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Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol Daniel Tarigan, Indra Masmur, Sabarmin Perangin-angin, Subur Pasaribu, Agustina Magdaleni, Hestina Hestina, Helmina Sembiring, Albert Pasaribu, Elvri Silinjak	ACS Omega	March 14, 2023	<b>In Peer Review</b> Your manuscript is being evaluated by researchers in your field.

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<p>Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol</p> <p>Daniel Tarigan, Indra Masmur, Sabarmin Perangin-angin, Subur Pasaribu, Agustina Magdaleni, Hestina Hestina, Helmina Sembiring, Albert Pasaribu, Elvri Silitjank</p>	ACS Omega	March 14, 2023	<p><b>Major Revision</b></p> <p>Your manuscript has received a Minor Revision decision. <b>May 02, 2023</b>. Submit Revision</p>

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<p>Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol</p> <p>Daniel Daniel, Indra Masmur, Sabarmin Perangin-angin, Subur Pasaribu, Agustina Magdaleni, Hestina Hestina, Helmina Sembiring, Albert Pasaribu, Elvri Silitjank</p>	ACS Omega	March 14, 2023	<p><b>Accept</b></p> <p>Your manuscript has been accepted for publication in this journal.</p>

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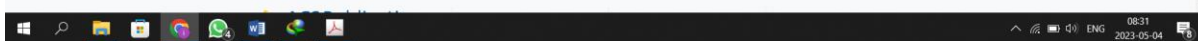
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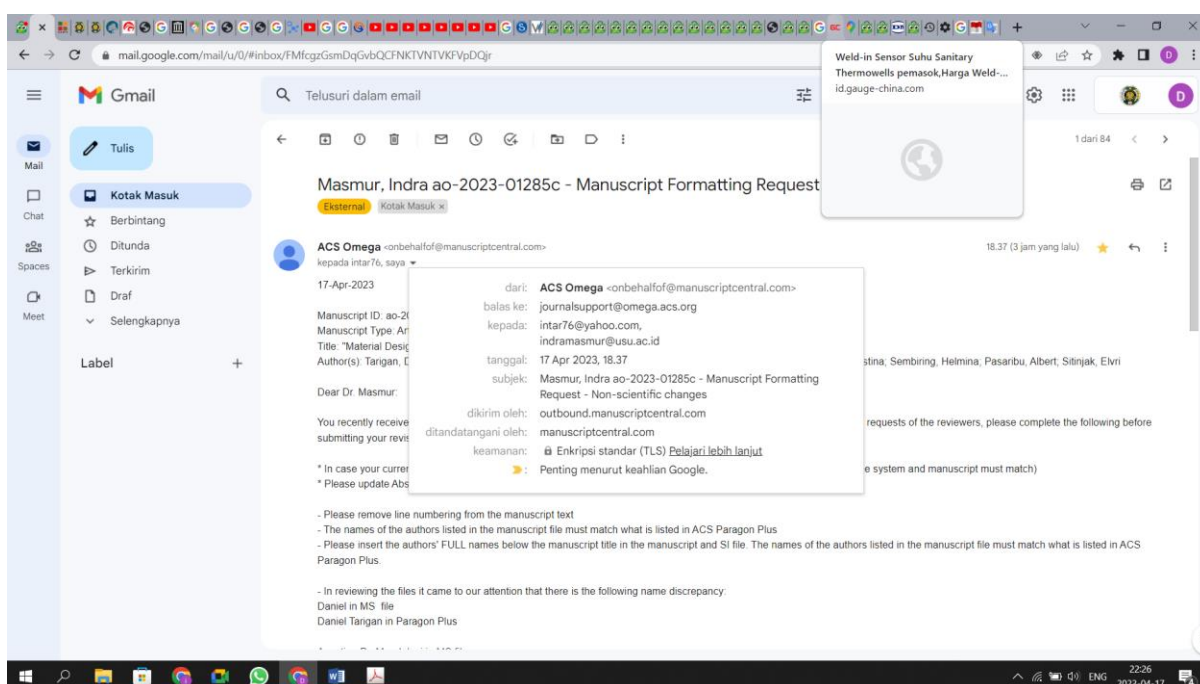
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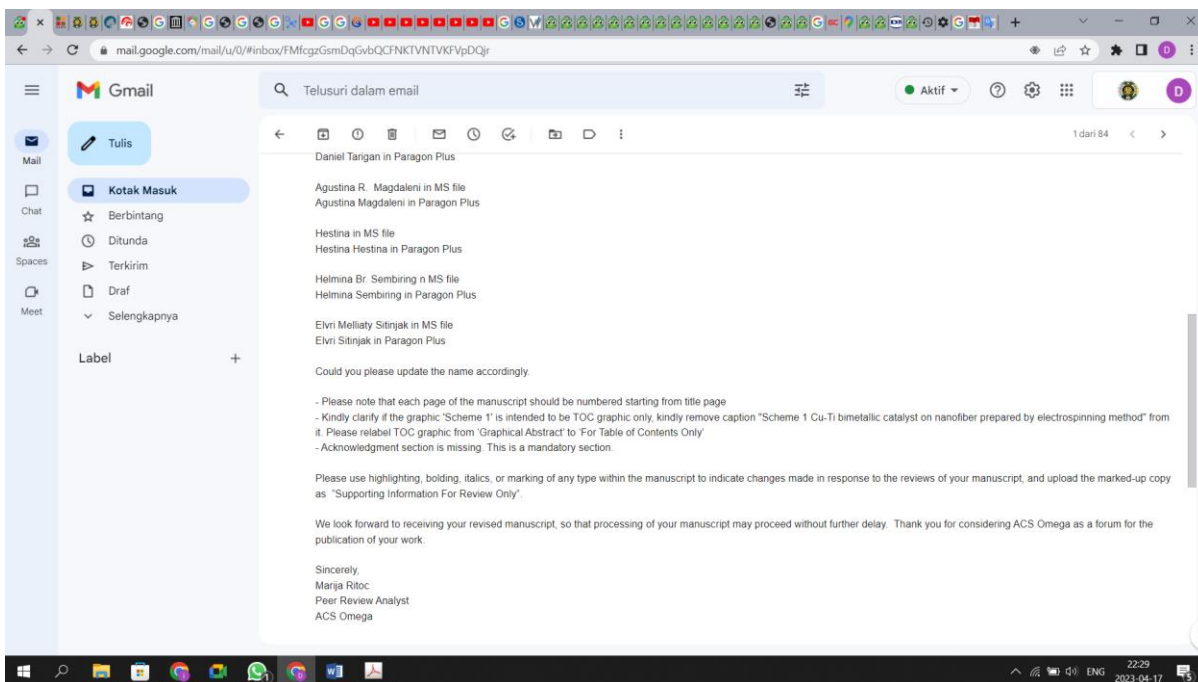
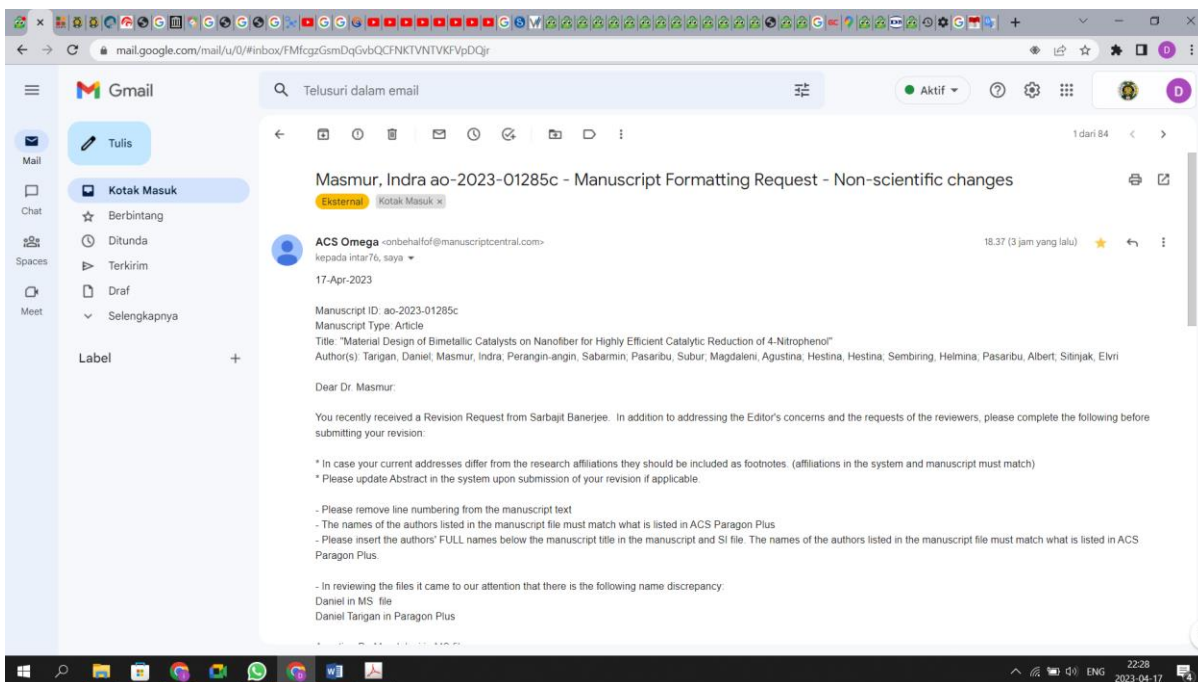
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Journal: ACS Omega  
Manuscript ID: ao-2023-01285c.R1  
Title: "Material Design of Bimetallic Catalysts on Nanolber for Highly Efficient Catalytic Reduction of 4-Nitrophenol"  
Author(s): Daniel, \*, Masmur, Indra, Perangin-angin, Sabarmin, Pasaribu, Subur, Magdaleni, Agustina, Hestina, \*, Sembiring, Helmina, Pasaribu, Albert, Sitingaj, Evri

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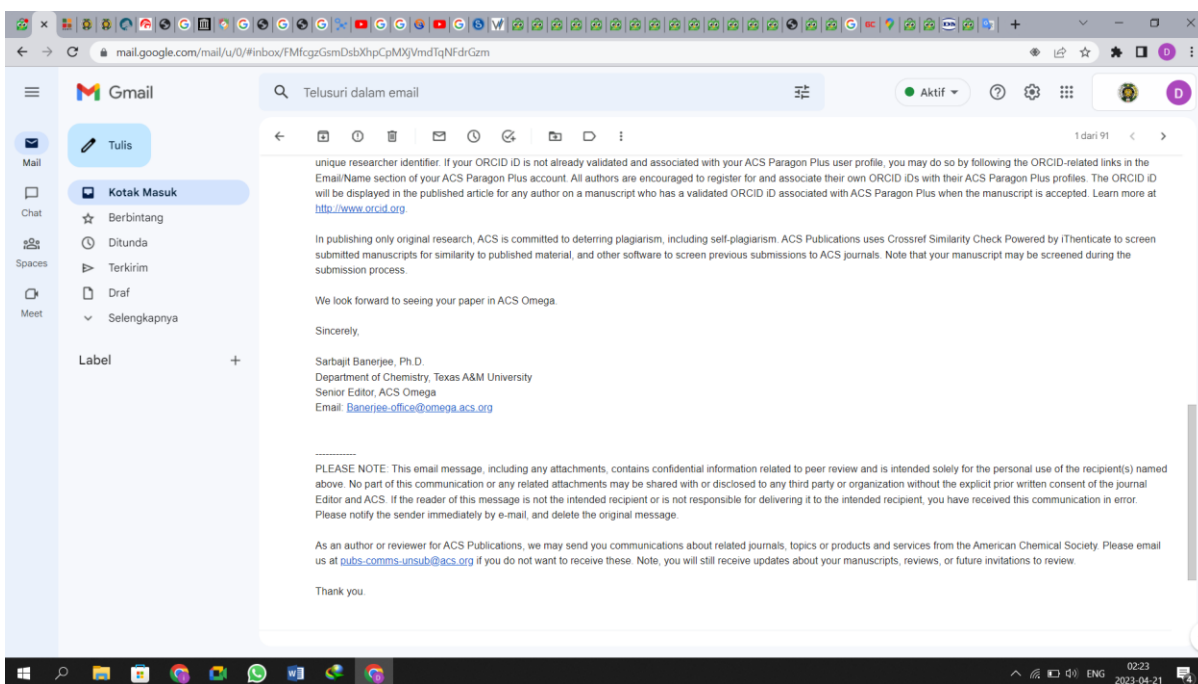
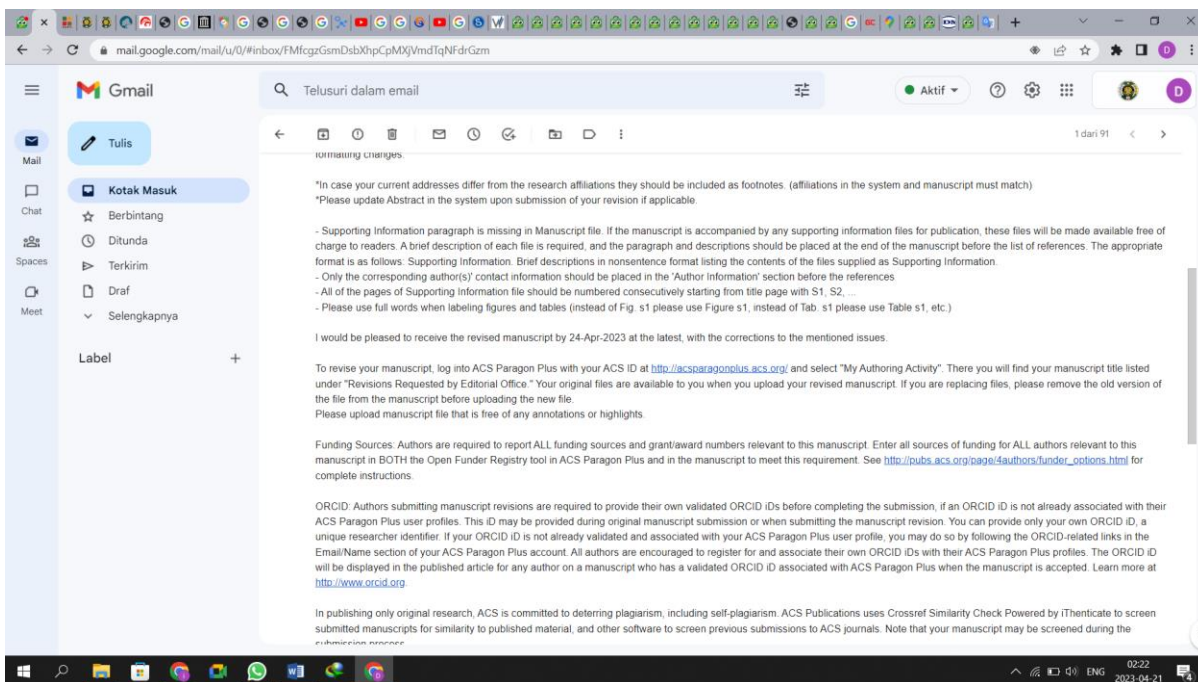
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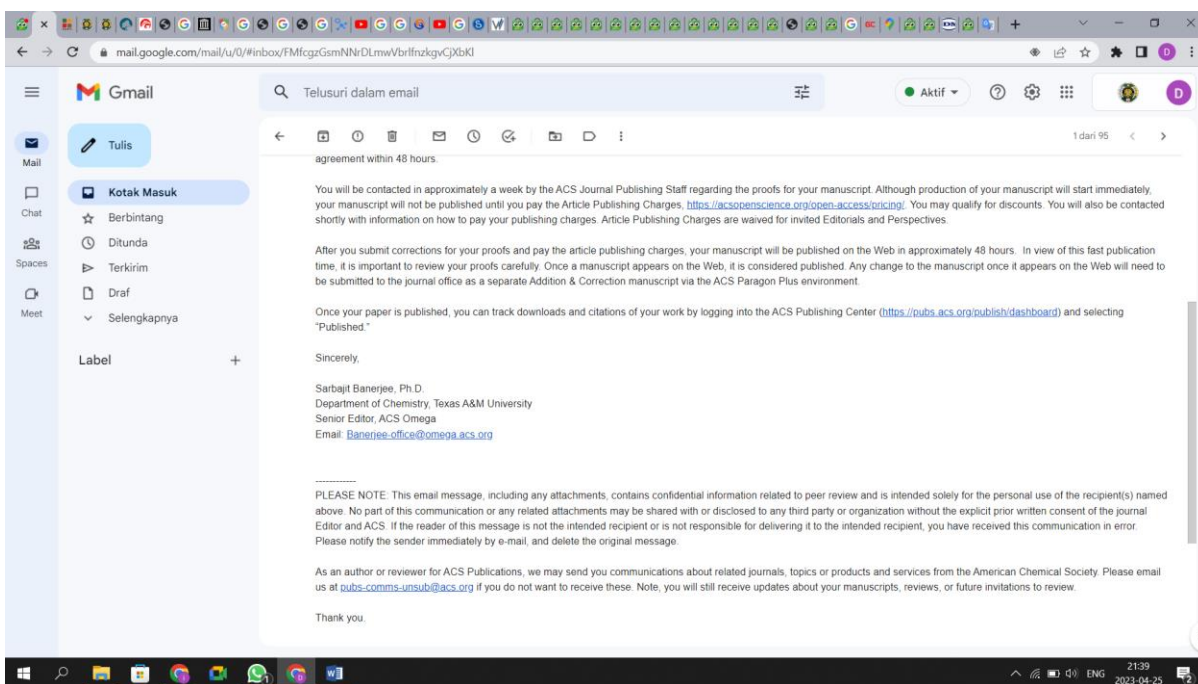
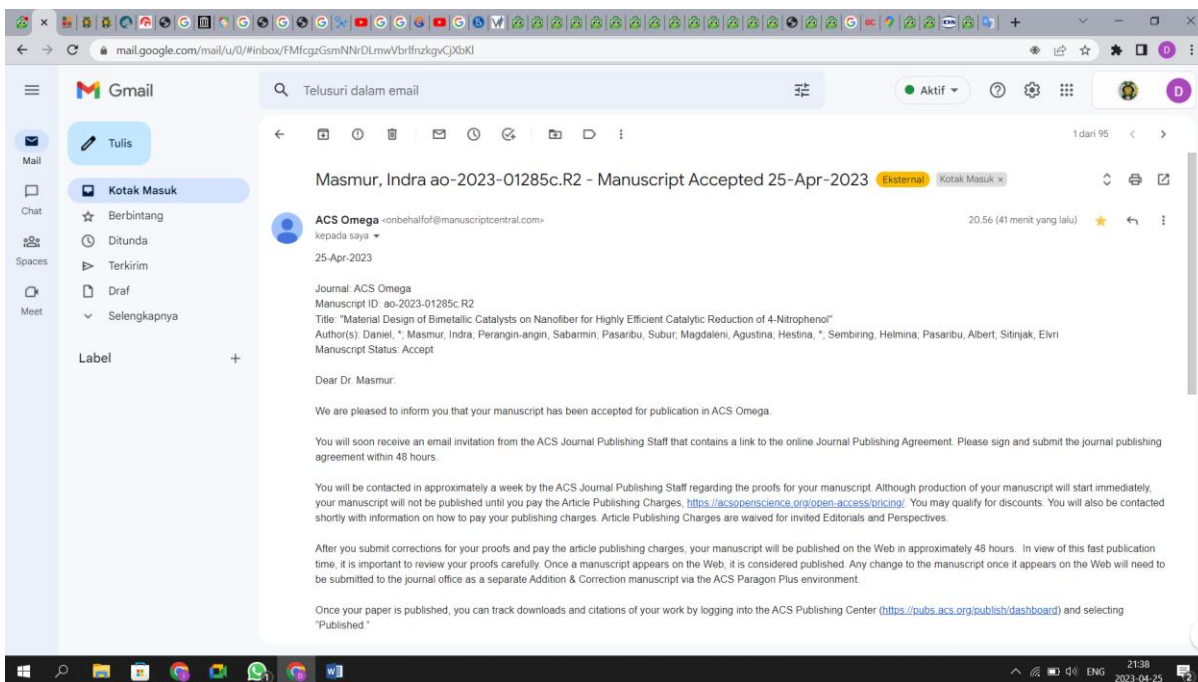
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Journal: ACS Omega  
Manuscript No.: ao-2023-01285c  
Title: Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol  
Authors: \* Daniel, Indra Masmur, Sabarmin Perangin-angin, Subur P. Pasaribu, Agustina R. Magdaleny, \* Hestina, Helmina Br. Sembiring, Albert Pasaribu, Elvri Meiliaty Sitiinjak  
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Title: Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol  
Authors: \* Daniel, Indra Masmur, Sabarmin Perangin-angin, Subur P. Pasaribu, Agustina R. Magdaleny, \* Hestina, Helmina Br. Sembiring, Albert Pasaribu, Elvri Meiliaty Sitiinjak  
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Manuscript No.: ao-2023-01285c (acsomega.3c01285)  
Title: Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol.  
Authors: \* Daniel, Indra Masmur, Sabarmin Perangin-angin, Subur P. Pasanbu, Agustina R. Magdaleni, \* Hestina, Helmina Br. Sembiring, Albert Pasanbu, Elvir Meliaty Sitjak.  
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Journal: ACS Omega  
Manuscript No.: ao-2023-01285c (10.1021/acsomega.3c01285)  
Title: Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol  
Authors: \* Daniel, Indra Masmur, Sabarmin Perangin-angin, Subur P. Pasaribu, Agustina R. Magdaleni, \* Hestina, Helmina Br. Sembiring, Albert Pasaribu, Elvri Melliaty Sitinjak  
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Journal: ACS Omega  
Manuscript No.: ao-2023-01285c (10.1021/acsomega.3c01285)  
Title: Material Design of Bimetallic Catalysts on Nanofibers for Highly Efficient Catalytic Reduction of 4-Nitrophenol  
Authors: Daniel, Indra Masmur, Sabarmin Perangin-angin, Subur P. Pasaribu, Agustina R. Magdaleni, Hestina, Helmina Br. Sembiring, Albert Pasaribu, Elvri Melliaty Sitinjak  
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Journal: ACS Omega  
Manuscript ID: ao-2023-01285c  
Title: "Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol"  
Author(s): Tarigan, Daniel; Masmur, Indra; Perangin-angin, Sabarmin; Pasaribu, Subur; Magdaleni, Agustina; Hestina, Hestina; Sembiring, Helmina; Pasaribu, Albert; Sitinjak, Elvri

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Reviewer(s)' Comments to Author:

Reviewer: 1

Recommendation: Publish after major revisions.

Comments:

Comments:

This manuscript reports "Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol to 4-aminophenol". It's intriguing that a simple and promising approach for synthesizing catalysts has been established. There have been very few characterizations technique used to understand the structure and properties of catalysts. there is no specific data on the relationship between catalytic activity and catalyst structural properties. It may be considered further after all the suitable modifications are done in the revision and queries are addressed properly.

1. The EDX spectra of CuO-TiO<sub>2</sub> and Cu-CuO-TiO<sub>2</sub> should be given and discussion should be included.
2. The metal content of the CuO-TiO<sub>2</sub> and Cu-CuO-TiO<sub>2</sub> bimetallic catalysts should be analyzed by other techniques, except EDX, and discussion should be included in the result and discussion section.
3. Page 7, line 106, "To reduce Cu<sup>2+</sup> to metallic copper (Cu<sup>0</sup>)....." Which technique was used to identify the oxidation state of copper, i.e. Cu<sup>2+</sup> and Cu<sup>0</sup>? How did you discover that copper's oxidation states are 2 and 0? please provide solid proof.
4. In catalysis, the surface area of heterogeneous catalysts is essential. Consequently, BET surface area study of CuO-TiO<sub>2</sub> and Cu-CuO-TiO<sub>2</sub> should be performed, and discussion should be included in the result and discussion section.
5. The authors should provide a table for comparison between the catalytic activities of their samples as compared to the previous competitor works relating to the reduction of 4-Nitrophenol to 4-aminophenol.

Additional Questions:

Is the technical quality of the research reported within valid and appropriate?: In Part (Please Elaborate in Your Review)

Please evaluate the degree of novelty and originality of the research reported: Fair

Are the conclusions adequately supported by the data presented?: No

Are the literature references appropriate and up to date?: No

Reviewer: 2

Recommendation: Publish after major revisions.

Comments:

In this work, the authors reported the synthesis of a series of copper-titania nanofiber catalysts and studied their catalytic performances in reduction of the 4-Nitrophenol. They found that the T1C3-4005 catalyst had the best catalytic performance and explained it by the synergistic interactions between the involved phases/species, which allow efficient charge separation and transfer. Overall, this work shows some interesting results that deserve to be published; however, some revisions are still needed before I recommend the publication. Here below show my comments:

- 1) Chemical and physical information about the catalysts is insufficiently provided in this work. I would suggest to perform additional characterizations (such as TEM, XPS, BET) to gain more information about the structure, composition, chemical state and surface areas of the catalysts. These results will greatly strengthen the work and allow to provide further insights into the structure-activity relationships of the catalysts.
- 2) I found some sentences hard to follow, for example "the presence of both Cu and CuO

species ... by acting as an electron" in line 29, page 3; What do you mean by "acting as an electron"?

There was no verb in the sentence "...new reflections associated to copper phases between 30 and 50°" in line 212, page 12.

I cannot understand the wording "with plane" appeared in line 219, Page 14.

I would suggest to rephrase the sentence "The high catalytic activity...as well as efficient electron transfer" in line 448-450, Page 24.

3) The fibers shown in Figure 2l was obtained at higher temperature compared to these shown in Figure 2k, yet they showed larger sizes, which does not make sense to me. This should be clarified.

4) The statement "...Cu nanoparticles are uniformly decorated on the surface..." was purely based on the SEM data. How did you know that the NPs were made of Cu? Note, XRD results have not been discussed yet.

5) XRD analysis can be improved. There were a few diffraction peaks remaining unassigned, for example the peaks shown at around 44° in Figure 3e and d.

6) The T1C3-4005 catalyst had the smallest diameter among all catalysts, suggesting that it might have the largest surface area. Would the surface area affect the catalytic activity? This may be worthy to discuss in the work.

**Additional Questions:**

Is the technical quality of the research reported within valid and appropriate?: In Part (Please Elaborate in Your Review)

Please evaluate the degree of novelty and originality of the research reported: Good

Are the conclusions adequately supported by the data presented?: Yes

Are the literature references appropriate and up to date?: Yes

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**To:** intar76@yahoo.com, indramasmur@usu.ac.id  
**CC:**  
**Subject:** Masmur, Indra ao-2023-01285c.R1 - Manuscript Revision Request - Formatting Changes 20-Apr-2023  
**Body:** 20-Apr-2023

Journal: ACS Omega  
Manuscript ID: ao-2023-01285c.R1  
Title: "Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol"  
Author(s): Daniel, \*; Masmur, Indra; Perangin-angin, Sabarmin; Pasaribu, Subur; Magdaleni, Agustina; Hestina, \*; Sembiring, Helmina; Pasaribu, Albert; Sitinjak, Elvri

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**Decision Letter (ao-2023-01285c.R2)****From:** Banerjee-office@omega.acs.org**To:** intar76@yahoo.com, indramasmur@usu.ac.id**CC:****Subject:** Masmur, Indra ao-2023-01285c.R2 - Manuscript Accepted 25-Apr-2023**Body:** 25-Apr-2023

Journal: ACS Omega

Manuscript ID: ao-2023-01285c.R2

Title: "Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol"

Author(s): Daniel, \*; Masmur, Indra; Perangin-angin, Sabarmin; Pasaribu, Subur; Magdaleni, Agustina; Hestina, \*; Sembiring, Helmina; Pasaribu, Albert; Sitinjak, Elvri

Manuscript Status: Accept

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# **Material Design of Bimetallic Catalysts on Nanofiber for Highly Efficient Catalytic Reduction of 4-Nitrophenol**

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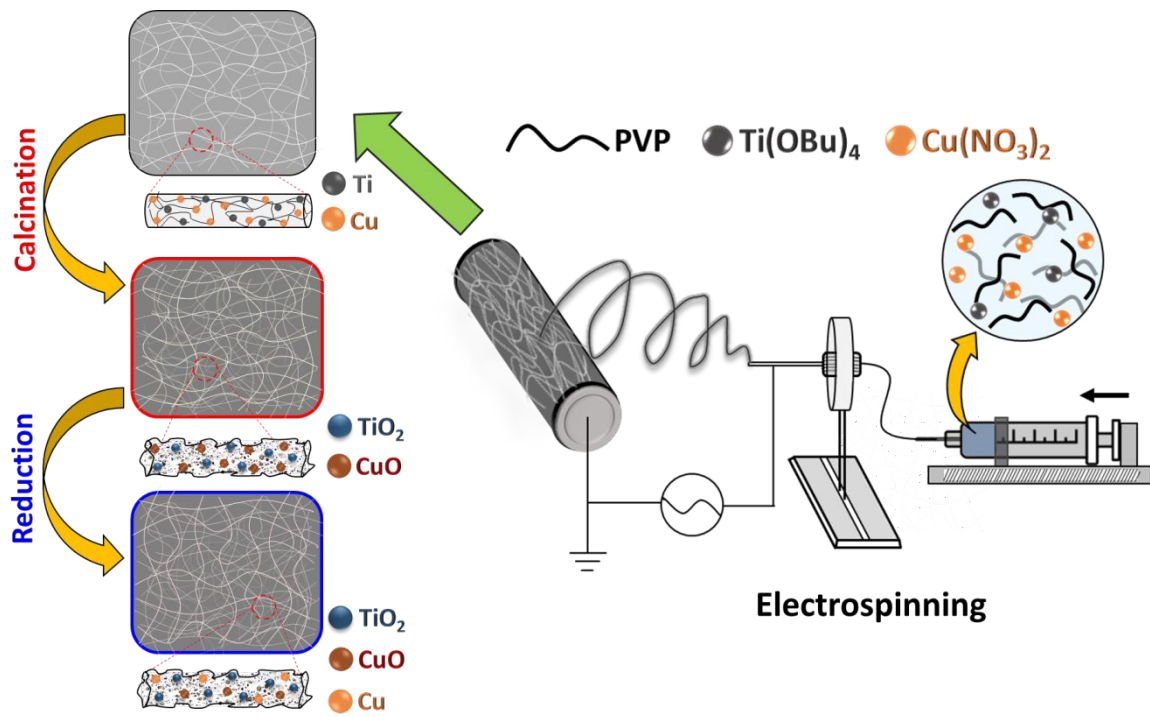
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## Graphical Abstract



**Scheme 1** Cu-Ti bimetallic catalyst on nanofiber prepared by electrospinning method

## Abstract

In this study, CuO-TiO<sub>2</sub> nanofiber catalysts were fabricated by an electrospinning process, followed by thermal annealing at various temperatures ranging from 300-700 °C. The phase transformation from CuO to metallic Cu was carried out through immersion treatment in NaBH<sub>4</sub> solution. The resulting CuO-TiO<sub>2</sub> and Cu-CuO-TiO<sub>2</sub> nanofibrous mats were characterized by scanning electron microscopy (SEM), [transmission electron microscopy \(TEM\)](#), [X-ray photoelectron spectroscopy \(XPS\)](#), X-ray diffraction (XRD) and [Brunauer-Emmett-Teller \(BET\) analysis](#). The results revealed that the crystalline phase composition of the nanofibrous mats considerably affected the efficiency of the photocatalytic reduction where the CuO-TiO<sub>2</sub> catalysts with predominant anatase content was found to be more photoactive than rutile phase. Similarly, the presence of both Cu and CuO species was more beneficial for promoting the activity of fibers by acting as an [interim location for facilitating the electron transfer](#). The fabricated Cu-CuO-TiO<sub>2</sub> nanofibrous mat with a ratio presented high conversion (~99%) within several minutes with the apparent pseudo-first-order rate constant of 0.42 and 0.50 min<sup>-1</sup> in the absence and presence of UV light irradiation, as well as excellent stability in recycling runs with stable conversion efficiency of 97% or higher over five successive catalytic cycles.

**Keywords:** Electrospinning; Nanofiber; Bimetallic; Reduction; 4-Nitrophenol

## 1. Introduction

The polluted freshwater resources remain as one of the global challenges in this century, which has directly impact to environmental and economic problems. Among the organic pollutants contained in the polluted water, nitroaromatic compounds had been found to be the most common and severely toxic chemicals, because of their highly stable, water soluble<sup>1</sup>, and induce carcinogenic effects even at low concentrations<sup>2, 3</sup>. Example of nitroaromatic compounds is 4-nitrophenol (4-NP) which are categorized as toxic pollutant by Environmental Protection Agency, with the limit concentration of 1 – 20 ppb<sup>1</sup>. It is because 4-NP has been widely used particularly for industrial applications (e.g. dyestuff, pesticide, explosives, etc.). The negative effects of nitrophenol exposure on human are dizziness, skin irritation, and organ disfunction. Even worse, the presence of this toxic organic chemical in water bodies could harm the marine biota, which further bring the domino-effect to human through the food chain<sup>4</sup>. Therefore, there has been a tremendous number of efforts dedicated to purify the contaminated water and wastewater to ensure a clean and healthy environment. Several methods are currently employed to remove nitrophenol in water bodies such as photolysis, electrolysis, adsorption, and Fenton reaction<sup>5-7</sup>. However, most of the aforementioned techniques are restricted for practical applications with low efficiency. Catalytic reduction approach has drawn attention from researchers owing to its highly efficient and large-scale process to convert 4-NP to 4-aminophenol (4-AP) on a nanostructured catalyst and is considered to be sustainable and economically friendly as well. Hence, materials design with high specific surface area, active sites, and robust durability is required to be developed<sup>8</sup>.

In the past few decades, the development of nanomaterials particularly for reduction of 4-NP to 4-AP involved nanosized noble metal<sup>9-11</sup>, carbon-based materials<sup>12, 13</sup>, and transition metals<sup>14, 15</sup>. Specifically, bimetallic material provides superior catalytic performances arising from their synergetic combination of two kinds of metals. For instance, Pt-Ni bimetallic



possessed better catalytic activity and corrosion resistance as compared to Pt metallic alone for 4-NP reduction assisted with  $\text{NaBH}_4$ <sup>16</sup>. Pozun *et. al.* reported higher reaction rate constant of bimetallic dendrimer encapsulated nanoparticles (DENs) where two metals were alloyed to trigger faster reaction rates as compared to their monometallic catalysts<sup>17</sup>. Regardless, previous works suffer from the expensive noble metal price and have serious issues for commercial production. Thus, the utilization of transition metals to replace noble metals not only would give benefit economically, but also potential for large-scale production. As for the transition metal, copper is a good choice since Cu is abundant resources, highly active element with varied oxidation states<sup>18</sup>. Another candidate is accompanied by titanium, Ti is low-cost material, highly stable, and strong oxidizer<sup>19</sup>. Furthermore, the improvement in terms of reusability purpose could be applied by embedding the bimetallic catalysts into a nanofibrous structure material which also enhance the surface area due to its highly porous network<sup>20</sup>.

To date, no studies reported the synthesis of copper-titania bimetallic catalyst on nanofibers with tunable phase compositions for catalytic reduction of 4-NP to 4-AP. With this regard in mind, a material design of copper-titania (Cu-Ti) bimetallic embedded in PVP nanofibers was synthesized by electrospinning process followed by reduction reaction. The as-prepared nanofibrous bimetallic catalyst was applied for catalytic reduction of 4-NP to 4-AP. In addition, the kinetics and thermodynamics of Cu-Ti bimetallic nanofibrous catalyst are thoroughly discussed in this study.

## 2. Materials and methods

### 2.1. Chemicals

PVP (MW= 40,000 g/mol), sodium borohydride (NaBH<sub>4</sub>, 98%), 4-NP (Echo chemicals, 99%), copper (II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Sigma Aldrich, 99.5%), and tetrabutyl titanate (TT, Sigma Aldrich, 97%) were used as received without any purification.

### 2.2. Preparation of Cu-Ti bimetallic nanofibers

In a typical experiment, Cu-Ti bimetallic nanofibrous catalyst was fabricated by mixing Cu(NO<sub>3</sub>)<sub>2</sub> and TT-PVP as copper and titanium sources, respectively. The titanium precursor solution was prepared via a sol-gel method by stirring ethanol, acetic acid, and TT at ambient temperature for min. Subsequently, 2 g of PVP was added and stirred until homogeneous. Then, Cu(NO<sub>3</sub>)<sub>2</sub> solution in ethanol was added into TT-PVP solution. The resulting viscous solution was transferred to a plastic syringe equipped with a stainless steel blunt-ended needle. Electrospinning was conducted at 20 kV, with a speed rate of 0.01 mL/h, and a distance of 15 cm between the tip of needle and drum collector. The as-obtained nanofibers were then stored in electric oven at 65 °C to avoid moisture and later used for further characterizations. The formulation of different copper and titanium precursors are tabulated in Table 1 and abbreviated as T<sub>n</sub>C<sub>m</sub>, where n and m represent the concentrations of titanium and copper precursors, respectively.

**Table 1.** Composition of electrospinning copper-titanium bimetallic nanofibers

Samples	Solution composition		Ø (nm)
	TT (wt%)	Cu(NO <sub>3</sub> ) <sub>2</sub> (wt%)	
T <sub>6</sub> C <sub>1</sub>	6	1	508 ± 143
T <sub>3</sub> C <sub>1</sub>	3	1	655 ± 74
T <sub>1</sub> C <sub>1</sub>	1	1	344 ± 70
T <sub>1</sub> C <sub>3</sub>	1	3	760 ± 220
TT-PVP	6	-	426 ± 67

Thermal crosslinking process of  $T_nC_m$  PVP nanofibers was carried out at 180 °C for 3 h in an electric muffle furnace under air atmosphere.  $T_nC_m$  PVP nanofibers were further annealed at 300 – 700 °C for 30 min with a heating ramp of 10 °C/min. The annealed nanofibers products were named as  $T_nC_m$ -X, where X denotes the annealing temperature. To reduce  $Cu^{2+}$  to metallic copper ( $Cu^0$ ),  $T_nC_m$ -X nanofibers was simply immersed in  $NaBH_4$  solution at different immersion time and the samples were named as  $T_nC_m$ -X<sub>r</sub>, where r represents reduction time.

### 2.3. Materials Characterizations

The surface morphology of prepared nanofibers was observed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7900) with an accelerating voltage of 30 kV equipped with energy dispersive X-ray (EDX) detector for elemental composition and transmission electron microscopy (TEM, JEOL 2000FX). The crystallinity and phase identification of samples was examined using X-ray diffraction (XRD, Bruker D2 Phaser) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250) analyses. Inductively Coupled Plasma Atomic Emission Spectra (ICP-AES, Shimadzu ICPE-9800) analysis was used to determine the titanium and copper content in the obtained nanofibers. The surface area of heterogeneous catalyst was further studied by BET analysis.

### 2.4. Catalytic experiments

The catalytic performances of bimetallic nanofibers were evaluated at dark and UV-light irradiated condition. In a typical experiment, ~2 mg of bimetallic nanofibers was dispersed in 4-NP solution with concentration of 0.5 mM. Prior to photocatalytic reaction, the dispersion was stirred for 30 min at dark condition to reach the adsorption-desorption

equilibrium. Afterwards, 5 mL of NaBH<sub>4</sub> 0.1 M was dropwise added and at the same time, irradiated with UV light while stirring. Aliquot was taken after a certain period of time and further analyzed using UV-vis spectrophotometer (Jasco V-650). The reusability performances of bimetallic nanofibers were also tested on five consecutive cycles experiments.

### 2.5. Kinetic and thermodynamic analysis

The kinetics of catalytic and photocatalytic 4-NP reduction reaction in the presence of bimetallic nanofibers were studied by monitoring the changes in absorbance of 4-nitrophenolate ions at  $\lambda_{\text{max}} = 400$  nm at different time intervals. In this model reaction, the kinetics of 4-NP reduction in the presence of excess NaBH<sub>4</sub> can be assumed to follow a pseudo-first-order model. The reaction rate constant with respect to 4-nitrophenolate ions can be expressed as follows (Eq 1):

$$-\ln \left( \frac{C_t}{C_0} \right) = -\ln \left( \frac{A_t}{A_0} \right) = kt \quad (1)$$

where  $A_t$  and  $A_0$  refer to the absorbance of 4-nitrophenolate ions at times  $t$  and 0, respectively, while  $C_t$  and  $C_0$  are the equivalent concentrations of the same species at times  $t$  and 0, respectively. The apparent rate constant ( $k_{\text{app}}$ ) can be obtained from the slope of the linear plot of  $-\ln(A_t/A_0)$  versus time.

The thermodynamic aspect of the reaction, such as predicting the apparent activation energy ( $E_a$ ), the enthalpy of activation ( $\Delta H^\ddagger$ ), and the Gibbs energy of activation ( $\Delta G^\ddagger$ ), was investigated by conducting the 4-NP reduction experiments at different temperatures (i.e., 303, 313, and 323 K). The  $E_a$  (kJ mol<sup>-1</sup>) can be calculated from the slope of the Arrhenius plot describing a linear relationship between the logarithm of the rate constant ( $k_{\text{app}}$ ) and the inverse of absolute temperature ( $1/T$ ) according to the following equation (Eq 2):

$$\ln k_{\text{app}} = -\frac{E_a}{RT} + \ln A \quad (2)$$

where  $R$  and  $A$  denote the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and pre-exponential factor related to the steric effect and collision frequency, respectively. The values of the enthalpy and entropy of activation ( $\Delta S^\ddagger$ ) can be obtained from the Eyring equation (Eq 3 And 4) describing a linear relationship between reaction rate and temperature<sup>21</sup>:

$$\ln\left(\frac{k_{\text{app}}}{T}\right) = \frac{-\Delta H}{R} \frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R} \quad (3)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (4)$$

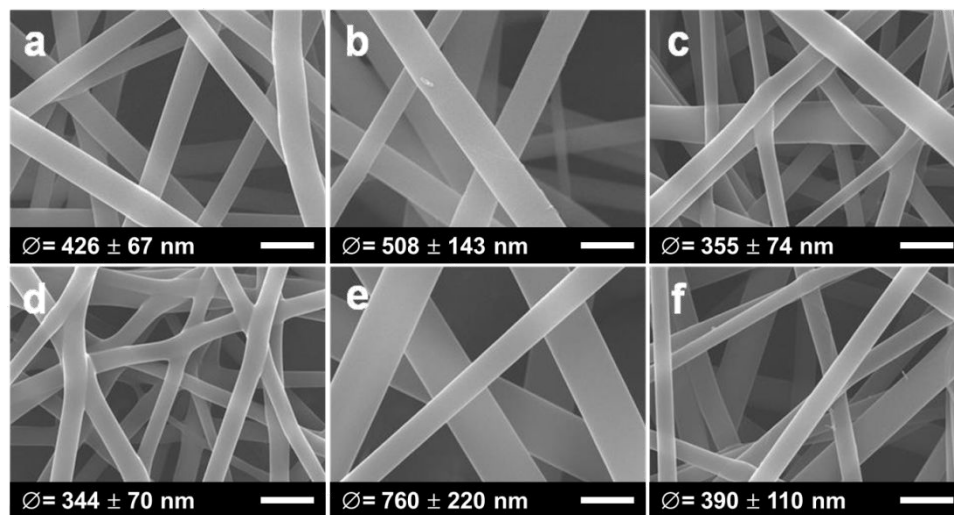
where  $k_B$  and  $h$  are the Boltzmann's ( $1.38 \times 10^{-23} \text{ J K}^{-1}$ ) and Planck's constant ( $6.63 \times 10^{-34} \text{ J s}$ ), respectively.

### 3. Results and discussion

#### 3.1. Morphology of bimetallic nanofibers

The surface morphology of  $T_nC_m$  PVP nanofibers is shown in Fig. 1. From this figure, it can be seen that all the fibers exhibited a smooth and uniform surface without discernable bead defects. The average diameter of  $T_nC_m$  PVP nanofibers was found to be affected by the precursor solution composition, particularly the titanium-to-copper ratio. The addition of metal salt into the polymer solution was also reported to affect the spinnability of the polymer jet since it will increase the number of ions and conductivity. Generally speaking, a more conductive and viscous solution results in the formation of thinner nanofiber. In this regard, the average diameter of the  $T_nC_m$  PVP nanofibers decreased from  $508 \pm 143$  to  $355 \pm 74$  and  $344 \pm 70$  nm with decreasing titanium content in the solution ( $T_6C_1$  to  $T_1C_1$ ), meanwhile, it is bigger in size with increasing copper content ( $T_1C_3$ ), which might be due to hygroscopic properties of copper nitrate precursors. As can be seen in Table 2, the average diameter of as-spun nanofibers was varied in between 94 – 513 nm. Moreover, BET results showed that T-400 possesses surface area of  $173.1 \text{ m}^2 \text{ g}^{-1}$ , pore volume of 19.6, and pore size of 3.1 nm. The surface area, pore volume, and pore size of nanofiber catalysts gradually decreased with

decreasing Ti concentration ( $T_6C_1$  to  $T_1C_1$ ) as shown in Table S1. Interestingly, surface area, pore volume, and pore size of nanofiber significantly increased after reducing by  $NaBH_4$  ( $T_1C_3-400_5$ ).



**Figure 1.** SEM images of as-spun fibers of (a) TT-PVP, (b)  $T_6C_1$ , (c)  $T_3C_1$ , (d)  $T_1C_1$ , (e)  $T_1C_3$ , and (f) Cu-PVP. The scale bar in all figures is 1  $\mu$ m.

**Table 2.** Average diameter and crystalline phase composition of  $T_nC_m-400$  and  $T_nC_m-400_5$  nanofiber catalysts.

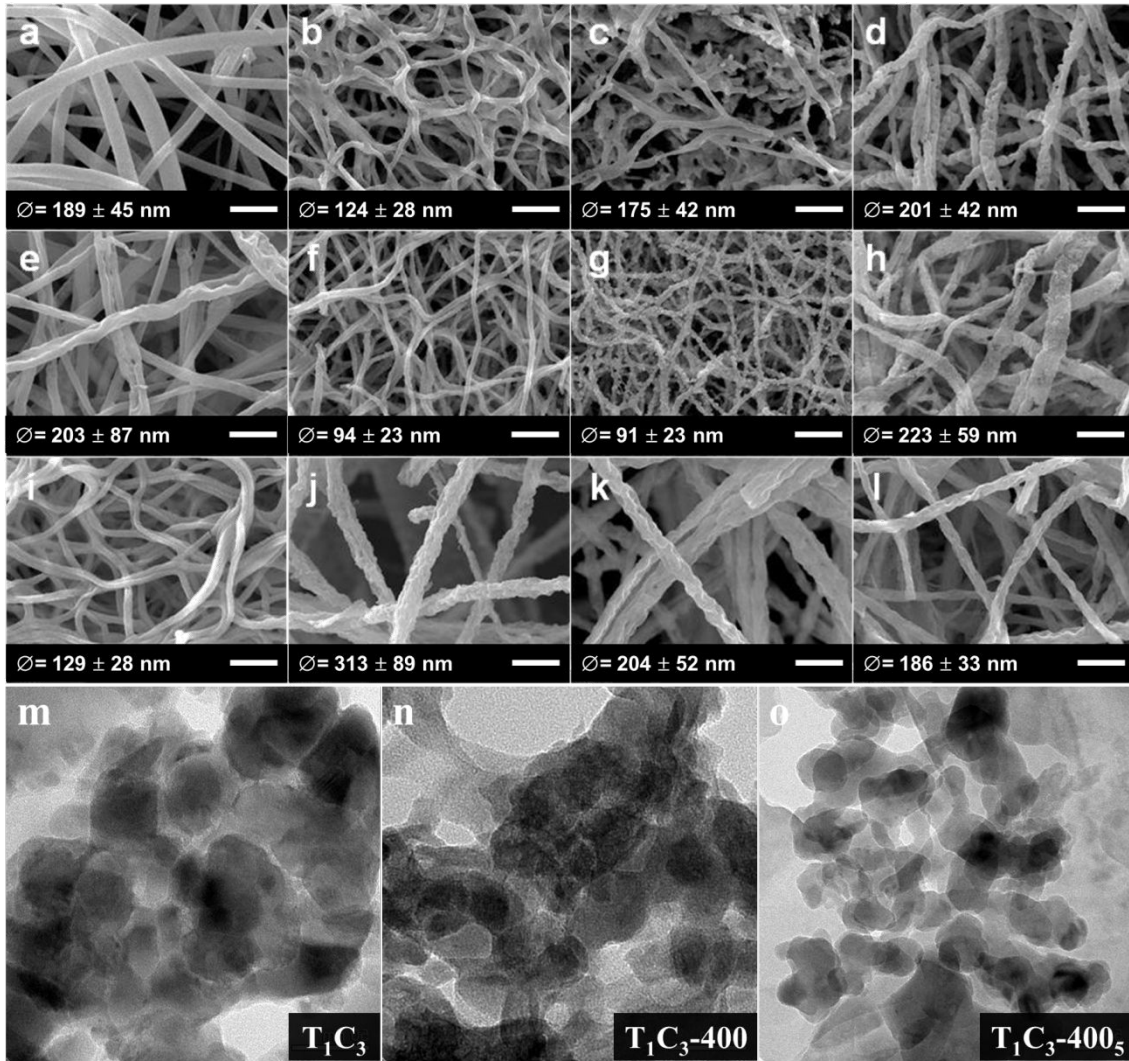
Catalyst	$\varnothing$ (nm)	Crystal phases	TiO <sub>2</sub> crystallinity	
			Anatase (wt%)	Rutile (wt%)
T-400	129 ± 28	TiO <sub>2</sub>	83.7	16.3
$T_6C_1-300$	513 ± 59	Amorphous	ND	ND
$T_6C_1-400$	189 ± 45		85.7	14.3
$T_6C_1-500$	313 ± 89	TiO <sub>2</sub>	72.4	27.6
$T_6C_1-600$	204 ± 52		27.8	72.2
$T_6C_1-700$	273 ± 74		ND	100
$T_3C_1-400$	124 ± 28	TiO <sub>2</sub> , CuO	83.4	16.6
$T_1C_1-400$	175 ± 42		86.2	13.8
$T_3C_1-400$	201 ± 87	TiO <sub>2</sub>	85.4	14.6
$T_6C_1-400_5$	203 ± 23		85.0	15.0

$T_3C_1-400_5$	$94 \pm 23$	TiO <sub>2</sub> , CuO, Cu	81.0	19.0
$T_1C_1-400_5$	$91 \pm 23$		83.6	26.4
$T_1C_3-400_5$	$223 \pm 59$		100	ND

Fig. 2 depicts the morphology of  $T_nC_m$  PVP nanofibers annealed at 400 °C. From this figure, it can be seen that all the annealed fibers had a significantly smaller diameter than the precursor fibers, which could be attributed to the thermal decomposition of the polymer matrix. Previous reports have shown that PVP decomposes upon heating in air at temperatures between 350 and 400 °C<sup>22, 23</sup>. The formation of such metal oxide agglomerates can be ascribed to the activation and diffusion-controlled neck growth of Ti and Cu atoms by thermal energy to form. This also suggests that thermal annealing at 400 °C can induce the formation of crystalline metal oxide phases (i.e., TiO<sub>2</sub> and CuO); both of which are beneficial for catalytic reactions. Additionally, one can also notice that Cu nanoparticles are uniformly decorated on the surface of  $T_nC_m-400_5$  nanofibers prepared from the electrospinning solutions with higher concentrations of copper salt, providing more catalytic active sites for 4-NP reduction.

Furthermore, TEM analysis shows that the nanostructure of  $T_1C_3$  (without annealing) was found to be agglomerated as shown in Fig. 2m. These agglomerates containing were then become slightly separated after annealing,  $T_1C_3-400$  (Fig. 2n) and after reducing by NaBH<sub>4</sub>, the obtained particles were irregular shape without any agglomeration with the average size of 20-30 nm as can be seen in Fig. 2o. In addition, the elemental composition of  $T_1C_3-400$  and  $T_1C_3-400_5$  nanofibers was analyzed by EDX analysis as the representatives of CuO-TiO<sub>2</sub> and Cu-CuO-TiO<sub>2</sub> crystal phases as shown in Fig. S1. The EDX spectra showed that the atomic % of O decreased after reducing by NaBH<sub>4</sub> from 17 % to 14.2 % and the amount of Ti and Cu slightly increased, indicating that CuO in  $T_1C_3-400$  was transformed into Cu<sup>0</sup> in  $T_1C_3-400_5$ .





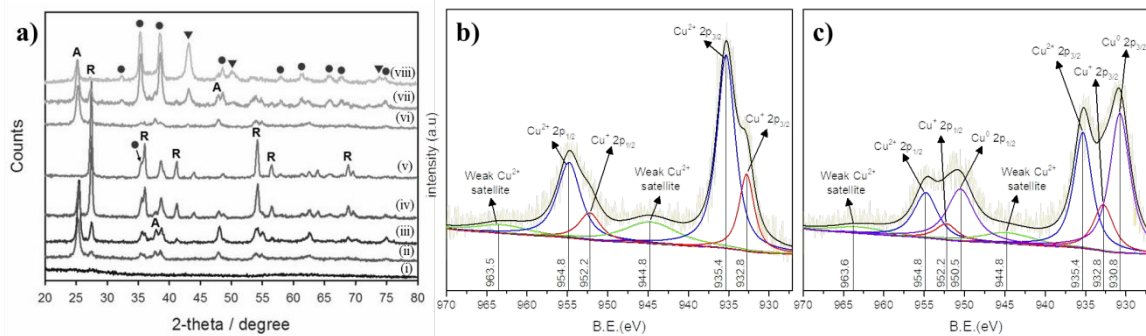
**Figure 2.** SEM images of annealed  $T_n C_m$  PVP nanofiber (a)  $T_6 C_1$ , (b)  $T_3 C_1$ , (c)  $T_1 C_1$ , and (d)  $T_1 C_3$ . SEM micrographs (e-h) of the nanofibrous mats corresponding to panels a-d after immersion in  $\text{NaBH}_4$  solution for 5 min to reduce  $\text{CuO}$  to metallic  $\text{Cu}$ . SEM images of (i) T-400 nanofiber and  $T_6 C_1$  nanofibers annealed at (j) 500 °C, (k) 600 °C, and (l) 700 °C. **TEM images of (m)  $T_1 C_3$ , (n)  $T_1 C_3$ -400, and (o)  $T_1 C_3$ -400<sub>5</sub> nanofibers.** The scale bar for SEM images represents 1  $\mu\text{m}$ .

### 3.2. Crystal phase and composition of the bimetallic nanofibrous mats

The XRD patterns of the fabricated bimetallic nanofibrous mats are presented in Fig. 3. As can be seen in the figure, there are no characteristic Bragg reflections associated with the

crystal structures of TiO<sub>2</sub> and copper oxides for T<sub>6</sub>C<sub>1</sub>-300 sample, indicating the amorphous nature of the fibers. On the contrary, the XRD patterns of T<sub>6</sub>C<sub>1</sub>-400, T<sub>6</sub>C<sub>1</sub>-500, T<sub>6</sub>C<sub>1</sub>-600, T<sub>6</sub>C<sub>1</sub>-700 nanofibers contain several sharp and intense Bragg reflections corresponding to the TiO<sub>2</sub> polymorphs following thermal annealing at higher temperatures. The assignment of the crystalline phases was based on the reference files Joint Committee on Powder Diffraction Standards (JCPDS) No. 21-1272, No. 21-1276, No. 45-0937, and No. 04-0836 for anatase TiO<sub>2</sub>, rutile TiO<sub>2</sub>, CuO, and metallic Cu, respectively. On the other hand, there is a tiny peak assigned for Cu<sub>2</sub>O observed at 44° after T<sub>6</sub>C<sub>1</sub> annealed at 600 and 700 °C as can be seen in Fig. 3iv and v. The results demonstrate that the formation of two crystalline phases strongly depends on the annealing temperature<sup>17,24</sup>, where T<sub>6</sub>C<sub>1</sub>-400, T<sub>6</sub>C<sub>1</sub>-500, and T<sub>6</sub>C<sub>1</sub>-600 samples exhibited mixed anatase-rutile phase and T<sub>6</sub>C<sub>1</sub>-700 sample comprised only the rutile phase (Table 2). Meanwhile, no appreciable copper oxide species could be observed in the XRD patterns of these samples, probably because of low concentration and also because the main reflections of copper oxides overlap those of anatase and rutile TiO<sub>2</sub>. Panels (vi), (vii), and (viii) show the diffraction patterns of T<sub>6</sub>C<sub>1</sub>-400, T<sub>1</sub>C<sub>1</sub>-400, and T<sub>1</sub>C<sub>3</sub>-400 nanofibers after the immersion treatment in NaBH<sub>4</sub> solution. In addition to reflections from TiO<sub>2</sub> polymorphs, new reflections associated to copper phases between 30° and 50° appear. Moreover, it can be observed that the Bragg peaks assigned to monoclinic CuO at 2θ become sharper and more intense in T<sub>1</sub>C<sub>1</sub>-400 and T<sub>1</sub>C<sub>3</sub>-400 nanofibers with higher amount of copper loading. For all T<sub>n</sub>C<sub>m</sub>-X samples, no traces of cubic Cu<sub>2</sub>O phase were found, indicating the complete thermal oxidation of amorphous Cu to CuO ( $2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}$ ) under annealing treatment at 400 °C and beyond in air atmosphere. This phase transition is in good agreement with results reported by De Los Santos Valladares *et. al.*<sup>25</sup>. Thus, it can be implied that the coexistence of both active TiO<sub>2</sub> with plane-predominant anatase phase and copper/copper oxide phases on T<sub>n</sub>C<sub>m</sub>-X nanofibers is beneficial for facilitating catalytic reduction of 4-NP to 4-AP.

Furthermore, Fig. 3b and c show the high resolution XPS spectra of Cu element in  $T_1C_3$ -400 and  $T_1C_3$ -400<sub>5</sub> nanofibers. Both XPS spectra exhibited  $Cu^+ 2p_{3/2}$ ,  $Cu^+ 2p_{1/2}$ ,  $Cu^{2+} 2p_{3/2}$ , and  $Cu^{2+} 2p_{1/2}$  peaks which located at 932.8, 952.2, 935.4, and 954.8 eV, respectively, and also accompanied by their satellite peaks of  $Cu^{2+}$  at 944.8 and 963.5 eV<sup>26</sup>. By comparing the peak intensity in Fig. 3b and c, the peaks for  $Cu^{2+}$  and  $Cu^+$  including the satellite peaks decreased after reduction using  $NaBH_4$ <sup>27</sup>. Also, there is one additional set of  $Cu^0 2p$  peaks located 930.8 and 950.5 eV in  $T_1C_3$ -400<sub>5</sub> nanofiber (Fig. 3c). Therefore, this phenomenon successfully revealed that  $Cu^{2+}$  in  $T_1C_3$ -400 was converted to  $Cu^0$  in  $T_1C_3$ -400<sub>5</sub> nanofiber.



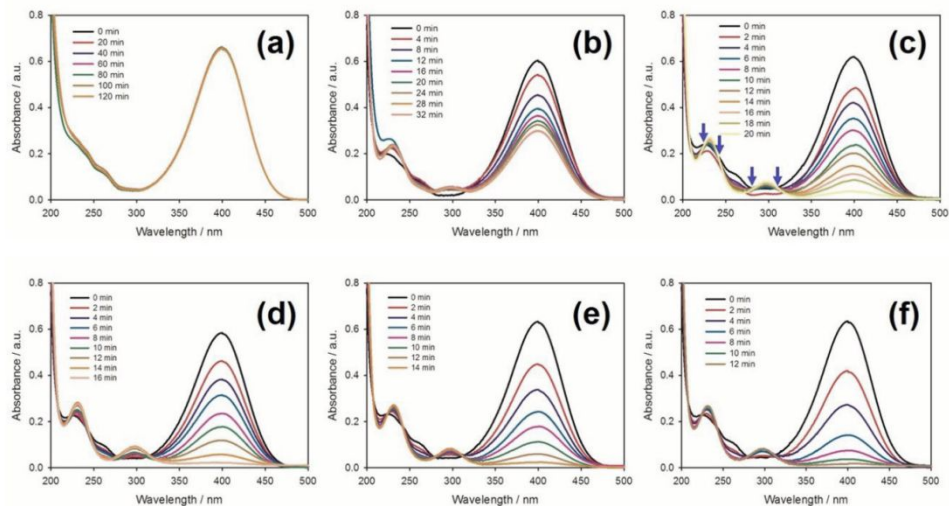
**Figure 3.** (a) Wide angle XRD patterns of  $T_6C_1$  nanofiber annealed at (i) 300, (ii) 400, (iii) 500, (iv) 600, and (v) 700 °C; (vi)  $T_6C_1$ , (vii)  $T_1C_1$ , and (viii)  $T_1C_3$  nanofibers after annealed at 400 °C for 30 min and immersed in  $NaBH_4$  solution for 5 min. Diffraction peaks corresponding to the anatase  $TiO_2$ , rutile  $TiO_2$ ,  $CuO$ , and metallic  $Cu$  phases are denoted by “A”, “R”, circles, and triangles, respectively. High resolution XPS spectra of Cu element in (b)  $T_1C_3$ -400 and (c)  $T_1C_3$ -400<sub>5</sub> nanofibers.

### 3.3. Photocatalytic activities of bimetallic nanofibers

The catalytic and photocatalytic activities of the fabricated electrospun samples were evaluated for reduction reaction of 4-NP to 4-AP in the aqueous phase at room temperature. The pH of the 4-NP solution before and after the addition of  $NaBH_4$  was measured using a

microelectrode pH meter and found to be around 7.2 and 9.6, respectively. In this model reaction, the reduction of 4-NP by  $\text{BH}_4^-$  does not occur in the absence of catalyst since there was neither color change from yellow to transparent observable by naked eyes nor a gradual decrease in the absorbance maxima of 400 nm corresponding to 4-nitrophenolate ions with time. Similar results were observed for  $\text{T}_6\text{C}_1$  sample with amorphous copper and  $\text{TiO}_2$  phases as the catalyst, showing negligible photocatalytic activity (Fig. 4a). Pure anatase-rich  $\text{TiO}_2$  nanofiber shows a rather moderate catalytic activity toward 4-NP reduction where only ~50% conversion was achieved after 32 min (Fig. 4b). On the contrary,  $\text{T}_n\text{C}_m$ -400 nanofibers with different bimetallic compositions and crystalline phases demonstrate high photocatalytic activity for 4-NP reduction, as shown in Fig. 4c-f. As can be seen from these figures, the complete conversion of 4-NP to 4-AP was achieved after 10-20 min of reaction at room temperature without formation of side products, as confirmed by two isosbestic points at 280 and 314 nm<sup>12</sup>. The results also indicate that the nanofibrous mats with higher Cu/Ti ratios, for example  $\text{T}_1\text{C}_1$ -400 and  $\text{T}_1\text{C}_3$ -400, demonstrate higher efficiency toward 4-NP reduction than  $\text{T}_6\text{C}_1$ -400 sample, which might be attributed to the presence of CuO phase. In this regard, CuO phase acts as a ‘shuttle bus’ to enhance separation efficiency of photogenerated electrons ( $e_{cb}^-$ ) and holes ( $h_{vb}^+$ ) by forming *p-n* heterojunction interface with the electron-rich (101) facet of  $\text{TiO}_2$ . Similar synergistic effect of photogenerated charge separation in CuO- $\text{TiO}_2$  heterojunction was observed for selective photo-oxidation of methanol to methyl formate<sup>28</sup> and degradation of 2,4-dichlorophenoxyacetic acid<sup>29</sup>. In addition, the positively charged CuO embedded in the surface of fiber catalysts may facilitate the adsorption of negatively charged 4-NP and hydrolyzed borohydride molecules on the surface through electrostatic interactions, leading to the elimination of induction period and increased reaction efficiency<sup>30</sup>. Since both copper and copper oxide phases in  $\text{T}_6\text{C}_1$ -X nanofibers were hardly recognized from the XRD results (Fig. 3, panels a-e), it can be implied that the photocatalytic activities of these samples

are mainly contributed by the TiO<sub>2</sub> polymorphs. The results show that the photocatalytic activity of the fibers becomes lower when the samples were annealed at higher temperatures, suggesting that anatase T<sub>6</sub>C<sub>1</sub> nanofiber catalyst is more active than its rutile counterpart toward the 4-NP reduction. The  $k_{app}$  value of T<sub>6</sub>C<sub>1</sub>-400 was about 2-fold higher compared to that of T<sub>6</sub>C<sub>1</sub>-700 sample. Similarly, Sclafani and Herrmann<sup>31</sup> and Tanaka *et. al.*<sup>32</sup> reported better photocatalytic performance of TiO<sub>2</sub> nanoparticles with higher anatase-to-rutile ratio for the degradation of organics in aqueous solutions. This can be attributed to the more negative conduction band energy minima of anatase that allows for a more facile electron transfer process to 4-NP and a lower recombination velocity of  $e_{cb}^-$  and  $h_{vb}^+$ , as well as a stronger adsorption affinity of 4-NP molecules toward the anatase (101) surface compared to that on rutile (110) surface<sup>33</sup>. The latter factor is thought to play a major role in the process since the reduction of 4-NP involves a key step in which the electron was transferred from donor BH<sub>4</sub><sup>-</sup> to the acceptor 4-NP<sup>8, 34</sup>. Moreover, the existence of a minor rutile phase in the T<sub>6</sub>C<sub>1</sub>-400 sample may also be beneficial for the separation of photogenerated charge carriers since  $h_{vb}^+$  will preferentially move to rutile owing to its higher valence band maximum energy<sup>25, 35</sup>. Therefore, an annealing temperature of 400 °C was chosen in this study to prepare photoactive anatase T<sub>n</sub>C<sub>m</sub> nanofibrous catalysts for subsequent catalytic testing and NaBH<sub>4</sub> reduction experiments. In addition, the use of lower annealing temperature is energetically more feasible for large-scale manufacturing of this nanofibrous catalyst.



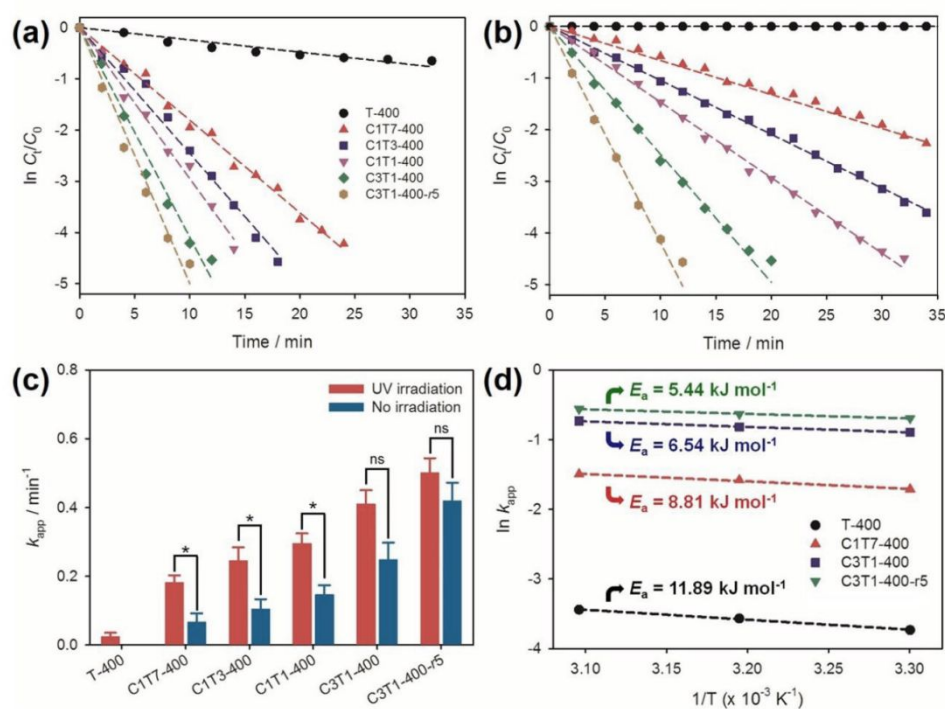
**Figure 4.** Time-dependent UV-vis absorption spectra of the reaction mixture consisting of 4-NP (0.2 mM), NaBH<sub>4</sub> (90 mM), and as-prepared nanofibrous catalysts (a) crosslinked T<sub>6</sub>C<sub>1</sub>, (b) T-400, (c) T<sub>6</sub>C<sub>1</sub>-400, (d) T<sub>3</sub>C<sub>1</sub>-400, (e) T<sub>1</sub>C<sub>1</sub>-400, and (f) T<sub>1</sub>C<sub>3</sub>-400 under UV irradiation. The blue arrows in panel (c) indicate representative four isosbestic points at 227, 244, 281, and 314 nm.

### 3.3.1. Effects of the copper phase compositions

The photocatalytic activities of the anatase T<sub>n</sub>C<sub>m</sub>-400 nanofibers with pure CuO phase and the mix phase Cu-CuO are shown in Fig. 5. The formation of a mixed Cu-CuO phase was carried out through immersion in NaBH<sub>4</sub>, which allows the reduction of CuO to Cu with H<sub>2</sub> according to the stoichiometric reactions. To explore the effect of immersion time of the C<sub>x</sub>T<sub>y</sub>-400 substrates in the NaBH<sub>4</sub> aqueous solution, the photocatalytic reduction activity of these substrates after the immersion treatments for 1, 5, and 10 min was evaluated. From our experiments, the optimized reduction time by NaBH<sub>4</sub> solution was found to be 5 min. From Fig. 5a and b, it can be shown that the T<sub>n</sub>C<sub>m</sub>-400<sub>5</sub> nanofiber catalysts exhibited better catalytic performance compared to their T<sub>n</sub>C<sub>m</sub>-400 containing only the CuO phase. The superior photocatalytic activity of T<sub>n</sub>C<sub>m</sub>-400<sub>5</sub> nanofiber might be attributed to the copresence of CuO and Cu active phases, leading not only to an enhanced charge carrier separation generated from



the CuO-TiO<sub>2</sub> heterojunction, but also a more efficient electron transfer between the adsorbed BH<sub>4</sub><sup>-</sup> and 4-NP molecules on the photocatalyst surface, which was facilitated by the high electrical conductivity (5.8 × 10<sup>7</sup> S m<sup>-1</sup>) of copper<sup>36</sup>. The presence of copper as a cocatalyst can also help suppress the recombination of the photoexcited electron-hole pairs in TiO<sub>2</sub> photocatalytic system, due to some e<sub>cb</sub><sup>-</sup> of TiO<sub>2</sub> could transfer directly to the Cu by ohmic interconnection<sup>37</sup>. Moreover, metallic Cu embedded in the surface of fibers can also serve as active sites to react with hydride (H<sup>+</sup>) ions generated from spontaneous hydrolysis of BH<sub>4</sub><sup>-</sup>, which upon contact with the catalyst surface donate its electrons to Cu and then combine to form H<sub>2</sub> gas.



**Figure 5.** Pseudo-first-order kinetic plots of the 4-NP reduction catalyzed by different nanofibrous mats (a) with and (b) without UV irradiation. The legend in (a) also applies to panel (b). The correlation fitted by Eq 1. is shown as colored dashed lines in panels (a) and (b). (c) Bar plot showing the comparisons of the  $k_{app}$  values for catalytic reduction of 4-NP in the presence and absence of UV exposure. Bars represent the mean value and error bars show standard error of the mean from three independent experiments ( $n = 3$ ). Asterisk (\*) and 'ns'



denote statistical significance at  $P < 0.05$  and no statistical significance, respectively based on unpaired two-tailed Welch's  $t$ -test using GraphPad Prism v6.01 software. (d) Arrhenius plots for photocatalytic 4-NP reduction by T-400, T<sub>6</sub>C<sub>1</sub>-400, T<sub>1</sub>C<sub>3</sub>-400, and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers. The  $E_a$  values are equal to the negative slopes of the respective linear fits multiplied by  $R$  (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) over three temperatures (303, 313, and 323 K).

### 3.3.2. Effects of UV irradiation

The effect of UV irradiation on the catalytic activity of T<sub>n</sub>C<sub>m</sub>-400 and T<sub>n</sub>C<sub>m</sub>-400<sub>5</sub> nanofibers is shown in Fig. 5a and b. From this figure, it can be seen that the reduction of 4-NP to 4-AP by T<sub>6</sub>C<sub>1</sub>-400, T<sub>3</sub>C<sub>1</sub>-400, T<sub>1</sub>C<sub>1</sub>-400, and T<sub>1</sub>C<sub>3</sub>-400 nanofiber catalysts was promoted under UV illumination. A complete conversion of 4-NP to 4-AP was achieved in shorter periods of time, within 5-10 min, compared to reactions without light irradiation. A similar trend was observed for the T<sub>n</sub>C<sub>m</sub>-400<sub>5</sub> nanofiber catalysts with ternary Cu-CuO-TiO<sub>2</sub> phase. The reason for the promotion effect of the UV light treatment is due to the generation of charge carriers in TiO<sub>2</sub> and CuO, where the photogenerated electrons serve as an additional source of electrons to reduce 4-NP, together with efficient electron relay and separation. Interestingly, T<sub>1</sub>C<sub>1</sub>-400 and T<sub>1</sub>C<sub>3</sub>-400 catalysts and their reduced samples, still showed decent catalytic activity in catalyzing reduction of 4-NP without UV irradiation. As can be seen from the bar graph in Fig. 5c, the effect of UV irradiation becomes insignificant in these nanofibrous catalysts since the obtained  $k_{app}$  values for reactions with and without UV irradiation are comparable and they were not significantly different ( $P > 0.05$ ) based on an unpaired  $t$ -test. The remarkable catalytic activity of T<sub>1</sub>C<sub>1</sub>-400<sub>5</sub> and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> samples could be attributed to the effective adsorption of 4-NP and borohydride anions on Cu-CuO-TiO<sub>2</sub> catalytic surface, which bears positively charged CuO, and a rapid interfacial electron transfer from donor BH<sub>4</sub><sup>-</sup> to acceptor 4-NP via Cu mediator. It is also worth noting that T-400 sample composed of pure

anatase gave no 4-NP conversion in the absence of UV irradiation, which implies that the reduction of 4-NP to 4-AP mediated by TiO<sub>2</sub> does not occur without the formation of photogenerated charge carriers.

### 3.3.3. Kinetic analysis of the 4-NP reduction reaction

Both catalytic and photocatalytic reduction of 4-NP to 4-AP in the presence of excess NaBH<sub>4</sub> were assumed to follow pseudo-first-order kinetics and the corresponding kinetic plots of  $\ln(C_t/C_0)$  versus time are depicted in Fig. 5. As can be seen, a good fit between experimental data and the kinetic model was obtained, which is confirmed by the coefficient of determination ( $R^2$ ) values greater than 0.98. Table 3 summarizes the obtained  $k_{app}$  values of the as-prepared nanofibrous catalysts in this study.

**Table 3.** The apparent pseudo-first-order rate constants ( $k_{app}$ ) for 4-NP reduction with NaBH<sub>4</sub> at room temperature catalyzed by various nanofibrous mats in the presence and absence of

UV irradiation

Samples	UV irradiation						
	T-400	T <sub>6</sub> C <sub>1</sub> -400	T <sub>3</sub> C <sub>1</sub> -400	T <sub>1</sub> C <sub>1</sub> -400	T <sub>1</sub> C <sub>3</sub> -400	T <sub>1</sub> C <sub>3</sub> -400 <sub>5</sub>	
$k_{app}$ (min <sup>-1</sup> )	UV	0.024	0.181	0.246	0.295	0.410	0.500
	No irradiation	-	0.066	0.104	0.146	0.248	0.419
$t_{99-UV}$ (min)*	Experimental		≈26	≈18	≈14	≈12	≈10
	Prediction RSE	191.9	25.4	18.7	15.6	11.2	9.2

\* $t_{99}$  represents the time required to achieve a 99% conversion for 4-NP. RSE was calculated from the difference between experimental and predicted values.

It is noted that the  $k_{app}$  values of T<sub>n</sub>C<sub>m</sub>-400<sub>5</sub> nanofiber samples are higher than those obtained for T<sub>n</sub>C<sub>m</sub>-400 samples and more interestingly, the difference in the rate constant values becomes greater (about fold) as the amount of copper loading in the catalyst increases. This result once again stresses the importance of metallic copper phase on the catalytic solid

surface to facilitate rapid interfacial electron transfer between 4-NP and  $\text{BH}_4^-$  anions. Among the fabricated nanofibrous catalysts,  $\text{T}_1\text{C}_3\text{-400}_5$  nanofiber sample exhibited the highest catalytic activity toward 4-NP reduction, with the  $k_{\text{app}}$  values of 0.50 and 0.42  $\text{min}^{-1}$  for reactions with and without UV irradiation, respectively. The catalytic activity of  $\text{T}_1\text{C}_3\text{-400}_5$  nanofiber is also comparable with some other metallic and non-metal catalysts reported in literatures<sup>1, 13, 15, 38, 39</sup>. For convenience of the catalytic performance comparison, the normalized kinetic parameter ( $k_n$ ) proposed by Liu *et. al*<sup>38</sup>. was used, which has the following mathematical expression (Eq 5):

$$k_n(\text{mmol g}^{-1} \text{min}^{-1}) = \frac{C_0}{m} \times k_{\text{app}} \quad (5)$$

where  $C_0$ ,  $V$ , and  $m$  refer to the initial concentration of 4-NP (mM), volume of 4-NP solution (L), and mass of the catalyst (g), respectively.

The catalytic activity of  $\text{T}_1\text{C}_3\text{-400}_5$  nanofiber outperforms that of many other 4-NP reduction catalysts reported so far in the literature, giving relatively high  $k_n$  values of 1.89 and 2.25  $\text{mmol g}^{-1} \text{min}^{-1}$  in the absence and presence of UV exposure. It is obvious that the catalysis performances are strongly influenced by Cu content in the nanofiber catalyst, in which as Cu content in the nanofiber increases, the  $k_{\text{app}}$  increases as shown by ICP results in Table S1. However, there is no significant alteration for metal content between  $\text{T}_1\text{C}_3\text{-400}$  and  $\text{T}_1\text{C}_3\text{-400}_5$  nanofibers. Other than that, the excellent catalytic activity by  $\text{T}_1\text{C}_3\text{-400}_5$  is also supported by the BET results which possesses the largest surface area, pore volume, and pore size. Compared with several noble-metal based composite nanocatalysts<sup>38-40</sup>, the present bimetallic catalytic system utilizing earth-abundant elements (Cu & Ti) exhibits a comparable or even better catalytic performance and, more importantly, is significantly cheaper in terms of the metal price. In addition, the fabricated  $\text{T}_1\text{C}_3\text{-400}_5$  nanofiber displayed superior activity for the reduction of 4-NP compared to the electrospun carbon nanofibers and PVDF nanofiber mats

surface-decorated with silver nanoparticles<sup>41, 42</sup> and Pd nanoparticles loaded cyclodextrin nanofibers<sup>42</sup>. Furthermore, the relatively straightforward and cost-effective fabrication method for T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber catalyst involving electrospinning, thermal annealing, and wet chemical reduction has the potential for upscaling and is likely to be adaptable for mass production.

### 3.3.4. Thermodynamic analysis

The Arrhenius plots corresponding to several nanofibrous catalysts are given in Fig. 5d. As can be seen in the figure, all the  $k_{app}$  values for photocatalytic 4-NP reduction increase with increasing reaction temperature, showing an endothermic nature of the reaction as expected. The slopes of the linear plots, which correspond to  $-Ea/R$ , are different in magnitude for each nanofibrous sample. The calculated  $Ea$  values for T-400, T<sub>6</sub>C<sub>1</sub>-400, T<sub>1</sub>C<sub>3</sub>-400, and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber catalysts were 11.89, 8.81, 6.54, and 5.44 kJ mol<sup>-1</sup>, respectively. In this regard, the lowest  $Ea$  value was obtained for the 4-NP reduction reaction catalyzed by T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber and this correlates well with the faster transfer reaction occurred on the catalyst surface. Moreover, all the  $Ea$  values are well within typical reported values for the surface catalyzed processes (8.3-41.8 kJ mol<sup>-1</sup>). From the point of view of liquid phase adsorption, it can be also inferred that the electrostatic interactions between anions and the catalyst surface belongs to a physisorption. The calculated thermodynamic parameters of activation including  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  are presented in Table 4.

**Table 4.** Thermodynamic parameters of activation for the photocatalytic reduction of 4-NP to 4-AP over designated nanofibrous catalysts at different temperatures.

Catalysts	T / K	$\Delta G^\ddagger$ / kJ mol <sup>-1</sup>	$\Delta H^\ddagger$ / kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ / J mol <sup>-1</sup> K <sup>-1</sup>	R <sup>2</sup>
T-400	303	54.64	9.29	-149.68	0.994

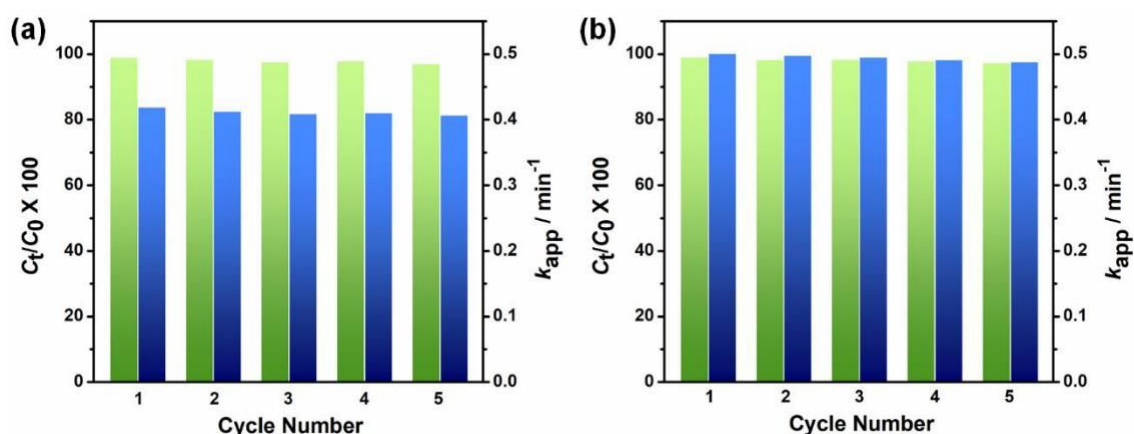
	313	56.13			
	323	57.64			
<b>T<sub>6</sub>C<sub>1</sub>-400</b>	303	53.59	6.21	-156.36	0.980
	313	55.15			
	323	56.71			
<b>T<sub>1</sub>C<sub>3</sub>-400</b>	303	51.09	3.94	-155.60	0.991
	313	52.64			
	323	54.20			
<b>T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub></b>	303	49.40	2.85	-153.64	0.982
	313	50.94			
	323	52.48			

As it can be observed, the photocatalytic reduction of 4-NP to 4-AP was nonspontaneous ( $\Delta G^\ddagger > 0$ ) and endothermic ( $\Delta H^\ddagger > 0$ ), thus this reaction requires energy or catalyst to promote the transformation of reactant to product. Further, the value of  $\Delta G^\ddagger$  becomes more positive with increasing temperature for all catalyst samples, indicating that the reduction of 4-NP becomes more facile and favorable at lower temperature. The positive value of  $\Delta G^\ddagger$  in this study also agrees well with the previous finding of Kohantorani and Gholami for catalytic reduction of 4-NP by CeO<sub>2</sub>-supported CuNi nanoparticles<sup>43</sup>, as well as for the Fenton-like photooxidation reaction<sup>44</sup>. The  $\Delta H^\ddagger$  values, which represent energy differences between the ground state and the transition state in a chemical reaction, are consistent and follow the same trend as the  $E_a$  results:  $T_1C_3-400_5 < T_1C_3-400 < T_6C_1-400 < T-400$ . The decrease in the positive values of  $\Delta H^\ddagger$  indicates less energy would be required for the reaction to proceed to completion using T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber than the other nanofibrous samples. Meanwhile, the negative values of  $\Delta S^\ddagger$  suggest loss of entropy due to a decrease in the randomness degree and the presence of an associative mechanism on forming the transition state for the catalytic reduction of 4-NP to 4-AP. This situation is frequently encountered in most bimolecular reactions, where two reactant molecules (i.e., 4-NP and BH<sub>4</sub><sup>-</sup>) come together on catalytic surfaces to form product (4-AP). Thus, from the chemical thermodynamics' viewpoint, it can be implied that T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub>

nanofiber was the best performing catalyst for facilitating the reduction of 4-NP to 4-AP, having the smallest  $E_a$  and  $\Delta H^\ddagger$  values.

### 3.4. Reusability test of the nanofibrous catalysts

The reusability and stability of the catalyst are important aspects to take into account for practical applications since they contribute toward lowering of the overall cost of the process. Therefore, the photocatalytic stability of  $T_1C_3-400$  and  $T_1C_3-400_5$  nanofibers was evaluated in five successive 4-NP reduction experiments. As can be seen in Fig. 6 (panels a and b), the as-prepared  $T_1C_3-400$  and  $T_1C_3-400_5$  nanofibers displayed satisfactory photocatalytic stability with respect to the  $k_{app}$  values and conversion efficiency after five consecutive catalytic runs. In this regard, the  $k_{app}$  values do not significantly change compared to the original one, while the catalytic conversion efficiency remains constant at 97% or above across the five runs for both nanofibrous catalysts. Moreover, the nanofibrous morphology of  $T_1C_3-400$  ( $CuO-TiO_2$ ) and  $T_1C_3-400_5$  ( $Cu-CuO-TiO_2$ ) catalysts may also facilitate the separation process of these solids from the solution after reaction, for example simply by filtration, compared to powdery catalysts that require tedious and time-consuming centrifugation/redispersion cycles. [Table 5 shows the kinetic parameter of 4-NP conversion using different catalysts as reported previously. This work using  \$T\_1C\_3-400\_5\$  nanofiber outperforms other catalysts for 4-NP reduction to 4-AP.](#)



**Figure 6.** Cycling tests of (a) T<sub>1</sub>C<sub>3</sub>-400 and (b) T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber for photocatalytic reduction of 4-NP to 4-AP over five cycles with respect to the apparent rate constant ( $k_{app}$ , blue bars) and conversion efficiency ( $C_t/C_0 \times 100$ , green bars).

**Table. 5** Comparison with the state-of-the-art literature of 4-NP conversion under different catalysts.

<u>Materials</u>	<u>Size (nm)</u>	<u><math>k_n</math> (mmol g<sup>-1</sup> min<sup>-1</sup>)</u>	<u>Light source</u>	<u>Ref.</u>
<u>Ag-TiO<sub>2</sub></u>	<u>19</u>	<u>0.036</u>	<u>Visible light</u>	45
<u>ZnO-NCP</u>	<u>100</u>	<u>0.0008</u>	<u>UV light</u>	46
<u>NdPc<sub>2</sub>-TiO<sub>2</sub></u>	<u>-</u>	<u>0.008</u>	<u>UV light</u>	47
<u>Pd-TiO<sub>2</sub></u>	<u>7</u>	<u>0.432</u>	<u>-</u>	48
<u>CuO</u>	<u>20</u>	<u>2.343</u>	<u>-</u>	49
<u>Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>-Ag</u>	<u>200</u>	<u>1.527</u>	<u>-</u>	50
<b><u>T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub></u></b>	<b><u>20-30</u></b>	<b><u>2.251</u></b>	<b><u>UV light</u></b>	<b><u>[this work]</u></b>

#### 4. Conclusions

In summary, we have successfully demonstrated in this study the composition-controlled fabrication of bimetallic copper-titania nanofibrous mats via a combination of electrospinning and thermal annealing processes. XRD results confirm the coexistence of Cu, CuO, and TiO<sub>2</sub> crystalline phases in the nanofibrous catalysts after NaBH<sub>4</sub> immersion treatment, meanwhile the conversion of Cu<sup>2+</sup> to Cu<sup>0</sup> after reduction by NaBH<sub>4</sub> was successfully revealed by XPS results. Among the fabricated bimetallic nanofibrous catalysts, T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> fiber mat with coexisting Cu, CuO, and TiO<sub>2</sub> phases was found to be the best performing catalyst toward 4-NP reduction reaction with and without UV irradiation, giving the  $k_{app}$  values of 0.50 and 0.42 min<sup>-1</sup>, respectively. The excellent catalytic activity demonstrated by The high catalytic activity of T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> could be attributed can be ascribed to the interplay of electron



separations from CuO and efficient ~~mediated by Cu species, as well as efficient~~ electron transfer ~~by Cu species. In addition, T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> also exhibits the largest surface area, pore volume, and pore size among other nanofiber catalysts as indicated by BET results.~~ Based on the thermodynamic analysis of the activation parameters, the photocatalytic reduction of 4-NP to 4-AP was endothermic and nonspontaneous where the reaction was favored at a low enthalpy value with T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> as the catalyst. The as-fabricated T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibrous catalyst is also stable and proved to be reusable for five consecutive reaction cycles without appreciable loss in activity, affording the 4-NP conversions of at least 97%. To this end, this free-standing and low cost bimetallic nanofibrous catalyst demonstrates its commercial potential to be implemented in industrial water and wastewater treatment containing nitroaromatic compounds.

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Material Design of Bimetallic Catalysts on Nanofibers for Highly Efficient Catalytic Reduction of 4-Nitrophenol

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**Graphical Abstract:**

**Abstract**

In this study, CuO-TiO<sub>2</sub> nanofiber catalysts were fabricated by an electrospinning process, followed by thermal annealing at various temperatures ranging from 300 to 700 °C. The phase transformation from CuO to metallic Cu was carried out through immersion treatment in NaBH<sub>4</sub> solution. The resulting CuO-TiO<sub>2</sub> and Cu-CuO-TiO<sub>2</sub> nanofibrous mats were characterized by scanning electron microscopy (SEM), ~~transmission~~transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) analysis. The results revealed that the crystalline phase composition of the nanofibrous mats considerably affected the efficiency of ~~the~~photocatalytic reduction, where the CuO-TiO<sub>2</sub> catalysts with a predominant anatase content was found to be more photoactive than ~~the~~rutile phase. Similarly, the presence of both Cu and CuO species was more beneficial for promoting the activity of fibers by acting as an interim location for facilitating the electron transfer. The fabricated Cu-CuO-TiO<sub>2</sub> nanofibrous mat with a ratio presented high conversion (~~~~~99%) within several minutes with the apparent pseudo-first-order rate constant of 0.42 and 0.50 min<sup>-1</sup> in the absence and presence of UV light irradiation, as well as excellent stability in recycling runs with a stable conversion efficiency of 97% or higher over five successive catalytic cycles.

## Keywords

~~e~~Electrospinning

~~n~~Nanofiber

~~b~~Bimetallic

~~r~~Reduction

4-~~Nitrophenol~~nitrophenol

## 1. Introduction



~~The p~~Polluted freshwater resources remain as one of the global challenges in this century, which ~~has~~ directly impact ~~to~~ ~~the~~ environmental and economy ~~ie problems~~. Among the organic pollutants contained in ~~the~~ polluted water, nitroaromatic compounds ~~are had been~~ found to be the most common and severely toxic chemicals, ~~because~~ of their highly ~~stabl~~stability~~e~~, water solubility~~e~~,<sup>1</sup> and ~~induce~~ carcinogenic effects even at low concentrations.<sup>2,3</sup> ~~An E~~Example of nitroaromatic compounds is 4-nitrophenol (4-NP), which ~~is are~~ categorized as ~~a~~ toxic pollutant by ~~the~~ Environmental Protection Agency, with ~~a the~~ limit concentration of 1—20 ppb<sup>1</sup>. ~~It is because~~ 4-NP has been widely used particularly for industrial applications (e.g., dyestuff, pesticide, explosives, etc.). The negative effects of nitrophenol exposure on human are dizziness, skin irritation, and organ disfunction.

~~Furthermore~~~~Even worse~~, the presence of this toxic organic chemical in water bodies could harm the marine biota, which further bring the domino-effect to humans ~~s~~ through the food chain.<sup>4</sup> Therefore, there has been a tremendous number of efforts dedicated to purify the contaminated water and wastewater to ensure a clean and healthy environment. Several methods are currently employed to remove nitrophenol in water bodies such as photolysis, electrolysis, adsorption, and Fenton reaction.<sup>5-7</sup> However, most of the aforementioned techniques are restricted for practical applications with low efficiency. Catalytic reduction approach has drawn attention from researchers owing to its highly efficient and large-scale process to convert 4-NP to 4-aminophenol (4-AP) on a nanostructured catalyst and is considered to be sustainable and economically friendly as well. Hence, materials design with high specific surface area, active sites, and robust durability is required to be developed.<sup>8</sup>

In the past few decades, the development of nanomaterials particularly for reduction of 4-NP to 4-AP involved ~~a~~ nanosized noble metal,<sup>9-11</sup> carbon-based materials,<sup>12,13</sup> and transition metals.<sup>14,15</sup> Specifically, bimetallic materials ~~s~~ provides superior catalytic performances arising from their synergetic combination of two kinds of metals. For instance,

Pt-Ni bimetallic possesses better catalytic activity and corrosion resistance as compared to Pt metallic alone for 4-NP reduction assisted with NaBH<sub>4</sub>.<sup>16</sup> Pozun *et al.* reported a higher reaction rate constant of bimetallic dendrimer encapsulated nanoparticles (DENS), where two metals were alloyed to trigger faster reaction rates as compared to their monometallic catalysts.<sup>17</sup> Regardless, previous works suffer from the expensive noble metal price and have serious issues for commercial production. Thus, the utilization of transition metals to replace noble metals not only would benefit economically, but is also potential for large-scale production. As for the transition metal, copper is a good choice since Cu is an abundant resource and a highly active element with varied oxidation states.<sup>18</sup> Another candidate is accompanied by titanium; Ti is a low-cost material, highly stable, and strong oxidizer.<sup>19</sup> Furthermore, the improvement in terms of reusability purpose could be applied by embedding the bimetallic catalysts into a nanofibrous structure material, which also enhances the surface area due to its highly porous network.<sup>20</sup>

To date, no studies reported the synthesis of the copper-titania bimetallic catalyst on nanofibers with tunable phase compositions for catalytic reduction of 4-NP to 4-AP. With this regard in mind, a material design of copper-titania (Cu-Ti) bimetallic embedded in PVP nanofibers was synthesized by electrospinning process followed by reduction reaction. The as-prepared nanofibrous bimetallic catalyst was applied for catalytic reduction of 4-NP to 4-AP. In addition, the kinetics and thermodynamics of Cu-Ti bimetallic nanofibrous catalysts are thoroughly discussed in this study.

## 2. Materials and Methods

### 2.1. Chemicals

PVP (MW = 40,000 g/mol), sodium borohydride (NaBH<sub>4</sub>, 98%), 4-NP (Echo chemicals, 99%), copper(II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Sigma Aldrich, 99.5%), and tetrabutyl titanate (TT, Sigma Aldrich, 97%) were used as received without any purification.

## 2.2. Preparation of Cu-Ti bimetallic nanofibers

In a typical experiment, the Cu-Ti bimetallic nanofibrous catalyst was fabricated by mixing Cu(NO<sub>3</sub>)<sub>2</sub> and TT-PVP as copper and titanium sources, respectively. The titanium precursor solution was prepared via a sol-gel method by stirring ethanol, acetic acid, and TT at an ambient temperature for min. Subsequently, 2-g of PVP was added and stirred until homogeneous. Then, Cu(NO<sub>3</sub>)<sub>2</sub> solution in ethanol was added into TT-PVP solution. The resulting viscous solution was transferred to a plastic syringe equipped with a stainless steel blunt-ended needle. Electrospinning was conducted at 20-kV, with a speed rate of 0.01-mL/h, and a distance of 15-cm between the tip of the needle and drum collector. The as-obtained nanofibers were then stored in an electric oven at 65-°C to avoid moisture and later used for further characterizations. The formulation of different copper and titanium precursors isare tabulated in Table 1 and abbreviated as T<sub>n</sub>C<sub>m</sub>, where n and m represent the concentrations of titanium and copper precursors, respectively.

Table 1. Composition of Electrospinning Copper-Titanium bimetallic nanofibers

Samples	Solution composition		Ø (nm)
	TT (wt %)	Cu(NO <sub>3</sub> ) <sub>2</sub> (wt %)	
T <sub>6</sub> C <sub>1</sub>	6	1	508 ± 143
T <sub>3</sub> C <sub>1</sub>	3	1	655 ± 74
T <sub>1</sub> C <sub>1</sub>	1	1	344 ± 70
T <sub>1</sub> C <sub>3</sub>	1	3	760 ± 220
TT-PVP	6	-	426 ± 67

The thermal crosslinking process of  $T_nC_m$  PVP nanofibers was carried out at 180 °C for 3 h in an electric muffle furnace under air atmosphere.  $T_nC_m$  PVP nanofibers were further annealed at 300–700 °C for 30 min with a heating ramp of 10 °C/min. The annealed nanofibers products were named as  $T_nC_m-X$ , where  $X$  denotes the annealing temperature. To reduce  $Cu^{2+}$  to metallic copper ( $Cu^0$ ),  $T_nC_m-X$  nanofibers were simply immersed in  $NaBH_4$  solution at different immersion times and the samples were named as  $T_nC_m-X_r$ , where  $r$  represents the reduction time.

### 2.3. Materials Characterizations

The surface morphology of the prepared nanofibers was observed using field emission scanning electron microscopy (FE-SEM, JEOL JSM-7900) with an accelerating voltage of 30 kV equipped with an energy dispersive X-ray (EDX) detector for elemental composition and transmission electron microscopy (TEM, JEOL 2000FX). The crystallinity and phase identification of samples were examined using X-ray diffraction (XRD, Bruker D2 Phaser) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250) analyses. Inductively coupled plasma atomic emission spectra (ICP-AES, Shimadzu ICPE-9800) analysis was used to determine the titanium and copper content in the obtained nanofibers. The surface area of the heterogeneous catalyst was further studied by BET analysis.

### 2.4. Catalytic Experiments

The catalytic performances of bimetallic nanofibers were evaluated at dark and UV-light irradiated conditions. In a typical experiment, ~2 mg of bimetallic nanofibers was dispersed in 4-NP solution with a concentration of 0.5 mM. Prior to photocatalytic reaction, the dispersion was stirred for 30 min under dark conditions to reach the adsorption-desorption equilibrium. Afterwards, 5 mL of 0.1 M  $NaBH_4$  was dropwise added and, at the same time, irradiated with UV light while stirring. The aliquot was taken after a

certain period of time and further analyzed using a UV-vis spectrophotometer (Jasco V-650). The reusability performances of bimetallic nanofibers were also tested on five consecutive cycles experiments.

## 2.5. Kinetic and Thermodynamic Analysis

The kinetics of catalytic and photocatalytic 4-NP reduction reaction in the presence of bimetallic nanofibers were studied by monitoring the changes in absorbance of 4-nitrophenolate ions at  $\lambda_{\max} = 400$  nm at different time intervals. In this model reaction, the kinetics of 4-NP reduction in the presence of excess  $\text{NaBH}_4$  can be assumed to follow a pseudo-first-order model. The reaction rate constant with respect to 4-nitrophenolate ions can be expressed as follows (Eq 1):

$$-\ln\left(\frac{C_t}{C_0}\right) = -\ln\left(\frac{A_t}{A_0}\right) = k_t t \quad (1)$$

where  $A_t$  and  $A_0$  refer to the absorbance of 4-nitrophenolate ions at times  $t$  and 0, respectively, while  $C_t$  and  $C_0$  are the equivalent concentrations of the same species at times  $t$  and 0, respectively. The apparent rate constant ( $k_{\text{app}}$ ) can be obtained from the slope of the linear plot of  $-\ln(A_t/A_0)$  versus time.

The thermodynamic aspect of the reaction, such as predicting the apparent activation energy ( $E_a$ ), the enthalpy of activation ( $\Delta H^\ddagger$ ), and the Gibbs energy of activation ( $\Delta G^\ddagger$ ), was investigated by conducting the 4-NP reduction experiments at different temperatures (i.e., 303, 313, and 323 K). The  $E_a$  ( $\text{kJ mol}^{-1}$ ) can be calculated from the slope of the Arrhenius plot describing a linear relationship between the logarithm of the rate constant ( $k_{\text{app}}$ ) and the inverse of absolute temperature ( $1/T$ ) according to the following equation (Eq 2):

$$\ln k_{\text{app}} = -\frac{E_a}{RT} + \ln A \quad (2)$$

where  $R$  and  $A$  denote the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and pre-exponential factor related to the steric effect and collision frequency, respectively. The values of the

enthalpy and entropy of activation ( $\Delta S^\ddagger$ ) can be obtained from the Eyring equation (Eq. 3 and 4), describing a linear relationship between the reaction rate and temperature<sup>21</sup>:

$$\ln\left(\frac{k_{app}}{T}\right) = \frac{-\Delta H}{R} \frac{1}{T} + \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S}{R} \quad (3)$$

$$\Delta G^\ddagger = -\Delta H^\ddagger - T\Delta S^\ddagger \quad (4)$$

where  $k_B$  and  $h$  are the Boltzmann's ( $1.38 \times 10^{-23} \text{ J K}^{-1}$ ) and Planck's constant ( $6.63 \times 10^{-34} \text{ J s}$ ), respectively.

### 3. Results and Discussion

#### 3.1. Morphology of Bimetallic Nanofibers

The surface morphology of  $T_nC_m$  PVP nanofibers is shown in Figure 1. From this figure, it can be seen that all the fibers exhibited a smooth and uniform surface without discernable bead defects. The average diameter of  $T_nC_m$  PVP nanofibers was found to be affected by the precursor solution composition, particularly the titanium-to-copper ratio. The addition of metal salt into the polymer solution was also reported to affect the spinnability of the polymer jet since it will increase the number of ions and conductivity. Generally speaking, a more conductive and viscous solution results in the formation of a thinner nanofiber. In this regard, the average diameter of the  $T_nC_m$  PVP nanofibers decreased from  $508 \pm 143$  to  $355 \pm 74$  and  $344 \pm 70$  nm with a decreasing titanium content in the solution ( $T_6C_1$  to  $T_1C_1$ ); meanwhile, it is bigger in size with increasing copper content ( $T_1C_3$ ), which might be due to hygroscopic properties of copper nitrate precursors. As can be seen in Table 2, the average diameter of as-spun nanofibers was varied in between 94 and 513 nm. Moreover, BET results showed that aT-400 possesses surface area of  $173.1 \text{ m}^2 \text{ g}^{-1}$ , pore volume of 19.6, and pore size of 3.1 nm. The surface area, pore volume, and pore size of nanofiber catalysts gradually decreased with a decreasing Ti concentration ( $T_6C_1$  to  $T_1C_1$ ) as

shown in Table S1. Interestingly, the surface area, pore volume, and pore size of nanofiber significantly increased after reducing by NaBH<sub>4</sub> (T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub>).

Figure 1. SEM images of as-spun fibers of (a) TT-PVP, (b) T<sub>6</sub>C<sub>1</sub>, (c) T<sub>3</sub>C<sub>1</sub>, (d) T<sub>1</sub>C<sub>1</sub>, (e) T<sub>1</sub>C<sub>3</sub>, and (f) Cu-PVP. The scale bar in all figures is 1 μm.

Table 2. Average diameter and crystalline phase composition of T<sub>n</sub>C<sub>m</sub>-400 and T<sub>n</sub>C<sub>m</sub>-400<sub>5</sub> nanofiber catalysts.

Catalyst	∅ (nm)	Crystal phases	TiO <sub>2</sub> crystallinity	
			Anatase anatase (wt %)	Rutile rutile (wt %)
T-400	129 ± 28	TiO <sub>2</sub>	83.7	16.3
T <sub>6</sub> C <sub>1</sub> -300	513 ± 59	Amorphous	ND	ND
T <sub>6</sub> C <sub>1</sub> -400	189 ± 45		85.7	14.3
T <sub>6</sub> C <sub>1</sub> -500	313 ± 89	TiO <sub>2</sub>	72.4	27.6
T <sub>6</sub> C <sub>1</sub> -600	204 ± 52		27.8	72.2
T <sub>6</sub> C <sub>1</sub> -700	273 ± 74		ND	100
T <sub>3</sub> C <sub>1</sub> -400	124 ± 28	TiO <sub>2</sub> , CuO	83.4	16.6
T <sub>1</sub> C <sub>1</sub> -400	175 ± 42		86.2	13.8
T <sub>3</sub> C <sub>1</sub> -400	201 ± 87	TiO <sub>2</sub>	85.4	14.6
T <sub>6</sub> C <sub>1</sub> -400 <sub>5</sub>	203 ± 23		85.0	15.0
T <sub>3</sub> C <sub>1</sub> -400 <sub>5</sub>	94 ± 23	TiO <sub>2</sub> , CuO, Cu	81.0	19.0
T <sub>1</sub> C <sub>1</sub> -400 <sub>5</sub>	91 ± 23		83.6	26.4
T <sub>1</sub> C <sub>3</sub> -400 <sub>5</sub>	223 ± 59		100	ND

Figure 2 depicts the morphology of T<sub>n</sub>C<sub>m</sub> PVP nanofibers annealed at 400 °C. From this figure, it can be seen that all the annealed fibers had a significantly smaller diameter than



the precursor fibers, which could be attributed to the thermal decomposition of the polymer matrix. Previous reports have shown that PVP decomposes upon heating in [the](#) air at temperatures between 350 and 400 °C.<sup>22,23</sup> The formation of such metal oxide agglomerates can be ascribed to the activation and diffusion-controlled neck growth of Ti and Cu atoms by thermal energy ~~to form~~. This also suggests that thermal annealing at 400 °C can induce the formation of crystalline metal oxide phases (i.e., TiO<sub>2</sub> and CuO); both of which are beneficial for catalytic reactions. Additionally, one can also notice that Cu nanoparticles are uniformly decorated on the surface of T<sub>n</sub>C<sub>m</sub>-400<sub>5</sub> nanofibers prepared from ~~the~~ electrospinning solutions with higher concentrations of copper salt, providing more catalytic active sites for 4-NP reduction. Furthermore, TEM analysis shows that the nanostructure of T<sub>1</sub>C<sub>3</sub> (without annealing) was found to be agglomerated as shown in Figure [2m](#). These agglomerates ~~containing were~~ then become slightly separated after annealing, T<sub>1</sub>C<sub>3</sub>-400 (Figure [2n](#)), and after reducing by NaBH<sub>4</sub>, the obtained particles were [of](#) irregular shape without any agglomeration with the average size of 20–30 nm as can be seen in Figure [2o](#). In addition, the elemental composition of T<sub>1</sub>C<sub>3</sub>-400 and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers was analyzed by EDX analysis as the representatives of CuO–TiO<sub>2</sub> and Cu–CuO–TiO<sub>2</sub> crystal phases as shown in [Figure S1](#). The EDX spectra showed that the atomic [percentage%](#) of O decreased after reducing [using](#) NaBH<sub>4</sub> from 17% to 14.2%, and the amount of Ti and Cu slightly increased, indicating that CuO in T<sub>1</sub>C<sub>3</sub>-400 was transformed into Cu<sup>0</sup> in T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub>.

**Figure 2.** SEM images of annealed T<sub>n</sub>C<sub>m</sub> PVP nanofiber: (a) T<sub>6</sub>C<sub>1</sub>, (b) T<sub>3</sub>C<sub>1</sub>, (c) T<sub>1</sub>C<sub>1</sub>, and (d) T<sub>1</sub>C<sub>3</sub>. SEM micrographs (e–h) of the nanofibrous mats corresponding to panels a–d after immersion in NaBH<sub>4</sub> solution for 5 min to reduce CuO to metallic Cu. SEM images of (i) T-400 nanofiber and T<sub>6</sub>C<sub>1</sub> nanofibers annealed at (j) 500 °C, (k) 600 °C, and (l) 700 °C. TEM images of (m) T<sub>1</sub>C<sub>3</sub>, (n) T<sub>1</sub>C<sub>3</sub>-400, and (o) T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers. The scale bar for SEM images represents 1 μm.

### 3.2. Crystal Phase and Composition of the Bimetallic Nanofibrous Mats

The XRD patterns of the fabricated bimetallic nanofibrous mats are presented in Figure 3. As can be seen in the figure, there are no characteristic Bragg reflections associated with the crystal structures of  $\text{TiO}_2$  and copper oxides for the  $\text{T}_6\text{C}_1$ -300 sample, indicating the amorphous nature of the fibers. On the contrary, the XRD patterns of  $\text{T}_6\text{C}_1$ -400,  $\text{T}_6\text{C}_1$ -500,  $\text{T}_6\text{C}_1$ -600, and  $\text{T}_6\text{C}_1$ -700 nanofibers contain several sharp and intense Bragg reflections corresponding to the  $\text{TiO}_2$  polymorphs following thermal annealing at higher temperatures. The assignment of the crystalline phases was based on the reference files Joint Committee on Powder Diffraction Standards (JCPDS) No. 21-1272, No. 21-1276, No. 45-0937, and No. 04-0836 for anatase  $\text{TiO}_2$ , rutile  $\text{TiO}_2$ ,  $\text{CuO}$ , and metallic  $\text{Cu}$ , respectively. On the other hand, there is a tiny peak assigned for  $\text{Cu}_2\text{O}$  observed at  $44^\circ$  after  $\text{T}_6\text{C}_1$  annealed at 600 and  $700^\circ\text{C}$  as can be seen in Figure 3iv and v. The results demonstrate that the formation of the two crystalline phases strongly depends on the annealing temperature,<sup>17,24</sup> where  $\text{T}_6\text{C}_1$ -400,  $\text{T}_6\text{C}_1$ -500, and  $\text{T}_6\text{C}_1$ -600 samples exhibited a mixed anatase-rutile phase and the  $\text{T}_6\text{C}_1$ -700 sample comprised only the rutile phase (Table 2). Meanwhile, no appreciable copper oxide species could be observed in the XRD patterns of these samples, probably because of low concentration and also because the main reflections of copper oxides overlap those of anatase and rutile  $\text{TiO}_2$ . Panels (vi), (vii), and (viii) show the diffraction patterns of  $\text{T}_6\text{C}_1$ -400,  $\text{T}_1\text{C}_1$ -400, and  $\text{T}_1\text{C}_3$ -400 nanofibers after the immersion treatment in  $\text{NaBH}_4$  solution. In addition to reflections from  $\text{TiO}_2$  polymorphs, new reflections associated to copper phases between  $30^\circ$  and  $50^\circ$  appear. Moreover, it can be observed that the Bragg peaks assigned to monoclinic  $\text{CuO}$  at  $2\theta$  become sharper and more intense in  $\text{T}_1\text{C}_1$ -400 and  $\text{T}_1\text{C}_3$ -400 nanofibers with a higher amount of copper loading. For all  $\text{T}_n\text{C}_m$ -X samples, no traces of the

cubic Cu<sub>2</sub>O phase were found, indicating the complete thermal oxidation of amorphous Cu to CuO ( $2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}$ ) under annealing treatment at 400 °C and beyond in air atmosphere. This phase transition is in good agreement with the results reported by De Los Santos Valladares *et al.*<sup>25</sup> Thus, it can be implied that the coexistence of both active TiO<sub>2</sub> with a predominant anatase phase and copper/copper oxide phases on T<sub>n</sub>C<sub>m</sub>-X nanofibers is beneficial for facilitating catalytic reduction of 4-NP to 4-AP.

Furthermore, Figure 3b and e, c shows show the high-resolution XPS spectra of the Cu element in T<sub>1</sub>C<sub>3</sub>-400 and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers. Both XPS spectra exhibited Cu<sup>+</sup> 2p<sub>3/2</sub>, Cu<sup>+</sup> 2p<sub>1/2</sub>, Cu<sup>2+</sup> 2p<sub>3/2</sub>, and Cu<sup>2+</sup> 2p<sub>1/2</sub> peaks which located at 932.8, 952.2, 935.4, and 954.8 eV, respectively, and were also accompanied by their satellite peaks of Cu<sup>2+</sup> at 944.8 and 963.5 eV.<sup>26</sup> By comparing the peak intensity in Figure 3b and e, c, the peaks for Cu<sup>2+</sup> and Cu<sup>+</sup> including the satellite peaks decreased after reduction using NaBH<sub>4</sub>.<sup>27</sup> Also, there is one additional set of Cu<sup>0</sup> 2p peaks located 930.8 and 950.5 eV in the T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber (Figure 3e), Therefore, this phenomenon successfully revealed that Cu<sup>2+</sup> in T<sub>1</sub>C<sub>3</sub>-400 was converted to Cu<sup>0</sup> in the T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber.

**Figure 3.** (a) Wide angle XRD patterns of the T<sub>6</sub>C<sub>1</sub> nanofiber annealed at (i) 300, (ii) 400, (iii) 500, (iv) 600, and (v) 700 °C; (vi) T<sub>6</sub>C<sub>1</sub>, (vii) T<sub>1</sub>C<sub>1</sub>, and (viii) T<sub>1</sub>C<sub>3</sub> nanofibers after being annealed at 400 °C for 30 min and immersed in NaBH<sub>4</sub> solution for 5 min.

Diffraction peaks corresponding to the anatase TiO<sub>2</sub>, rutile TiO<sub>2</sub>, CuO, and metallic Cu phases are denoted by “A”, “R”, circles, and triangles, respectively. High-resolution XPS spectra of the Cu element in (b) T<sub>1</sub>C<sub>3</sub>-400 and (c) T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers.

### 3.3. Photocatalytic Activities of Bimetallic Nanofibers

The catalytic and photocatalytic activities of the fabricated electrospun samples were evaluated for reduction reaction of 4-NP to 4-AP in the aqueous phase at room temperature. The pH of the 4-NP solution before and after the addition of NaBH<sub>4</sub> was measured using a

microelectrode pH meter and found to be around 7.2 and 9.6, respectively. In this model reaction, the reduction of 4-NP by  $\text{BH}_4^-$  does not occur in the absence of [the](#) catalyst since there was neither color change from yellow to transparent observable by naked eyes nor a gradual decrease in the absorbance maxima of 400-nm corresponding to 4-nitrophenolate ions with time. Similar results were observed for [the](#)  $\text{T}_6\text{C}_1$  sample with amorphous copper and  $\text{TiO}_2$  phases as the catalyst, showing negligible photocatalytic activity (Figure [4aa](#)). [The](#) [P](#)pure anatase-rich  $\text{TiO}_2$  nanofiber shows a rather moderate catalytic activity toward 4-NP reduction, where only  $\sim$ 50% conversion was achieved after 32-min (Figure [4bb](#)). On the contrary,  $\text{T}_n\text{C}_m$ -400 nanofibers with different bimetallic compositions and crystalline phases demonstrate high photocatalytic activity for 4-NP reduction, as shown in Figure [4e-fc-f](#). As can be seen from these figures, the complete conversion of 4-NP to 4-AP was achieved after 10–20-min of reaction at room temperature without formation of side products, as confirmed by two isosbestic points at 280 and 314-nm.<sup>12</sup> The results also indicate that the nanofibrous mats with higher Cu/Ti ratios, for example,  $\text{T}_1\text{C}_1$ -400 and  $\text{T}_1\text{C}_3$ -400, demonstrate higher efficiency toward 4-NP reduction than [the](#)  $\text{T}_6\text{C}_1$ -400 sample, which might be attributed to the presence of [the](#) CuO phase. In this regard, [the](#) CuO phase acts as a ‘shuttle bus’ to enhance separation efficiency of [the](#) photogenerated electrons ( $e_{\text{cb}}^-$ ) and holes ( $h_{\text{vb}}^+$ ) by forming a *p-n* heterojunction interface with the electron-rich (101) facet of  $\text{TiO}_2$ . [A](#) [S](#)similar synergistic effect of photogenerated charge separation in [the](#)  $\text{CuO-TiO}_2$  heterojunction was observed for selective photo-oxidation of methanol to methyl formate<sup>28</sup> and degradation of 2,4-dichlorophenoxyacetic acid.<sup>29</sup> In addition, the positively charged CuO embedded in the surface of fiber catalysts may facilitate the adsorption of negatively charged 4-NP and hydrolyzed borohydride molecules on the surface through electrostatic interactions, leading to the elimination of [the](#) induction period and increased reaction efficiency.<sup>30</sup> Since both copper and copper oxide phases in  $\text{T}_6\text{C}_1$ -X nanofibers were hardly recognized from the

XRD results (Figure 3, panels a–e), it can be implied that the photocatalytic activities of these samples are mainly contributed by the TiO<sub>2</sub> polymorphs. The results show that the photocatalytic activity of the fibers becomes lower when the samples were annealed at higher temperatures, suggesting that [the](#) anatase T<sub>6</sub>C<sub>1</sub> nanofiber catalyst is more active than its rutile counterpart toward ~~the~~ 4-NP reduction. The  $k_{app}$  value of T<sub>6</sub>C<sub>1</sub>-400 was about 2-fold higher compared to that of [the](#) T<sub>6</sub>C<sub>1</sub>-700 sample. Similarly, Sclafani and Herrmann<sup>31</sup> and Tanaka [et al.](#)<sup>32</sup> reported better photocatalytic performance of TiO<sub>2</sub> nanoparticles with [a](#) higher anatase-to-rutile ratio for the degradation of organics in aqueous solutions. This can be attributed to the more negative conduction band energy minima of anatase that allows for a more facile electron transfer process to 4-NP and a lower recombination velocity of  $e_{cb}^-$  and  $h_{vb}^+$ , as well as a stronger adsorption affinity of 4-NP molecules toward the anatase (101) surface compared to that on [the](#) rutile (110) surface.<sup>33</sup> The latter factor is thought to play a major role in the process since the reduction of 4-NP involves a key step in which the electron was transferred from donor BH<sub>4</sub><sup>-</sup> to the acceptor 4-NP.<sup>8,34</sup> Moreover, the existence of a minor rutile phase in the T<sub>6</sub>C<sub>1</sub>-400 sample may also [be](#) beneficial for the separation of photogenerated charge carriers since  $h_{vb}^+$  will preferentially move to rutile owing to its higher valence band maximum energy.<sup>25,35</sup> Therefore, an annealing temperature of 400 °C was chosen in this study to prepare photoactive anatase T<sub>n</sub>C<sub>m</sub> nanofibrous catalysts for subsequent catalytic testing and NaBH<sub>4</sub> reduction experiments. In addition, the use of [a](#) lower annealing temperature is energetically more feasible for large-scale manufacturing of this nanofibrous catalyst.

**Figure 4.** Time-dependent UV–vis absorption spectra of the reaction mixture consisting of 4-NP (0.2 mM), NaBH<sub>4</sub> (90 mM), and as-prepared nanofibrous catalysts, (a) crosslinked T<sub>6</sub>C<sub>1</sub>, (b) T-400, (c) T<sub>6</sub>C<sub>1</sub>-400, (d) T<sub>3</sub>C<sub>1</sub>-400, (e) T<sub>1</sub>C<sub>1</sub>-400, and (f) T<sub>1</sub>C<sub>3</sub>-400, under UV irradiation.

The blue arrows in panel (c) indicate representative four isosbestic points at 227, 244, 281, and 314 nm.

### 3.3.1. Effects of the Copper Phase Compositions

The photocatalytic activities of the anatase  $T_nC_m$ -400 nanofibers with the pure CuO phase and the mix phase Cu-CuO are shown in Figure 5. The formation of a mixed Cu-CuO phase was carried out through immersion in NaBH<sub>4</sub>, which allows the reduction of CuO to Cu with H<sub>2</sub> according to the stoichiometric reactions. To explore the effect of immersion time of the  $C_xT_y$ -400 substrates in the NaBH<sub>4</sub> aqueous solution, the photocatalytic reduction activity of these substrates after the immersion treatments for 1, 5, and 10 min was evaluated. From our experiments, the optimized reduction time by NaBH<sub>4</sub> solution was found to be 5 min. From Figure 5a and 5b, it can be shown that the  $T_nC_m$ -400<sub>5</sub> nanofiber catalysts exhibited better catalytic performance compared to their  $T_nC_m$ -400 containing only the CuO phase. The superior photocatalytic activity of the  $T_nC_m$ -400<sub>5</sub> nanofiber might be attributed to the copresence of CuO and Cu active phases, leading not only to an enhanced charge carrier separation generated from the CuO-TiO<sub>2</sub> heterojunction, but also a more efficient electron transfer between the adsorbed BH<sub>4</sub><sup>-</sup> and 4-NP molecules on the photocatalyst surface, which was facilitated by the high electrical conductivity ( $5.8 \times 10^7 \text{ S m}^{-1}$ ) of copper.<sup>36</sup> The presence of copper as a cocatalyst can also help suppress the recombination of the photoexcited electron-hole pairs in the TiO<sub>2</sub> photocatalytic system, because due to some  $e_{cb}^-$  of TiO<sub>2</sub> could transfer directly to the Cu by ohmic interconnection.<sup>37</sup> Moreover, metallic Cu embedded in the surface of the fibers can also serve as active sites to react with hydride (H<sup>+</sup>) ions generated from spontaneous hydrolysis of BH<sub>4</sub><sup>-</sup>, which upon contact with the catalyst surface donate its electrons to Cu and then combine to form H<sub>2</sub> gas.

**Figure 5.** Pseudo-first-order kinetic plots of the 4-NP reduction catalyzed by different nanofibrous mats (a) with and (b) without UV irradiation. The legend in (a) also applies to

panel (b). The correlation fitted by Eq. 1. is shown as colored dashed lines in panels (a) and (b). (c) Bar plot showing the comparisons of the  $k_{app}$  values for catalytic reduction of 4-NP in the presence and absence of UV exposure. Bars represent the mean value, and error bars show the standard error of the mean from three independent experiments ( $n=3$ ). Asterisk (\*) and 'ns' denote statistical significance at  $P < 0.05$  and no statistical significance, respectively, based on unpaired two-tailed Welch's  $t$ -test using GraphPad Prism v6.01 software. (d) Arrhenius plots for photocatalytic 4-NP reduction by T-400, T<sub>6</sub>C<sub>1</sub>-400, T<sub>1</sub>C<sub>3</sub>-400, and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers. The  $E_a$  values are equal to the negative slopes of the respective linear fits multiplied by  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) over three temperatures (303, 313, and 323 K).

### 3.3.2. Effects of UV Irradiation

The effect of UV irradiation on the catalytic activity of T<sub>n</sub>C<sub>m</sub>-400 and T<sub>n</sub>C<sub>m</sub>-400<sub>5</sub> nanofibers is shown in Figure 5a and b. From this figure, it can be seen that the reduction of 4-NP to 4-AP by T<sub>6</sub>C<sub>1</sub>-400, T<sub>3</sub>C<sub>1</sub>-400, T<sub>1</sub>C<sub>1</sub>-400, and T<sub>1</sub>C<sub>3</sub>-400 nanofiber catalysts was promoted under UV illumination. A complete conversion of 4-NP to 4-AP was achieved in shorter periods of time, within 5–10 min, compared to reactions without light irradiation. A similar trend was observed for the T<sub>n</sub>C<sub>m</sub>-400<sub>5</sub> nanofiber catalysts with the ternary Cu–CuO–TiO<sub>2</sub> phase. The reason for the promotion effect of the UV light treatment is due to the generation of charge carriers in TiO<sub>2</sub> and CuO, where the photogenerated electrons serve as an additional source of electrons to reduce 4-NP, together with efficient electron relay and separation. Interestingly, T<sub>1</sub>C<sub>1</sub>-400 and T<sub>1</sub>C<sub>3</sub>-400 catalysts and their reduced samples, still showed decent catalytic activity in catalyzing reduction of 4-NP without UV irradiation. As can be seen from the bar graph in Figure 5c, the effect of UV irradiation becomes insignificant in these nanofibrous catalysts since the obtained  $k_{app}$  values for reactions with and without UV irradiation are comparable and they were not significantly different

( $P > 0.05$ ) based on the unpaired  $t$ -test. The remarkable catalytic activity of T<sub>1</sub>C<sub>1</sub>-400<sub>5</sub> and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> samples could be attributed to the effective adsorption of 4-NP and borohydride anions on the Cu-CuO-TiO<sub>2</sub> catalytic surface, which bears positively charged CuO<sub>x</sub> and a rapid interfacial electron transfer from donor BH<sub>4</sub><sup>-</sup> to acceptor 4-NP via the Cu mediator. It is also worth noting that the T-400 sample composed of pure anatase gave no 4-NP conversion in the absence of UV irradiation, which implies that the reduction of 4-NP to 4-AP mediated by TiO<sub>2</sub> does not occur without the formation of photogenerated charge carriers.

### 3.3.3. Kinetic Analysis of the 4-NP Reduction Reaction

Both catalytic and photocatalytic reduction of 4-NP to 4-AP in the presence of excess NaBH<sub>4</sub> were assumed to follow pseudo-first-order kinetics, and the corresponding kinetic plots of  $\ln(C_t/C_0)$  versus time are depicted in Figure 5. As can be seen, a good fit between experimental data and the kinetic model was obtained, which is confirmed by the coefficient of determination ( $R^2$ ) values greater than 0.98. Table 3 summarizes the obtained  $k_{app}$  values of the as-prepared nanofibrous catalysts in this study.

Table 3. The apparent pseudo-first-order rate constants ( $k_{app}$ ) for 4-NP reduction with NaBH<sub>4</sub> at room temperature catalyzed by various nanofibrous mats in the presence and absence of UV irradiation

Sample		T-400	T <sub>6</sub> C <sub>1</sub> -400	T <sub>3</sub> C <sub>1</sub> -400	T <sub>1</sub> C <sub>1</sub> -400	T <sub>1</sub> C <sub>3</sub> -400	T <sub>1</sub> C <sub>3</sub> -400 <sub>5</sub>
$k_{app}$ (min <sup>-1</sup> )	UV	0.02	0.18	0.24	0.29	0.41	0.50
	No-irradiation	-	0.06	0.10	0.14	0.24	0.41
			6	4	6	8	9



$t_{99}$ -UV (min) <sup>a</sup>	<del>Experimental</del> experimental		≈26	≈18	≈14	≈12	≈10
	<del>Prediction</del> prediction	191.	25.4	18.7	15.6	11.2	9.2
	RSE	9					

<sup>a</sup> $t_{99}$  represents the time required to achieve a 99% conversion for 4-NP. RSE was calculated from the difference between experimental and predicted values.

It is noted that the  $k_{app}$  values of  $T_nC_m-400_5$  nanofiber samples are higher than those obtained for  $T_nC_m-400$  samples, and more interestingly, the difference in the rate constant values becomes greater (about fold) as the amount of copper loading in the catalyst increases. This result once again stresses the importance of the metallic copper phase on the catalytic solid surface to facilitate rapid interfacial electron transfer between 4-NP and  $BH_4^-$  anions. Among the fabricated nanofibrous catalysts, the  $T_1C_3-400_5$  nanofiber sample exhibited the highest catalytic activity toward 4-NP reduction, with the  $k_{app}$  values of 0.50 and 0.42  $\text{min}^{-1}$  for reactions with and without UV irradiation, respectively. The catalytic activity of the  $T_1C_3-400_5$  nanofiber is also comparable with some other metallic and non-metal catalysts reported in the literatures.<sup>1,-13,-15,-38,-39</sup> For convenience of the catalytic performance comparison, the normalized kinetic parameter ( $k_n$ ) proposed by Liu *et al.*<sup>38</sup> was used, which has the following mathematical expression (Eq-5):

$$k_n (\text{mmol g}^{-1} \text{min}^{-1}) = \frac{C_0}{m} \times k_{app} \quad (5)$$

where  $C_0$ ,  $V$ , and  $m$  refer to the initial concentration of 4-NP (mM), volume of 4-NP solution (L), and mass of the catalyst (g), respectively.

The catalytic activity of the  $T_1C_3-400_5$  nanofiber outperforms that of many other 4-NP reduction catalysts reported so far in the literature, giving relatively high  $k_n$  values of 1.89 and 2.25  $\text{mmol g}^{-1} \text{min}^{-1}$  in the absence and presence of UV exposure. It is obvious that the catalysis performances are strongly influenced by the Cu content in the nanofiber catalyst,

in which as [the](#) Cu content in the nanofiber increases, the  $k_{app}$  increases as shown by ICP results in [Table S1](#). However, there is no significant alteration [in the](#) metal content between T<sub>1</sub>C<sub>3</sub>-400 and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers. Other than [this](#), the excellent catalytic activity by T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> is also supported by the BET results, which possesses the largest surface area, pore volume, and pore size. Compared with several noble-metal-based composite nanocatalysts,<sup>38-40</sup> the present bimetallic catalytic system utilizing earth-abundant elements (Cu [and](#) Ti) exhibits a comparable or even better catalytic performance and, more importantly, is significantly cheaper in terms of [the](#) metal price. In addition, the fabricated T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber displayed superior activity for the reduction of 4-NP compared to the electrospun carbon nanofibers and PVDF nanofiber mats surface-decorated with silver nanoparticle-[s](#)<sup>41,42</sup> and Pd nanoparticle-[s](#)-loaded cyclodextrin nanofibers.<sup>42</sup> Furthermore, the relatively straightforward and cost-effective fabrication method for [the](#) T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber catalyst involving electrospinning, thermal annealing, and wet chemical reduction has the potential for upscaling and is likely to be adaptable for mass production.

### 3.3.4. Thermodynamic [A](#)nalysis

The Arrhenius plots corresponding to several nanofibrous catalysts are given in [Figure 5d](#). As can be seen in the figure, all the  $k_{app}$  values for photocatalytic 4-NP reduction increase with increasing reaction temperature, showing an endothermic nature of the reaction as expected. The slopes of the linear plots, which correspond to  $-E_a/R$ , are different in magnitude for each nanofibrous sample. The calculated  $E_a$  values for T-400, T<sub>6</sub>C<sub>1</sub>-400, T<sub>1</sub>C<sub>3</sub>-400, and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber catalysts were 11.89, 8.81, 6.54, and 5.44  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively. In this regard, the lowest  $E_a$  value was obtained for the 4-NP reduction reaction catalyzed by [the](#) T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber and this correlates well with the faster transfer reaction [that](#) occurred on the catalyst surface. Moreover, all the  $E_a$  values are well within [the](#) typical reported values for the surface catalyzed processes (8.3–41.8  $\text{kJ}\cdot\text{mol}^{-1}$ ). From the point of

view of liquid phase adsorption, it can be also inferred that the electrostatic interactions between anions and the catalyst surface belongs to physisorption. The calculated thermodynamic parameters of activation including  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  are presented in Table 4.

**Table 4.** Thermodynamic parameters of activation for the photocatalytic reduction of 4-NP to 4-AP over designated nanofibrous catalysts at different temperatures.

Catalysts	T-/K	$\Delta G^\ddagger$ -/kJ mol <sup>-1</sup>	$\Delta H^\ddagger$ -/kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ -/J mol <sup>-1</sup> K <sup>-1</sup>	R <sup>2</sup>
T-400	303	54.64	9.29	-149.68	0.994
	313	56.13			
	323	57.64			
T <sub>6</sub> C <sub>1</sub> -400	303	53.59	6.21	-156.36	0.980
	313	55.15			
	323	56.71			
T <sub>1</sub> C <sub>3</sub> -400	303	51.09	3.94	-155.60	0.991
	313	52.64			
	323	54.20			
T <sub>1</sub> C <sub>3</sub> -400 <sub>5</sub>	303	49.40	2.85	-153.64	0.982
	313	50.94			
	323	52.48			

As it can be observed, the photocatalytic reduction of 4-NP to 4-AP was nonspontaneous ( $\Delta G^\ddagger > 0$ ) and endothermic ( $\Delta H^\ddagger > 0$ ); thus, this reaction requires energy or catalyst to promote the transformation of the reactant to product. Further, the value of  $\Delta G^\ddagger$  becomes more positive with increasing temperature for all catalyst samples, indicating that the

reduction of 4-NP becomes more facile and favorable at a lower temperature. The positive value of  $\Delta G^\ddagger$  in this study also agrees well with the previous findings of Kohantorani and Gholami for catalytic reduction of 4-NP by CeO<sub>2</sub>-supported CuNi nanoparticles,<sup>43</sup> as well as for the Fenton-like photooxidation reaction.<sup>44</sup> The  $\Delta H^\ddagger$  values, which represent energy differences between the ground state and the transition state in a chemical reaction, are consistent and follow the same trend as the  $E_a$  results: T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> < T<sub>1</sub>C<sub>3</sub>-400 < T<sub>6</sub>C<sub>1</sub>-400 < T-400. The decrease in the positive values of  $\Delta H^\ddagger$  indicates that less energy would be required for the reaction to proceed to completion using the T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber than the other nanofibrous samples. Meanwhile, the negative values of  $\Delta S^\ddagger$  suggest loss of entropy due to a decrease in the randomness degree and the presence of an associative mechanism in forming the transition state for the catalytic reduction of 4-NP to 4-AP. This situation is frequently encountered in most bimolecular reactions, where two reactant molecules (i.e., 4-NP and BH<sub>4</sub><sup>-</sup>) come together on catalytic surfaces to form a product (4-AP). Thus, from the chemical thermodynamics' viewpoint, it can be implied that the T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber was the best performing catalyst for facilitating the reduction of 4-NP to 4-AP, having the smallest  $E_a$  and  $\Delta H^\ddagger$  values.

### 3.4. Reusability Test of the Nanofibrous Catalysts

The reusability and stability of the catalyst are important aspects to take into account for practical applications since they contribute toward lowering of the overall cost of the process. Therefore, the photocatalytic stability of T<sub>1</sub>C<sub>3</sub>-400 and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers was evaluated in five successive 4-NP reduction experiments. As can be seen in Figure 6 (panels a and b), the as-prepared T<sub>1</sub>C<sub>3</sub>-400 and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers displayed satisfactory photocatalytic stability with respect to the  $k_{app}$  values and conversion efficiency after five consecutive catalytic runs. In this regard, the  $k_{app}$  values do not significantly change compared to the original one, while the catalytic conversion efficiency remains constant at

97% or above across the five runs for both nanofibrous catalysts. Moreover, the nanofibrous morphology of T<sub>1</sub>C<sub>3</sub>-400 (CuO-TiO<sub>2</sub>) and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> (Cu-CuO-TiO<sub>2</sub>) catalysts may also facilitate the separation process of these solids from the solution after reaction, for example, simply by filtration, compared to powdery catalysts that require tedious and time-consuming centrifugation/redispersion cycles. Table 5 shows the kinetic parameter of 4-NP conversion using different catalysts as reported previously. This work using the T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofiber outperforms other catalysts for 4-NP reduction to 4-AP.

Figure 6. Cycling tests of (a) T<sub>1</sub>C<sub>3</sub>-400 and (b) T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers for photocatalytic reduction of 4-NP to 4-AP over five cycles with respect to the apparent rate constant ( $k_{app}$ , blue bars) and conversion efficiency ( $C_t/C_0 \times 100$ , green bars).

Table 5. Comparison with the state-of-the-art literature of 4-NP conversion under different catalysts.

Materials	Size (nm)	$k_n$ (mmol·g <sup>-1</sup> ·min <sup>-1</sup> )	Light source	Ref.
Ag-TiO <sub>2</sub>	19	0.036	Visible light	45
ZnO-NCP	100	0.0008	UV light	46
NdPc <sub>2</sub> -TiO <sub>2</sub>	-	0.008	UV light	47
Pd-TiO <sub>2</sub>	7	0.432	-	48
CuO	20	2.343	-	49
Fe <sub>3</sub> O <sub>4</sub> @SiO <sub>2</sub> -Ag	200	1.527	-	50
T <sub>1</sub> C <sub>3</sub> -400 <sub>5</sub>	20-30	2.251	UV light	[this work]

## 4. Conclusions

In summary, we have successfully demonstrated in this study the composition-controlled fabrication of bimetallic copper–titania nanofibrous mats via a combination of electrospinning and thermal annealing processes. XRD results confirm the coexistence of Cu, CuO, and TiO<sub>2</sub> crystalline phases in the nanofibrous catalysts after NaBH<sub>4</sub> immersion treatment; meanwhile, the conversion of Cu<sup>2+</sup> to Cu<sup>0</sup> after reduction by NaBH<sub>4</sub> was successfully revealed by XPS results. Among the fabricated bimetallic nanofibrous catalysts, [the](#) T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> fiber mat with coexisting Cu, CuO, and TiO<sub>2</sub> phases was found to be the best performing catalyst toward 4-NP reduction reaction with and without UV irradiation, giving the  $k_{app}$  values of 0.50 and 0.42 min<sup>-1</sup>, respectively. The excellent catalytic activity demonstrated by T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> could be attributed to the electron separations from CuO and efficient electron transfer by Cu species. In addition, T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> also exhibits the largest surface area, pore volume, and pore size among other nanofiber catalysts as indicated by BET results. Based on the thermodynamic analysis of the activation parameters, the photocatalytic reduction of 4-NP to 4-AP was endothermic and nonspontaneous, where the reaction was favored at a low enthalpy value with T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> as the catalyst. The as-fabricated T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibrous catalyst is also stable and proved to be reusable for five consecutive reaction cycles without appreciable loss in activity, affording [the](#) 4-NP conversions of at least 97%. To this end, this free-standing and low-cost bimetallic nanofibrous catalyst demonstrates its commercial potential to be implemented in industrial water and wastewater treatment containing nitroaromatic compounds.

## ~~ASSOCIATED CONTENT~~

### Supporting Information

~~The Supporting Information is available free of charge at:~~

~~The~~ [Elemental composition by EDX analysis of T<sub>1</sub>C<sub>3</sub>-400 and T<sub>1</sub>C<sub>3</sub>-400<sub>5</sub> nanofibers; \(Figure S1\) \(PDF\); BET surface ~~are~~ and pore size analysis for various composite nanofibers; \(Table](#)

[S1\)-\(PDF\)](#); and [a](#)Actual metal content in composite nanofibers determined by ICP-AES ([Table S2\)-\(PDF\)](#);

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## Notes

The authors declare no competing financial interest.

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