Green approach for photocatalytic Cu(II)-EDTA degradation over TiO₂ : toward environmental sustainability

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For

A green approach of photocatalytic Cu(II)-EDTA degradation over TiO₂ nanofibers: Towards environmental sustainability

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A) Determination of the optimum calcinations temperature for TiO₂ nanofibers

Researchers have adopted calcinations temperature ranging from between 400°C to 550°C for pristine TiO₂. Xu et al. (2011) had prepared TiO₂ nanotube (TNT) via hydrothermal method and calcinations at as low as 400°C.¹ The anatase crystal structure of TNT had been well evidenced via XRD pattern. Furthermore, this TNT had been used as the support to synthesize TiO₂/CuO composite photocatalysts via wet-impregnation and adsorption-calcination methods; where calcinations at 400°C were employed. Both TiO₂/CuO composite photocatalysts showed well-crystalline structure with good H₂ generation efficiency from 10%v/v methanol-water mixture. Where electrospinning is concerned, Chuangchote S. et al. (2009) had reported that electrospun pristine TiO₂ nanofibers which were calcined at 450°C demonstrated the highest H₂ generation efficiency from 10%v/v methanol-water mixture, compared to those which were calcined at 400°C, 500°C, 600°C and 700°C.² This was attributed to the lower or absence of rutile phase in the nanofibers calcined at 450°C and sufficient specific surface area.² Madhugiri, S. et al. (2004) reported that calcinations at 400°C yielded a more efficient TiO₂ nanofibers for photo-degradation of phenol and formic acid than that at 600°C, due to presence of higher anatase phase and enhanced specific surface area.³ Meanwhile, Choi et al. (2010) has adopted the calcinations temperature of 500°C, which eventually demonstrated higher H₂ generation capability than that of P25 TiO₂ nanoparticles from 10%v/v methanol-water mixture.⁴

Herein, a supplementary experimental work has been undertaken to determine an optimum temperature for synthesis of TiO₂ nanofibers. TiO₂ nanofibers were prepared via electrospinning by adopting the same precursor preparation and synthesis procedure as reported in our previous work.⁵⁻⁷ The as-spun nanofibers were calcined in the air at 400 °C, 450 °C and 500 °C for 1 hr, at temperature rising rate of 0.5°C/min to obtain TiO₂ nanofibers

from different temperature; namely T-400, T-450, and T-500. XRD analysis, BET specific surface area analysis, and H₂ generation test were undertaken to gain a better in-sight, as follows:

Figure S1. XRD patterns for TiO₂ nanofibers calcined at 400 °C (T-400), 450 °C (T-450), and 500 °C (T-500)

XRD patterns in Fig. S1 show that all calcinations temperature yielded anatase TiO₂ crystal (JCPDS 21-1272). T-500 possessed the highest anatase peak, indicating the highest degree of crystallinity among all thus lower crystalline defects, than that of T-400 and T-450. High degree of crystallinity is beneficial to promote charge transfer.

Table S1. Summary of BET specific surface area of photocatalysts (T-400, T-450, T-500: TiO₂ nanofibers produced from calcinations at 400 °C, 450 °C, and 500 °C, respectively; T-C: Cu-adsorbed used TiO₂ nanofibers; R-TC: Reclaimed TiO₂/CuO composite)

Materials	BET specific surface area (m ² /g)
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(a) T-400 (Bare TiO ₂ @ 400 °C)	22.15
(b) T-450 (Bare TiO ₂ @ 450 °C)	72.12
(c) T-500 (Bare TiO ₂ @ 500 °C)	36.58
(d) T-C	3.02
(f) R-TC (from calcination of (b))	15.73
(g) Regenerated R-TC	13.11
(h) P25 TiO ₂	59.54

Nevertheless, BET specific surface area of T-500 was observed to be lower than that of T-450 (Table S1); which possibly would result in a lower adsorption efficiency of reactants as well as lower light utilization ability by T-500.² Similar observation was reported by Chuangchote S. et al. (2009) where 450 °C yielded the highest specific surface area thus exhibited the highest H₂ evolution rate.² Higher temperature could promote fusion and growth of the granular nanocrystals into larger crystals⁸ thus possibly resulting in a smoother surface structure, also verified by one of our past work.⁷ T-400 exhibited the lowest specific surface area due to the incomplete removal of PVP which resulted in the insufficient formation of porosity required to enhance surface area of the nanostructures.⁷

Table S2. Photocatalytic H₂ evolution rate over TiO₂ nanofibers calcined at different temperature

Materials	Sacrificial reagents	H ₂ evolution rate (μmol h ⁻¹)
(a) T-400	10% v/v methanol	40.27
	0.8 mM Cu-EDTA	121.35
(b) T-450	10% v/v methanol	92.66
	0.8 mM Cu-EDTA	250.90

(c) T-500	10% v/v methanol	89.75
	0.8 mM Cu-EDTA	240.18

As shown in Table S2, T-450 exhibited the highest H₂ generation from 10% v/v methanol and 0.8 mM Cu-EDTA. On the other hand, T-400 exhibited the lowest H₂ generation, possibly attributed to its lowest degree of crystallinity and specific surface area for reactant adsorption and light utilization.⁹ In all reaction involving Cu-EDTA, more than 90% Cu²⁺ was removed within 1 hour of reaction. Overall, both T-450 and T-500 have exhibited comparable H₂ generation rate likely attributed to a synergistic balance between crystallinity and specific surface area in each photocatalyst. A high degree of crystallinity at the expense of specific surface area may not necessarily favor H₂ generation, rather it is the balance of synergy among the physicochemical properties and the type of pollutant as sacrificial or electron donor.⁷

With this, we postulated that the determination of calcinations temperature to be used could varies depending on the overall objective of a research, the synthesis method and raw materials used, and the overall physicochemical properties of the TiO₂ photocatalyst desirable for an application of interest in a study. Hence, based on the experimental work and literature review done, 450°C was reasonably sufficient to produce efficient TiO₂ nanofibers for the purpose of our research on environmental sustainability via TiO₂ photocatalysis. Higher calcinations temperature which entailed more energy resource was not necessary.

B) Verification and discussion on efficiency of TiO₂ nanofibers in EDTA

TiO₂ has been widely demonstrated to show good photocatalytic H₂ production with enhancement by one or more co-catalyst(s). Nevertheless, the ability of TiO₂ in generating H₂ without co-catalyst have been interestingly reported in the recent years. In general, this phenomena could be attributed to the following two factors:

1. *The superiority of one-dimensional (1D) nanostructures* - Unlike the 0-dimensional (0D) nanoparticles, the unique 1D nanostructures have been demonstrated to exhibit enhancement in the interparticle charge transfer thus the photo-generated charges separation, as well as the mesoporous property facilitating adsorption and light utilization. Chuangchote, S. et al. (2009) reported a significant H₂ generation over TiO₂ nanofibers from 10%v/v methanol-water mixture, which was approximately 3 times more than that by TiO₂ nanoparticles.² Choi S.K. et al. (2010) also reported similar enhancement in H₂ generation (which was approximately 7.5 times more than TiO₂ nanoparticles) over pristine TiO₂ nanofibers from 10%v/v methanol owing to its 1D nanostructures which enhanced the charge transfer as well as enhanced adsorption ability given by the mesoporosity, enhanced specific surface area and lack of tendency to agglomerate during reaction.⁴

In this study, to verify the efficiency of the as-synthesized 1D TiO₂ nanofibers (using T-450), additional study using P25 TiO₂ (0D nanoparticles) as comparison have been carried out using N₂ adsorption-desorption isotherm technique, BJH analysis, BET specific surface area analysis, photoluminescence (PL) analysis, and H₂ generation efficiency from 10%v/v methanol-water mixture and EDTA solution.

Figure S2. N₂ adsorption/desorption isotherm curve of (a) TiO₂ nanofibers (black) and (b) P25 TiO₂; and (c) BJH pore size distribution for both TiO₂ nanofibers and P25 TiO₂

A surface analysis using the N₂ adsorption-desorption isotherm technique showed that the TiO₂ nanofibers were mesoporous as characterized by the type IV isotherm curve with obvious H3-type hysteresis, while no mesoporosity was suggested by that of P25 TiO₂ (Fig. S2).^{10, 11} The BJH analysis further affirmed the mesoporosity nature of the bare TiO₂ nanofibers since they showed a narrow pore size distribution of between 2-20 nm (Fig. S2).¹⁰ A mesoporous structure is desirable to enhance the photocatalytic reaction as it enables fast diffusion of reactants through the photocatalysts thus facilitating access to the reactive sites.

BET specific surface area of TiO₂ nanofibers was 72.12 m²/g (Table S1), which was approximately 1.2 times more than that of P25 TiO₂, supporting the benefits of mesoporosity in enhancing specific surface area for photocatalysis.

Figure S3. Photoluminescence spectra of photocatalysts (TiO₂ nanofibers, P25 TiO₂, Cu-deposited TiO₂ (T-C), reclaimed TiO₂/CuO composite nanofibers (R-TC), and recycled R-TC (after 3 times of reaction))

PL analysis as shown in Fig. S3 further evidenced the enhanced separation of photogenerated charges possibly attributed to the long 1D nanofibrous structure of TiO₂ nanofibers since the PL spectra is relatively lower than that of P25.⁴ Therefore, unlike 0D TiO₂ nanoparticles (P25), the electrospun 1D TiO₂ nanofibers was a more potential and efficient photocatalyst as it possessed a beneficial synergy between (1) its 1D long nanofibrous structure (**Figs. 1(a)-(b)**) which would have low aggregation tendency thus ensuring optimum specific surface area for pollutants adsorption, facilitating recovery and reusability of the spent photocatalysts¹³ as well as enhancing charges separation for oxidation and reduction processes⁴, and (2) its

mesoporous structure which would promote diffusivity of reactants through the photocatalysts hence high reactants mass transfer; as well as facilitate light utilization ability¹².

Table S3. Comparison of photocatalytic H₂ evolution rate over TiO₂ nanofibers and P25 from different sacrificial reagents

Materials	Sacrificial reagents	H ₂ evolution rate ($\mu\text{mol h}^{-1}$)
(a) TiO ₂ nanofibers	10% v/v methanol	92.66
	50 ppm EDTA	146.40
	Acid orange 7 (AO7)	13.60
	5% v/v glycerol	173.36
(b) P25	10% v/v methanol	36.40
	50 ppm EDTA	40.01
	Acid orange 7 (AO7)	0.42
	5% v/v glycerol	49.40

As shown in Table S3, TiO₂ nanofibers have demonstrated a more superior H₂ generation capability than that of P25 TiO₂. Approximately 2.5 times and 3.7 times H₂ generation was evolved from methanol and EDTA over TiO₂ nanofibers compared to P25 TiO₂. This observation was in consistent with the superiority of TiO₂ nanofibers over P25 TiO₂ in terms of mesoporosity and enhanced specific surface area (Fig. S2, Table S1) and enhanced charges separation (Fig. S3).

2. *Type of sacrificial reagent used* - Different sacrificial reagent employed might result different H₂ evolution rate. EDTA has been demonstrated to be one of the best sacrificial candidates for photocatalytic H₂ generation.¹⁴ Nada, A.A. et al. (2005) demonstrated that amount of photocatalytic H₂ generated over modified TiO₂ was in the following sequence: EDTA>methanol>ethanol>lactic acid (all with 4% v/v concentration in water).¹⁵ In consistent with this, our data from Table S3 depicted similar trend where the use of EDTA has yielded more H₂ than that of methanol. We postulate that different sacrificial reagent would require different photocatalyst for an efficient photocatalytic H₂ generation. Depending on the type of photocatalysts used, some sacrificial reagent may not yield significant H₂ while some others may. As demonstrated in our study, the integration of the superior 1D TiO₂ nanofibers (instead of 0D nanoparticles) and EDTA (which was one of the potential sacrificial reagents) has given an enhanced synergy and made it possible to yield significant H₂ via photocatalysis. Nevertheless, we also observed that TiO₂ alone could not yield significant H₂ when a more complex electron donor such as azo-dye, was used (Table S3). The simpler molecular structure and chemical property of EDTA might be the facilitating factors.¹⁶⁻¹⁹ In this case, a modified or doped TiO₂ may be required. This had been demonstrated in our previous work where TiO₂ nanofibers showed negligible H₂ generation despite its enhanced physical properties while TiO₂/CuO composite nanofibers were required to generate H₂ from water with azo-dye as pollutant, owing to its TiO₂/CuO heterojunctions and better physicochemical properties than that of TiO₂ nanofibers⁶.

In summary, base on the literature review and the supplementary experimental work done, it is reasonable that 1D TiO₂ nanofibers itself (without any doping), possesses enhanced photocatalytic efficiency given by the merits of its physicochemical properties which

possibly endowed it with the capability to evolve H_2 from water under suitable sacrificial condition.

C) Verification and discussion on advantage of R-TC over T-C

Cu^0 , along with Cu_2O and CuO , have been well-demonstrated as good co-catalysts for TiO_2 in photocatalytic H_2 generation.¹⁶⁻²⁰ Nevertheless, some studies have shown that CuO was a better co-catalyst among all Cu species (Cu^0 , Cu_2O , and CuO) in the case of photocatalytic H_2 generation owing to: (1) its smallest band gap energy of 1.35 eV thus extended light sensitivity and harvesting efficiency, and (2) its stability.²¹⁻²³ CuO/TiO_2 has been reported to give the highest H_2 generation from glycerol compared to its reduced species.²⁴ In other study, Cu^0 and Cu^+ were shown to de-activate TiO_2 efficiency but not Cu^{2+} .^{25, 26} Moreover, CuO has higher affinity for electron compared to Cu^0 due to the different oxidation states thus higher redox potential of CuO than Cu^0 .^{21, 27} This would give a better electron-hole separation efficiency in TiO_2/CuO than that in TiO_2/Cu^0 .

Additionally, we have carried out supplementary experiments to verify the efficiency of R-TC and rationale of its synthesis and reclamation. A comparison was made between the freshly recovered used TiO_2 with Cu^0 deposited on it (herein after termed as T-C) and R-TC, using PL analysis, leachability study, and H_2 generation test from 5% v/v glycerol.

Table S4. Comparison of photocatalytic H_2 evolution rate over R-TC and T-C

Materials	Sacrificial reagents	H_2 evolution rate ($\mu\text{mol h}^{-1}$)
(a) R-TC	5% v/v glycerol	270.00
(b) T-C	5% v/v glycerol	265.12

Figure S3 shows that R-TC exhibited relatively lower PL spectra than T-C, suggesting better separation between the photogenerated charges by R-TC thus an enhanced photocatalytic efficiency, which was evidenced by the relatively higher H₂ generation rate over R-TC as seen in Table S4. Both R-TC and T-C were however rather competitive towards the end of the reaction, possibly ascribing to the cyclical kinetic transformation of Cu species on T-C. During photocatalysis under anaerobic condition, a cyclical kinetic transformations of Cu species had been postulated: Cu²⁺ from EDTA would be reduced by photogenerated electrons to form Cu⁺ and then Cu⁰ on the surface of TiO₂ nanofibers. Subsequently, Cu⁰ was oxidized back into Cu⁺ and finally Cu²⁺ by the photogenerated holes.^{21, 28} Thermal treatment of the used TiO₂ photocatalysts was therefore employed to remove the organics to obtain both active and stable TiO₂/CuO heterojunctions.¹⁸ It has been claimed that calcinations at low temperature of 450°C might served to minimize Cu dissolution into the oxide lattice as dissolution of Cu into TiO₂ lattice thus reducing the H₂ efficiency of the photocatalysts.^{29, 30}

Table S5 Summary of leachability of Ti and Cu from photocatalysts

Photocatalyst	Medium	Ti (mg/L)	Cu (mg/L)
R-TC	Diluted HNO ₃ (pH 2)	0.376	33.68
	Diluted NaOH (pH 12)	1.474	0.135
	5% v/v Glycerol	0.004	0.538
T-C	Diluted HNO ₃ (pH 2)	0.354	39.24
	Diluted NaOH (pH 12)	1.503	0.937
	5% v/v Glycerol	0.012	0.689

Moving forward, a leachability study was carried out and Table S5 indicated that despite negligible difference of Cu dissolution in 5% v/v glycerol, R-TC exhibited relatively lower Cu leaching in acidic medium i.e. pH2 and alkaline medium i.e. pH12; indicating its better stability compared to T-C.

This supplementary study has demonstrated that through the thermal treatment, not only the used TiO_2 photocatalysts could be regenerated, the separation of photogenerated charges could also be enhanced in the heterojunctions due to the lower CB of CuO than that of TiO_2 and the greater affinity for electrons on the surface of TiO_2 , thus increasing the availability of photogenerated electrons for reduction of H_2O or H^+ into H_2 , while the cyclical kinetic transformations of the free Cu species which might interfere with the H_2 generation (although seems negligible from the experiment i.e. Fig. 3), could be minimized if not eliminated. With this, it is therefore reasonable for this study to adopt the calcinations step to obtain R-TC which possessed better efficiency and stability.

Figure S4. N_2 adsorption/desorption isotherm curve of TiO_2 nanofibers (black) and reclaimed TiO_2 -CuO composite nanofibers (R-TC) (red), and BJH pore size distribution (inset) of TiO_2 nanofibers (black) and R-TC (red)

Figure S5. (a) High magnification dark field FESEM-STEM image of a single R-TC, (b)-(c) EDX spectrums for the indicated points on the nanofiber in (a), Elemental mapping for the selected area in (a) for (d) Ti element, (e) Cu element, and (f) O element

(b) A - Anatase TiO_2 Cu^0 - metallic Cu C - CuO

Figure S6. (a) High magnification HRTEM image showing the corresponding crystal lattice of anatase TiO₂ and CuO with an inset showing the full range XRD patterns for TiO₂ nanofibers, T-C, R-TC, and recycled R-TC; and (b) Close-up XRD patterns for from $2\theta = 30^\circ - 45^\circ$

Inset of Fig. S6(a) illustrates the XRD patterns for the pure TiO₂ nanofibers, T-C, R-TC and used R-TC after 3 cycles of reaction. The XRD patterns have revealed the changes in the chemical state of Cu over TiO₂ nanofibers albeit the weak detection which was possibly due to the high dispersion of Cu species on the TiO₂ nanofibers.⁶ It revealed that in addition to anatase TiO₂ (JCPDS file No. 21-1272)³¹, Cu⁰ and CuO was present in T-C and R-TC, respectively. A close-up XRD pattern plotted across the region of $2\theta = 30^\circ - 50^\circ$ (Fig. S6(b)) provided a clear view where the peaks observed at $2\theta = 36.5^\circ$ and $2\theta = 38.8^\circ$ could be ascribed to the (111) plane and (002) plane of CuO, respectively³², in consistent with the observed HRTEM image. After 3 cycles of reaction, the XRD diffraction peaks of Cu species was weaker, albeit observable. This could be attributed to combined effect from the minor leaching and more dispersion of CuO on the TiO₂ nanofibers which has rendered it not detectable by XRD after the photocatalytic reactions.¹

Figure S7. The UV-visible spectra of TiO_2 nanofibers and R-TC

Figure S8. (a) XPS survey spectrum for R-TC; High resolution XPS spectrum of R-TC for (b) Ti 2p, (c) Cu 2p, and (d) O 1s

Figure S9. FESEM-STEM image of a single strain of R-TC which has been used for reaction in 5% v/v glycerol and regenerated (a) low magnification and (b) high magnification

Figure S10. (a) High magnification dark field FESEM-STEM image of a single R-TC (recycled), (b) EDX spectrums for the indicated points on the nanofiber in (a), Elemental mapping for the selected area in (a) for (c) Ti element, (d) Cu element, and (e) O element

Additional EDX analysis which affirmed the existence of highly dispersed Cu on recycled R-TC .

Table S6 Summary of leachability of Ti and Cu from R-TC after being used for photocatalysis of 5%v/v glycerol

Photocatalyst	Medium	Ti (mg/L)	Cu (mg/L)
R-TC	Cycle 1	0.004	0.538
	Cycle 2	0.010	0.481
	Cycle 3	0.001	0.106

Table S6 showed that the leach-out concentration of Ti and Cu were consistently below 1 ppm in 5%v/v glycerol even at the 3rd use, implying the potential reusability of R-TC.

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