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Author(s)	Lee, Siew Siang; Bai, Hongwei; Liu, Zhaoyang; Sun, Darren Delai
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A green approach for photocatalytic Cu(II)-EDTA degradation over TiO$_2$: Towards environmental sustainability

Siew Siang Lee,[a] Hongwei Bai,[a,b] Zhaoyang Liu,[c] and Darren Delai Sun*[a]

[a] School of Civil & Environmental Engineering, Nanyang Technological University, Singapore 639798

Tel: +65-6790-6273; Fax: +65-6790-0676

[b] Energy Research Institute@NTU, Nanyang Technological Univeristy, Singapore 637141

[c] Qatar Environment and Energy Research Institute, Qatar Foundation, PO Box 5825, Doha, Qatar

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ABSTRACT. A green approach was successfully developed to reap three environmental benefits simultaneously: (1) clean water production, (2) hydrogen (H$_2$) generation and (3) well-dispersed *in-situ* Cu^{2+} recovery for direct TiO$_2$-CuO composite reclamation; by exploiting the synergistic integration of photocatalytic reaction of Cu-EDTA and one-dimensional (1D)

ultralong and ultrathin TiO_2 nanofibers. In this light-initiated system, Cu-EDTA was oxidized by TiO_2 thus releasing Cu^{2+} which was reduced and recovered through uniform adsorption onto the long and porous TiO_2 surface. A win-win platform was thus attained, on which Cu was recovered while providing active sites for H_2 generation via photo-reduction of H_2O and enhancing photo-oxidation of remaining intermediate oxidation by-products. Experimental results showed a H_2 generation rate of 251 μmol/hr concomitantly with TOC reduction. The used TiO_2 nanofibers deposited with Cu were reclaimed directly as TiO_2-CuO composite after a facile heat treatment without additional chemical, and subsequently reusable for photocatalytic treatment of other wastewater (glycerol) to cogenerate H_2 and clean water under both UV-visible and visible light. This study expounds a significant advancement through an ingenious integration which enhance the environmental sustainability of Cu-EDTA treatment via TiO_2 photocatalysis. It also represents a promising and adoptable approach to synthesize other functional composite nanomaterials in a green manner thus broadening its environmental application spectrum, as it promotes industrial environmental management via waste segregation and motivates research to recover more resources from wastewater.

Introduction

The worldwide burgeoning population, urbanization and industrialization have resulted in rising concerns among the community today on major environmental issues, in particular (1) water scarcity [1], as well as (2) generation of variable waste or wastewater which are becoming more and more challenging to manage and treat. [2] These exigencies have thus obliged more aggressive review, research and development endeavors in various technologies especially for water/wastewater treatment and reclamation.[3-9]

Copper(II)- ethylene diamine tetra acetic acid (Cu-EDTA), a type of organometallic wastewater usually generated from textile, electroplating, and nuclear industries, has been one of the major environmental pollutants of concern because it is very stable over a wide range of pH and highly resistant to degradation. [10, 11] Cu-EDTA wastewater must be treated before discharge, because its persistence in the environment can be detrimental to life as it increases the mobility of Cu elements which can be toxic at high concentration. [12] Nonetheless, Cu is also a useful and valuable resource for various applications such as in the electronics and nanomaterials fields. [13-15] Unlike the conventional physical-chemical and biological treatments which entail complex operation and maintenance procedures, high resources demand, as well as challenges in treatment efficiency and post-treatment [16-20], photocatalytic treatment of Cu-EDTA over TiO_2 may represents a simpler and more promising technology as (1) it taps into the clean and renewable solar energy for photocatalytic oxidation (PCO) of Cu-EDTA, (2) it spontaneously recover the Cu^{2+} *via* photocatalytic reduction (PCR), (3) it does not require additional chemical, and (4) it does not generate secondary pollutant. [11, 21, 22] Eventually, Cu could be recovered from the used photocatalysts using acid extraction. [21] Despite the benefits of concurrent organic degradation and Cu recovery which produce clean water, environmental challenges remain where the post-treatment and complexity of the recovery steps entail intensive use of chemicals, high resources demand and secondary wastewater generation. The challenge is further compounded as exploration to recover the deposited Cu *via* a greener approach seems to be very few. In view of this, one-dimensional (1D) TiO_2 nanofibers, which have not been used before for Cu-EDTA photocatalytic treatment, may offer a more sustainable recovery option by facilitating direct reclamation of the used TiO_2 photocatalyst with Cu deposited on it, owing to its superior properties: (1) high porosity and long aspect ratio [23] which would enhance adsorption

and uniform dispersion of reactants, and (2) low aggregation tendency which facilitate separation and reusability of the photocatalysts as well as reduce recombination of photogenerated charges. [23] Meanwhile, the extent of research on photocatalytic treatment of Cu-EDTA over TiO_2 remains limited with other possible sought-after opportunities; one of which is the hydrogen (H_2) generation. While EDTA solution itself has been proven to enhance H_2 generation [24-27], no study on possible photocatalytic H_2 generation from Cu-EDTA was ever reported to date. Past research have showed that Cu was a good co-catalyst and candidate to modify TiO_2 thus enhancing its photocatalytic H_2 generation significantly. [28-31] Hence, in principle, the remaining intermediate oxidation by-products (after the PCO of Cu-EDTA) as the hole scavengers [32] should enhance the electrons-holes separation, thereby enabling further extension of PCR to generate H_2 from water (H_2O), with a boost of efficiency from the photo-reduced Cu on TiO_2. In general, derivatives of acetic acid, glyoxilic acid, oxalic acid, glycolic and formic acids were major intermediate degradation products while NH_4^+, NO_3^-, CO_2, Cu^{2+}, and some carbon fragments were the common final products of Cu-EDTA photo-degradation. [32-35] Hypothetically, this may pave an avenue to harvest clean energy simultaneously in addition to clean water production and material reclamation, addressing the looming environmental-energy issues in particular depletion of fossil fuels [36, 37] and climate change from the use of fossil fuels.

Herein for the first time, a green approach was developed to co-generate H_2, clean water, and TiO_2-CuO composite from Cu-EDTA wastewater, by exploiting the integration synergy from PCO and PCR extension and the merits of 1D TiO_2 nanofibers. Cu-EDTA played a dominant role in promoting the photocatalytic reaction over TiO_2 by: (1) providing EDTA as the photogenerated holes scavenger thus enhancing the charges separation, and (2) providing Cu as the co-catalyst for H_2 production, to extend the visible light sensitivity as well as to enhance the

separation of the photogenerated charges. What is more, the used TiO_2 nanofibers were utilized directly to synthesize TiO_2-CuO composite nanomaterials via facile calcinations. Photocatalytic efficiency of the reclaimed composite nanofibers for treatment of other organic pollutant such as glycerol, was shown and discussed to predict the application future. In addition, through an in-depth characterization of the reclaimed TiO_2-CuO composite, a comprehensive mechanism for this synergistic system was unravelled to bridge the research gap.

Experimental Section

Materials

Ethanol, acetic acid, tetra n-butyl titanate (Ti(oBu)$_4$), polyvinylpyrolidone (PVP; M_W=1 300 000), copper nitrate (Cu(NO$_3$)$_2$.3H$_2$O), sodium-EDTA (C$_{10}$H$_{14}$N$_2$Na$_2$O$_8$.2H$_2$O), sodium hydroxide (NaOH) and nitric acid (HNO$_3$) were of analytical grade and used directly without further purification. Deionized (DI) water of 18 µS/cm was used in all reagents and samples preparation.

Preparation of TiO_2 nanofibers

TiO_2 nanofibers were prepared via electrospinning by adopting the same precursor preparation and synthesis procedure as reported in our previous work. [13, 38, 39] Briefly, 7 wt% of PVP and 20 wt% of Ti(oBu)$_4$ were added into a solution of CH$_3$CH$_2$OH and CH$_3$COOH) (V/V = 4:1. Subsequently, the mixture was magnetically mixed for 6 hrs to obtain a clear sol-gel solution for the electrospinning of TiO_2. Facilitated by a syringe pump, the precursor solution was injected at a rate of 0.4 mL/hr through a hypodermic syringe with a stainless steel nozzle diameter of 1.1 mm. Under an electrical potential of 1.1 kV/cm, a non-woven nanofiber webs of PVP/Ti($_o$Bu)$_4$

composite was obtained on a grounded aluminum foil which was located 18 cm away from the nozzle of the syringe. The as-spun nanofibers were calcined in the air at 450 ºC for 1 hr, at temperature rising rate of 0.5°C/min to obtain TiO_2 nanofibers. A series of comparative study was conducted to determine the optimum calcinations temperature for TiO_2 nanofibers (extensively discussed in the Supporting Information (SI)).

Cogeneration of H_2 and clean water

Concurrent photocatalytic H_2 and clean water generation test was carried out in 0.8 mM Cu-EDTA solution containing 0.5 g/L of suspended bare TiO_2 nanofibers as the photocatalyst in an inner irradiation type Pyrex reactor with a 400W high pressure Hg lamp (Riko, UVL-400HA) as the UV-visible light source. [38] Synthetic Cu-EDTA wastewater solution was prepared by dissolving equal molar amounts of $Cu(NO_3)_2.3H_2O$ and $C_{10}H_{14}N_2Na_2O_8.2H_2O$ in DI water. Diluted NaOH and HNO_3 were used to adjust the Cu-EDTA solution to pH 4, 6, and 10 to investigate the effect of pH on the reaction. Following a purge with N_2 gas for 30 min to de-aerate the reactor, dark and photolysis experiments were carried out for 4 hrs to obtain a baseline for organic removal and H_2 generation. In all subsequent photocatalysis reaction test, the suspension was stirred in the dark for 1 hr to achieve a dark adsorption-desorption equilibrium between the organometallic substrates and the photocatalysts prior to light irradiation. An aliquot of 5 mL was sampled and immediately filtered through a Millipore filter of 0.45 μm every 10 min for water quality analysis. The filtered aliquot was measured for its total organic carbon (TOC) and Cu content using a Shimadzu TOC analyzer model TOC-V CSH and inductively coupled plasma optimal emission spectrometry (ICP OES) (Dionex ISC-1000), respectively. A thermal conductivity detector (TCD)-type gas chromatography (Agilent 7890A,

HP-PLOT MoleSieve/5A) was used to measure the gas produced from the photocatalytic reaction. [29, 30] All experiments were carried out in triplicates to get averaged data for analysis. EDTA solution without the presence of Cu ions was tested under the same experimental conditions as comparison.

Reclamation of used TiO_2 into TiO_2-CuO composite nanofibers and its usability

The used TiO_2 nanofibers with Cu deposited on them (herein after termed as Cu-TiO_2 nanofibers (T-C)) were collected and washed briefly with DI water to remove excess organic oxidation by-products. Subsequently they were dried overnight at 105ºC in an oven and stabilized via calcinations at 450 °C for 1 hr to yield TiO_2-CuO composite nanofibers (herein after termed as reclaimed TiO_2-CuO composite (R-TC)). R-TC were tested for its photocatalytic H_2 and clean water production efficiency from glycerol solution (5% v/v) using the same reactor setup for 3 cycles. Photocatalytic efficiency of R-TC under the visible light source (360 W high pressure Na lamp, Riko HNL-360A) was also tested using the same equipment setup. [39] The amount of Cu in the reaction solution was determined after each reaction cycle using the ICP OES. Leachability test was carried out additionally at pH 2 and pH 12 in diluted HNO_3 and diluted NaOH respectively, to predict the operational pH spectrum for R-TC. A comparison of the was done with the innovative TiO_2-CuO composite nanofibers (6-TC) from our previous work. [13]

Characterization of nanofibers (TiO_2 and R-TC)

The morphologies of photocatalysts were observed and characterized using the field-emission scanning electron microscope (FESEM, JEOL JSM-7600F) coupled with high-end scanning transmission electron microscopy, STEM (working at an accelerated voltage of 30 kV). The

elemental content of the photocatalysts were analysed by an energy dispersive X-ray spectrometer (EDX) (Oxford Instrument, X-Max, 80 mm^2) attached to the FESEM (JEOL, JSM-7600F). The microstructure of the nanofibers were analysed using the high resolution transmission electron microscopy (HRTEM, JEOL JEM-2010) working at an accelerated voltage of 200 kV. The crystal phases were analyzed by the Bruker D8 Advance X-ray diffractometer (XRD) with monochromated high-intensity Cu Kα radiation (λ = 1.5418 Å). The UV-Vis spectra were obtained using a Thermo Scientific Evolution 300 UV-Vis spectrometer (Thermo Fisher Scientific, Massachusetts, USA). The Brunauer, Emmett, and Teller (BET) specific surface area of the photocatalysts were determined at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2040 system. The samples were degassed at 200°C for 3 hrs prior to BET measurement. The pore size distribution was estimated by employing the Barret-Joyner-Halenda (BJH) method. The Fluorolog-3 spectrofluorometer (Horiba Scientific, New Jersey, USA) was used to conduct the photoluminescence (PL) analysis at an excitation wavelength of 300 nm [40]. X-ray photoelectron spectroscopy (XPS) measurement were done using a Kratos Axis Ultra Spectrometer with a monochromic Al Kα source at 1486.7 eV, a voltage of 15 kV and an emission current of 10 mA; where the carbonaceous C 1s line at 284.6 eV was used as the reference to calibrate the binding energies.

Results and Discussion

Co-generation of H$_2$ and clean water

H$_2$ and clean water generation from Cu-EDTA was investigated using electrospun TiO$_2$ nanofibers under UV-visible irradiation. Its efficiency is compared against that of a pure EDTA solution without the presence of Cu^{2+} ions to gain more insights of the reaction. TOC and Cu^{2+}

removal were monitoring parameters for the degradation of Cu-EDTA thus the clean water generation. In the case of EDTA, only TOC was monitored. As shown in Figure 1(a), at the end of the 4-hrs irradiation, nearly 2 times more H_2 generation rate of approximately 251 µmol/hr was obtained from Cu-EDTA than that from EDTA over TiO_2 nanofibers. TOC removal from Cu-EDTA was observed to be nearly 1.5 times higher than that from EDTA. No appreciable H_2 generation and TOC removal was observed both in the dark and during photolysis (in the absence of photocatalysts) signifying the essential role of TiO_2 nanofibers for photocatalytic treatment of both Cu-EDTA and EDTA (the efficiency of TiO_2 nanofibers in EDTA was discussed in the SI). Figure 1(b) shows the continuous percentage removal of TOC and Cu^{2+} from Cu-EDTA over TiO_2 nanofibers throughout the 4-hrs reaction. The more superior H_2 generation rate and TOC removal in Cu-EDTA than EDTA have signified the dominant role of Cu from Cu-EDTA in promoting the photocatalytic reaction. Similar observation on the positive effect of Cu^{2+} on photodegradation of EDTA was reported before in the literature; however with no further explanation included. [11] The effect of pH on the was also investigated and results are depicted in Table 1. Shortest time was required at pH 4 for 90% of the Cu^{2+} to be removed from the solution. Protonated TiO_2 surface under acidic condition facilitated the adsorption of the anionic Cu-EDTA [17, 32], thus promoting the PCO of the adsorbed Cu-EDTA by the photogenerated holes, and subsequently the decomplexation and PCR of Cu^{2+} on TiO_2 by the photogenerated electrons. Meanwhile, possible protonation of Cu-EDTA could happen at low pH, leading to decomplexation in the bulk solution prior to adsorption on TiO_2. [41] TOC removal, nevertheless, was more favourable at pH 6 and 10 compared to that at pH 4. Even though the presence of OH^- would pose a competition with Cu-EDTA for adsorption and reaction sites on TiO_2 [17], its formation as OH radical (OH·) by the photogenerated holes [19] would eventually

facilitate Cu-EDTA oxidation in the bulk solution. The low TOC removal at pH 4 further suggested that the overall TOC reduction could be enhanced by OH^-, in addition to the adsorption and oxidation by the holes. In the case where PCO of Cu-EDTA took place in the bulk solution, the PCR of Cu^{2+} could be delayed due to the additional path required for the decomplexed Cu^{2+} to reach and adsorb onto TiO_2, as evidenced by the longer Cu^{2+} removal at pH 6 and 10. However, negatively charged TiO_2 under basic condition might counter this effect by favouring the adsorption of Cu^{2+}. [17, 42] Overall, regardless of solution pH, approximately 50% TOC and 90% of Cu^{2+} removal was achieved within 1 hr. Meanwhile, the combined effect of H^+ as the precursor to H_2 production [30, 43] as well as photo-reduction of Cu^{2+} as reduction sites on TiO_2 [44] seemed to have promoted H_2 generation at pH 4; despite the small differences on H_2 evolution rate between all pH values. This part of work showed that H_2 and clean water can be generated concurrently and more efficiently from Cu-EDTA through PCO of the remaining oxidation by-products and PCR of H_2O or H^+.

Reclamation of T-C and its characterization

At the end of the photocatalytic reaction, T-C were filtered from the reacted solution for direct synthesis into R-TC via facile calcinations at 450 °C for 1 hr, to regenerate the photocatalysts by removing any excess organics by-product and to oxidize Cu into CuO. An in-depth characterizations of TiO_2 and R-TC were carried out following the photocatalytic reaction in the Cu-EDTA solution to compare, to gain an insight of any physicochemical properties changes, and to verify the formation of R-TC. Figure 2(a) shows that TiO_2 nanofibers possessed a rough and porous structure given by the loss of PVP during calcinations [45], as well as high aspect ratio of around 30-50 (inset). This would render the photocatalysts with high specific surface area thus reaction sites for adsorption and photocatalytic reaction of the reactants. [46] As shown in

Figure 2(b), the sustained length and diameter in R-TC will be advantageous for the subsequent application and recovery because these properties facilitate inter-particle charges transfer and prevent agglomeration of the nanofibers. [47] A porous structure analysis using the N_2 adsorption-desorption isotherm technique showed that R-TC has remained a mesoporous property like TiO_2 nanofibers, as characterized by the type IV isotherm curve with obvious H3-type hysteresis (Fig. S4). [48] The mesoporous nature of R-TC was further corroborated by the BJH analysis where a narrow pore size distribution of between 2-20 nm was observed (Inset of Fig. S4). [48] Figure S5(a) shows a high-magnification STEM-FESEM image of a single strain of R-TC. Figure S5(b) depicts the possible aggregation of Cu which was however generally rare as seen in the inset of Fig. S5(b), while Fig. S5(c) confirms the presence of both Ti and Cu on R-TC. The mapping images as shown in Figs. S5(d)-(f) further supported the co-existence of well-dispersed Ti, Cu, and O elements, facilitated by the mesoporosity and the ultralong 1D structure of the nanofibers (Figs. 2). A good Cu dispersion is highly desirable to attain an optimized elemental contact between TiO_2 and CuO heterojunctions which thus would enhance the transfer and separation of the photogenerated charges for a more efficient photocatalytic reaction. [49, 50] The reduced BET specific surface area in R-TC compared to TiO_2 nanofibers (Table S1) is consistent with the observation in Figs. S5, further affirming the deposition of Cu elements on and within TiO_2 nanofibers. Meanwhile, the increased BET specific surface area of R-TC compared to T-C has suggested that the organics have been removed during calcinations. The HRTEM image (Fig. S6(a)) further elucidates the closely contacted TiO_2-CuO heterojunctions. Both the (101) plane of anatase TiO_2 and the (111) plane of CuO were well-evidenced by the lattice fringes of 0.325 nm and 0.253 nm, respectively. [40, 51, 52] The XRD pattern (inset of Fig. S6(a)) revealed that in addition to anatase TiO_2 (JCPDS file No. 21-1272) [40], CuO was present. A close-up

XRD pattern plotted across the region of $2\theta = 30\degree - 45\degree$ (Fig. S6(b)) provided a clear view where the peaks observed at $2\theta = 36.5\degree$ and $2\theta = 38.8\degree$ could be ascribed to the (111) plane and (002) plan of CuO, respectively [52], in consistent with the observed HRTEM image. The absorbance spectra of TiO_2 and R-TC in the UV-Vis light region of between 350-800 nm (Fig. S7) illustrated that the absorption edge in the UV light region has been red-shifted for R-TC, suggesting the successful incorporation of the CuO into TiO_2 nanofibers as well-witnessed in the HRTEM image and XRD patterns in Figs. S6. In addition, the photoresponse in the visible light region was significantly intensified likely due to the presence of CuO which has a small bandgap of 1.2 eV thus capable of absorbing both the UV and visible regions of the solar spectrum. [53] The enhanced sensitivity and absorption in the visible light region could enhance the photogeneration of electrons and holes for photocatalytic reaction. The addition of CuO has resulted in a lower PL spectra by R-TC than that by TiO_2 nanofibers (Fig. S3). A lower PL spectra intensity implies a lower recombination tendency of the photogenerated charges. [40] The energy potential differences which existed between the conduction band (CB) of TiO_2 and that of the CuO have promoted the migration of the photogenerated electrons from the CB of TiO_2 to that of CuO. This has further corroborated the advantage of good elemental dispersion and close proximity between TiO_2 and CuO heterojunctions as shown in Figs. S5 and Figs. S6; which implied that the separation and hence the life span and utilization of photogenerated charges could be enhanced for photocatalytic reaction. The chemical composition and elemental states of R-TC were analyzed using the XPS analysis (Fig. S8). The binding energy for C1s peak at 284.6 eV was used as the reference for calibration. The survey spectrum (Fig. S8(a)) witnesses the existence of Ti, Cu, and O in the regenerated TiO_2 nanofibers. The characteristic peaks for Ti^{4+} at the binding energy of 458.0 eV and 464.0 eV (Fig. S8(b)) which were indicative of Ti $2p_{3/2}$

and Ti $2p_{1/2}$, respectively. The peaks at binding energy of 529.5 eV which was evidence of O 1s in TiO_2 and CuO [29] (Fig. S8(c)) implied contamination by atmospheric hydroxides onto the surface of the composite nanofibers. [29] The valence state of Cu was +2, as corroborated by the peaks around the binding energy of 933.9 eV and 953.9 eV ascribing to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu^{2+} in CuO [31], respectively (Fig. S8(d)). The existence of Cu^{2+} from CuO in the composite nanofibers was further confirmed by the characteristic shakeup satellite peaks around 942.0 eV and 962.0 eV. [54] On the basis of the characterizations and analysis, it is reasonable to state that Cu has been successfully loaded into the TiO_2 nanofibers and after calcinations, formed TiO_2-CuO composite (R-TC) which exhibited rather similar properties as our previously reported innovative TiO_2-CuO nanofibers (6TC). [13] Hence, R-TC could be a potential nanomaterial candidate for photocatalytic reaction. Unlike the conventionally adopted method such as wet-impregnation, hydrothermal and sol-gel which entail use of additional chemical or complex synthesis steps to incorporate Cu on the surface of the TiO_2 photocatalysts [29, 30, 49, 55], the recovered Cu from Cu-EDTA wastewater can be utilized directly as the precursor to synthesize TiO_2-CuO composite almost instantly in a more sustainable manner by tapping into the benefits of 1D TiO_2 nanofibers. With this, not only the non-renewable chemical resource could be conserved, there was also opportunity for attaining zero waste discharge from the wastewater treatment, assuming that a proper drain segregation has been implemented upstream at the point of wastewater generation to prevent mixing of variety of waste components.

R-TC - photocatalytic efficiency and stability

The R-TC were tested for their photocatalytic function to co-generate H_2 and clean water generation from glycerol, a primary waste product from the biodiesel production industry.[28] The

mechanism involved in the photocatalytic treatment of glycerol using TiO_2 to cogenerate H_2 and clean water has been proposed elsewhere.[28, 56] Despite the reduced specific surface area, R-TC exhibited efficient H_2 generation rate of approximately 2627 μmol/hr under UV-visible light and 407 μmol/hr under visible light, as shown in Fig. 3(a). This is almost comparable with the capability of 6TC which showed 2647 μmol/hr and 562 μmol/hr H_2 evolution rate from glycerol under UV-visible and visible light, respectively (Fig. 3(b)). Rhoads K. et al (2004) however reported that the used TiO_2 exhibited similar efficiency with or without adsorbed Cu, thus implying the significant use of 1D TiO_2 nanofibers to facilitate the green synthesis of usable R-TC directly.[21] It is thus postulated that the synergy between all the enhanced physicochemical properties of R-TC could have driven the net photocatalytic reaction. [39] Albeit offering similar role as Cu^0 in T-C before calcinations, CuO in R-TC exhibited enhanced charge separation and stability, thus enhancing photocatalytic H_2 production. [13, 30, 44, 57-59] Advantage of R-TC over T-C is elaborated in the SI. Repeated use of R-TC were feasible owing to its sustainable 1D long nanofibrous structure which thus have enabled the ease of recovery and reuse; corroborated by the FESEM-STEM images (Fig. S9) showing sustained morphology of the used R-TC. XRD and EDX analysis for used R-TC are available in SI. Negligible reduction in photocatalytic H_2 generation was observed in the subsequent two cycles (Fig. 3(c)). The specific surface area could be easily recovered via facile calcinations at 450 °C overnight (Table S1). Moreover, Cu^{2+} ion was constantly below the detection limit of 1.0 mg/L in the reacting solution after every cycle (Table S6), complying with the industrial wastewater effluent standard for Cu as specified by the US EPA. [60] While the leachability study reveals that more than 1.0 mg/L Cu^{2+} could be leached out at pH 2, further study is undergoing to identify the optimization possibility in order to extend the operational pH range for R-TC as well as to build the fundamental of this approach.

In essence, the exhibited photocatalytic efficiency and stability imply the potential of this green approach to synthesize TiO_2-CuO composite, which subsequently could promote industrial symbiosis when the reclaimed photocatalyst is used for remediation of waste water from other industry.

Mechanism explanation

Based on the experimental data and characterization studies, the mechanism of producing clean water, H_2, and R-TC simultaneously via the photocatalytic treatment of Cu-EDTA was postulated and illustrated in Scheme 1. The mechanism comprised the reaction that takes place in the bulk solution and on the photocatalysts. Upon harvesting of the photon energy from the simulated solar irradiation, electrons and holes responsible for the photocatalytic reaction were generated in the CB and valence band (VB) of the TiO_2 nanofibers, respectively. The photogenerated holes would react with the hydroxyl groups in the aqueous phase or on the surface of the photocatalysts, yielding the reactive oxidation species (ROS) which possess strong oxidation ability. The PCO of Cu-EDTA was initiated either by the ROS in the bulk solution, or by the photogenerated holes and/or the ROS on the surface of the TiO_2 nanofibers where Cu-EDTA was adsorbed onto. Subsequently, decomplexation of the Cu^{2+} from Cu-EDTA complexes would take place, followed by the adsorption of Cu^{2+} onto TiO_2 nanofibers. [10, 32] Cu^{2+} ions in the bulk solution however would need to travel in order to access the photocatalysts prior to adsorption, especially under high pH condition where adsorption of Cu-EDTA was challenged. Thereafter, Cu^{2+} could be reduced into Cu metal (Cu^0) by the photogenerated electrons to yield T-C. [42, 44] XRD pattern and leachability analysis for T-C are available in SI. A uniform dispersion and adsorption of Cu^{2+} was facilitated by the mesoporosity and long

nanofibrous structure of the TiO$_2$ nanofibers. [42] H$_2$ could be harvested by extending PCO of the remaining intermediate oxidation by-products and PCR of H$_2$O or H$^+$. The extensive analysis of reaction products from the PCO of Cu-EDTA which was well-discussed in other literature, is not included in this research. [32, 33, 35, 61] Meanwhile, since the redox potential of Cu^0 is more electronegative than H$_2$O reduction potential, the migration of photogenerated electrons was promoted from the CB of TiO$_2$ to Cu^0 following which the electrons would be rapidly and efficiently used up for H$_2$O reduction into H$_2$.[44] Under acidic condition, additional H$^+$ would enhance the H$_2$ generation. On the surface of the TiO$_2$ nanofibers, Cu^0 rendered several advantages as follows: (1) it served as an efficient reduction co-catalyst for H$_2$ production, (2) it promoted the separation of photogenerated charges thus a longer lifetime of the charge carriers, and (3) it extended the light sensitivity and absorption thus the charges photogeneration ability of TiO$_2$ nanofibers. [44] Hence, H$_2$ generation rate from Cu-EDTA was more efficient than that from EDTA. While the Cu^0 could also be possibly oxidized by the holes into Cu^{2+} [19, 44], and while the PCR of the Cu^{2+} into Cu^0 would result in the competition for electrons to generate H$_2$ [44], the overall net effect of Cu^0/Cu^{2+} and Cu^{2+}/Cu^0 redox reactions were seen to be insignificant and would become negligible at one stage, especially as the reaction progressed beyond 1 hr after which almost 90% of Cu^{2+} were removed along with a continuous H$_2$ evolution. Briefly, this study has showed that clean water, clean energy fuel, and R-TC could be co-generated from photocatalytic treatment of Cu-EDTA through the excellent synergy rendered by extending PCO and PCR of Cu-EDTA coupled with TiO$_2$ nanofibers of superior physicochemical properties. With the elimination of (1) prior complex synthesis process to modify and enhance TiO$_2$, (2) sacrificial reagent to enhance reaction efficiency for clean water and clean energy production, and (3) additional chemical to recover Cu, this approach has enhanced the sustainability of Cu-

EDTA treatment via TiO$_2$ photocatalysis significantly. What is more, this ingenious synergistic integration represents an adoptable approach to synthesize other functional composite nanomaterials from other organometallic wastewater streams in a green manner, possibly broadening its environmental application prospect. While this approach is being pursued; the monitoring of and identification of suitable treatment technology for NH$_4^+$, NO$_3^-$, and dissolved organic carbon may be necessary to close the loop in the later stage as this research matures, since their excessive existence in the water body would adversely impact the health of aquatic ecosystem and its surrounding living community.
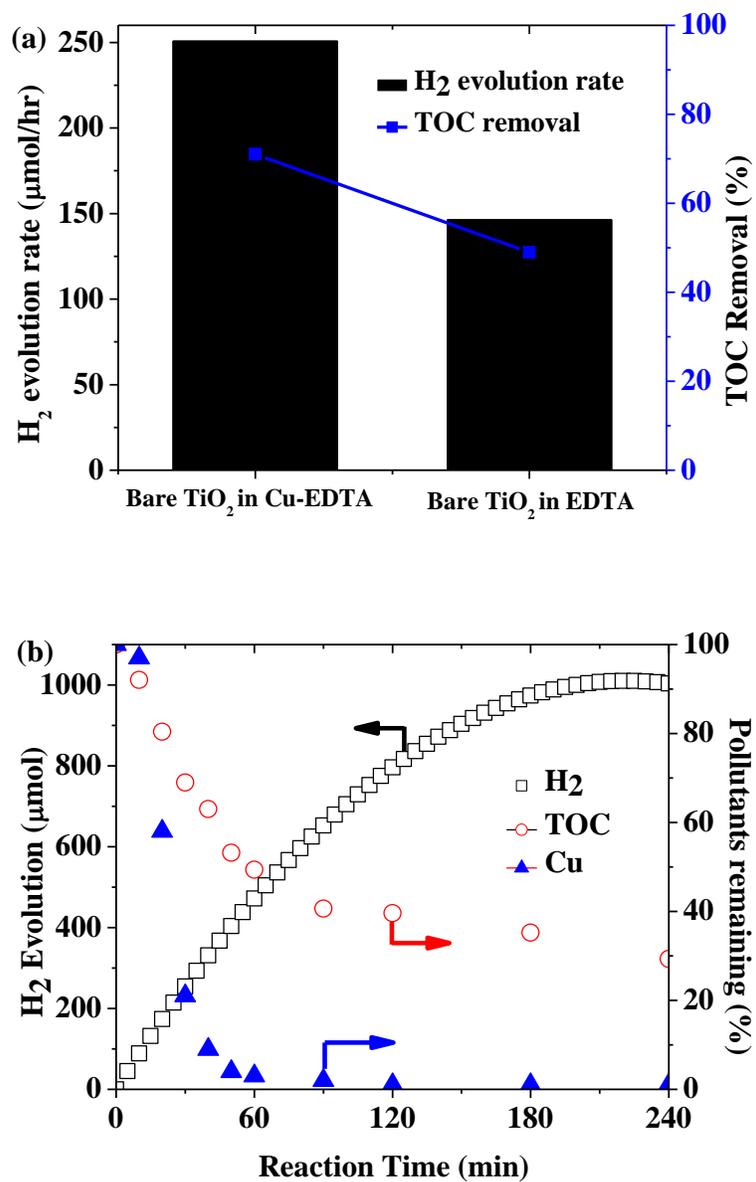
Figures

Figure 1. (a) Photocatalytic TOC removal (%) and H_2 generation rate for Cu-EDTA and EDTA, and (b) Photocatalytic removal of TOC (%), Cu (%), and H_2 generation over 4 hr reaction in Cu-EDTA
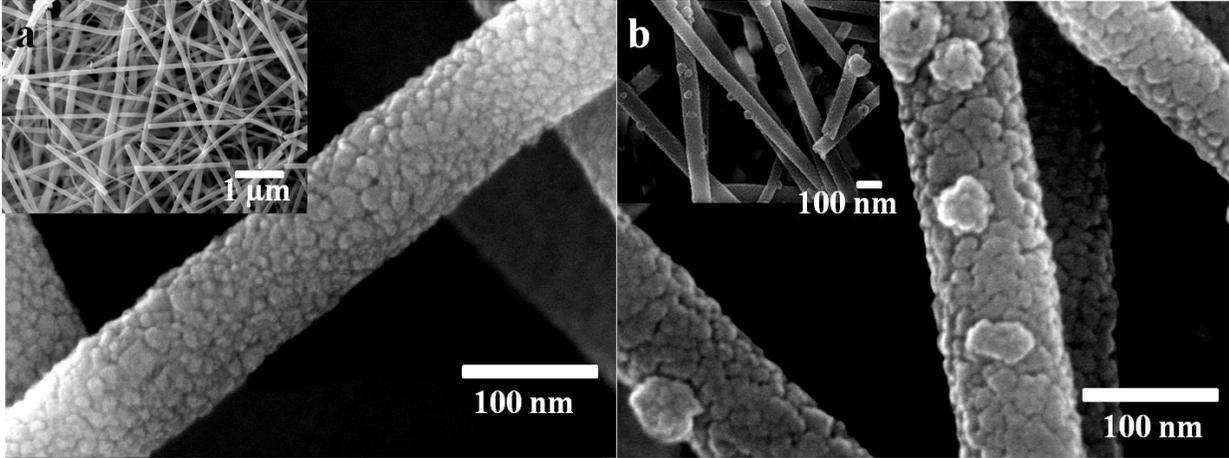
Figure 2. (a) High magnification and low magnification (inset) FESEM images of ultralong and ultrathin electrospun 1D TiO$_2$ nanofibers and (b) High magnification and low magnification (inset) FESEM images of reclaimed TiO$_2$-CuO composite nanofibers (R-TC)
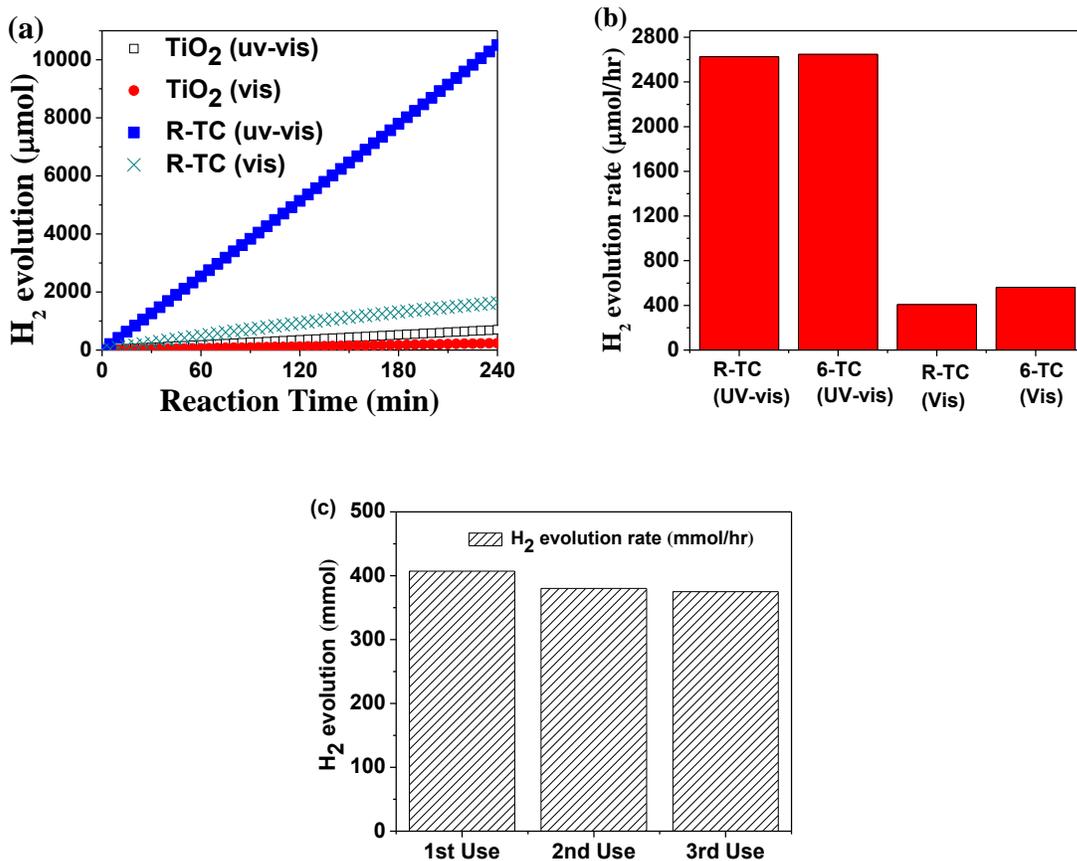
Figure 3. (a) Photocatalytic H$_2$ generation from 5%(v/v) glycerol using R-TC under UV-visible and visible lights and (b) Comparison of H$_2$ evolution rate from 5% v/v glycerol under UV-visible and visible lights between R-TC and innovative TiO$_2$-CuO composite (6-TC), and (c) Reusability experiment for photocatalytic H$_2$ generation by R-TC

Schemes

Scheme 1. Mechanism behind the cogeneration of H_2, clean water and R-TC from the photocatalytic treatment of Cu-EDTA using 1D TiO_2 nanofibers
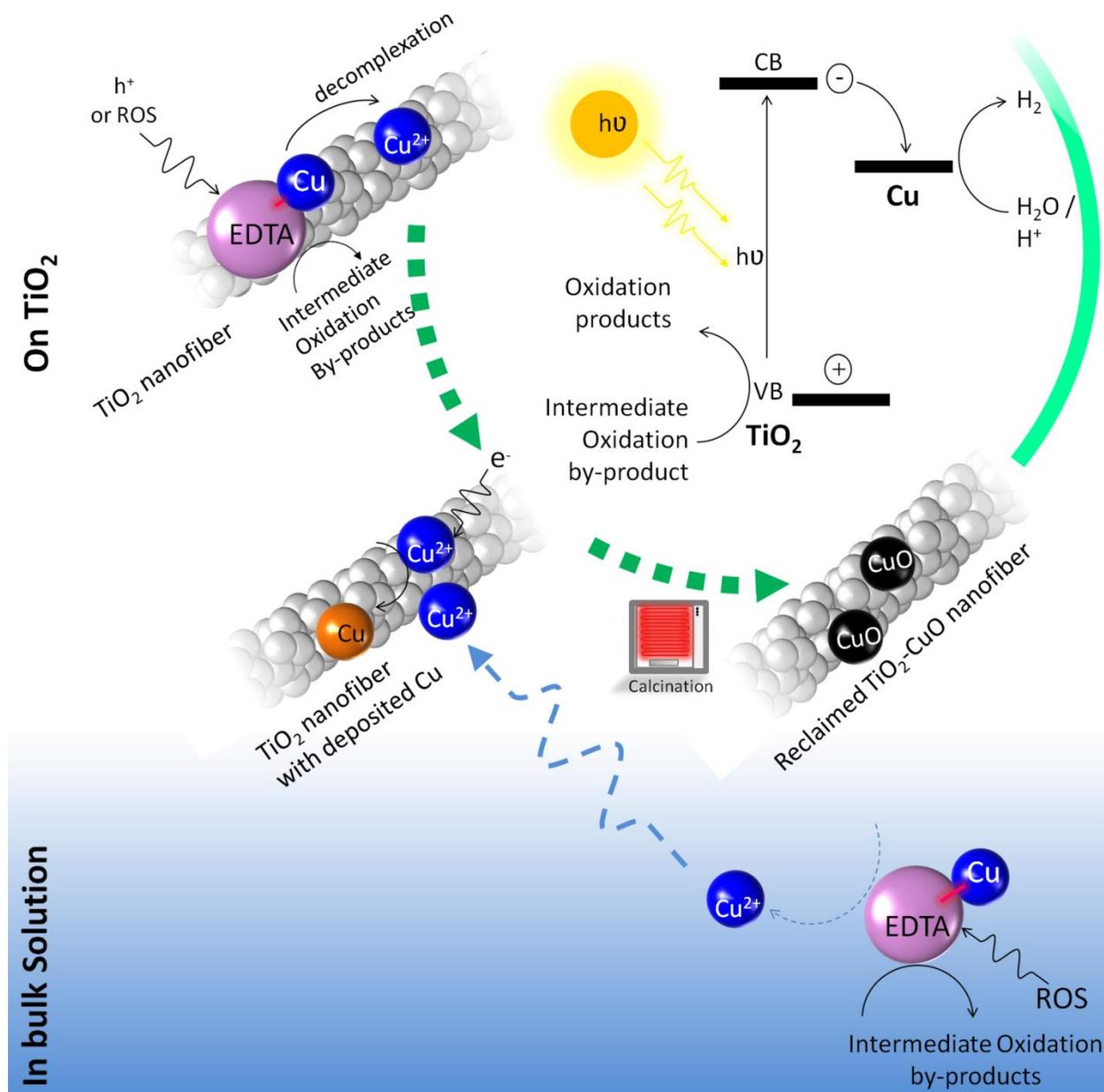
Tables

Table 1. Effect of solution pH on photocatalytic reaction

pH condition (Cu-EDTA)	Time to achieve 90% Cu reduction (min)	TOC removal after 4 hours reaction (%)	H_2 evolution (μmol/hr/g)
pH 4	10	57.5	2293.0
pH 6	40	71.0	1930.3
pH 10	50	70.0	2196.6

ASSOCIATED CONTENT

Supporting Information

Supporting Information for characterization and verification studies as noted in the text available: Figure S1-S10 and Table S1-S6. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table of Contents (TOC)/Abstract Graphic