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2013

Lee, S. S., Bai, H., Liu, Z., & Sun, D. D. (2013). Novel-structured electrospun TiO₂/CuO composite nanofibers for high efficient photocatalytic cogeneration of clean water and energy from dye wastewater. *Water Research*, 47(12), 4059-4073.

<https://hdl.handle.net/10356/80040>

<https://doi.org/10.1016/j.watres.2012.12.044>

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Novel-Structured Electrospun TiO₂/CuO Composite Nanofibers for High Efficient Photocatalytic Cogeneration of Clean Water and Energy from Dye Wastewater

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Abstract. It is still a challenge to photocatalytically cogenerate clean water and energy from dye wastewater owing to the relatively low photocatalytic efficiency of photocatalysts. In this study, novel-structured TiO₂/CuO composite nanofibers were successfully fabricated via facile electrospinning. For the first time, the TiO₂/CuO composite nanofibers demonstrated multifunctional ability for concurrent photocatalytic organic degradation and H₂ generation from dye wastewater. The enhanced photocatalytic activity of TiO₂/CuO composite nanofibers was ascribed to its excellent synergy of physicochemical properties: 1) mesoporosity and large specific surface area for efficient substrate adsorption, mass transfer and light harvesting; 2) red-shift of the absorbance spectra for enhanced light utilization; 3) long nanofibrous structure for efficient charge transfer and ease of recovery, 4) TiO₂/CuO heterojunctions which enhance the separation of electrons and holes and 5) presence of CuO which

serve as co-catalyst for the H₂ production. The TiO₂/CuO composite nanofibers also exhibited rapid settleability by gravity and uncompromised reusability. Thus, the as-synthesized TiO₂/CuO composite nanofibers represent a promising candidate for highly efficient concurrent photocatalytic organic degradation and clean energy production from dye wastewater.

Keywords: Cogeneration, Dye wastewater, Electrospinning, Hydrogen generation, Nanofibers, TiO₂/CuO

1. Introduction

Dye wastewater discharge from the textile and dye industries has been one of the major environmental pollution concerns (Anliker, 1977). Owing to its large and complex molecular structure, dye's high recalcitrance to degradation has posed a great challenge for colour removal and complete mineralization, which are both crucial to the aquatic life and human health ultimately (Anliker, 1977). Thus, vast research has been undertaken in order to develop an effective treatment process for dye wastewater. Physical-chemical process such as ozonation-coagulation and adsorption as well as biological anaerobic-aerobic process have been demonstrated for purification of dye wastewater (Davies et al., 2006; Lin and Lin, 1993; Méndez-Paz et al., 2005; Meshko et al., 2001; Van Der Zee and Villaverde, 2005; Wang et al., 2005). However, the remarkable results from these treatment methods entail high operation and maintenance cost comprising of either the treatment chemicals, post-treatment management of the resulting sludge or maintenance of the strict operating condition for microorganism's survival (Crittenden et al., 1997; Forgacs et al., 2004). Above all, the physical-chemical and biological processes are also energy-intensive in nature thus making them less desirable options because fossil fuel consumption is one of the major causes of climate change (Tassou, 1988). Consequently, water scarcity problem which is already afflicted by the dye pollutant and burgeoning population and industrialization will be further aggravated as climate change is also associated with the risk of reducing freshwater supply and its quality (Sophocleous, 2004). Therefore, existing dye wastewater treatment can

exacerbate both water and energy crisis which necessitate the continuous research and development of an alternative treatment method which is both environmentally and economically viable.

Photocatalytic oxidation over TiO_2 represents a promising technology to treating dye wastewater since this process is relatively low-cost, does not generate harmful secondary by-product, operable under standard atmospheric condition and utilizes the renewable solar energy for its activation (Chong et al., 2010). Furthermore, TiO_2 is non-toxic and exhibits high chemical and thermal stability (Hernández-Alonso et al., 2009). However, TiO_2 possesses large band-gap energy and rapid recombination of photogenerated electron-hole pairs thus resulting in limited utilization of the solar irradiation and low photocatalytic efficiency (Chen and Mao, 2007). These are among the factors which impede the practical application of TiO_2 for dye wastewater treatment and thus need to be overcome.

TiO_2 can be synthesized to improve its photocatalytic performance by doping of noble metals nanoparticle such as Pt (Kudo and Miseki, 2009). An interesting phenomenon was reported by Patsoura et al. (2006) where enhanced simultaneous hydrogen (H_2) generation was observed over Pt-loaded TiO_2 when wastewater containing Acid Orange 7 (AO7) was being purified (Patsoura et al., 2006). This defines a sustainable and economical avenue for alleviating the water scarcity and climate change issue concurrently because dye wastewater is readily available from the industry. H_2 is a very attractive fuel source due to its zero carbon emission, high conversion efficiencies, and it can be easily produced and stored on site (Hightower and Pierce, 2008). Since the first discovery of H_2 generation over TiO_2 (Fujishima and Honda, 1972), photocatalytic H_2 generation has been the subject of intensive research. However, more work is still needed in search for possible substitute to noble metal as the cost and sustainability concerns have rendered noble metals such as Pt not the ideal choice for long term solution (Chong et al., 2010).

Transition metal such as Cu may be a more economical option for enhancing TiO₂ photocatalytic activity. Recently, our group has developed TiO₂/CuO composite nanoparticles for H₂ generation and reported significant enhancement of photocatalytic H₂ generation than that of TiO₂/Pt from 10% v/v aqueous methanol (Xu and Sun, 2009). CuO played a similar role as Pt in promoting photocatalytic H₂ generation by serving as the electron trapping site good for H₂O reduction (Xu and Sun, 2009). However, the H₂ generation efficiency over the TiO₂/CuO composite nanoparticles from the more realistic dye wastewater was not demonstrated. Meanwhile, TiO₂/CuO nanoparticles have also been reported to show enhanced degradation of organic pollutants owing to the modified optical property which has enabled the composite material to tap into the visible light range of the solar irradiation (Helaïli et al., 2009). Nevertheless, photocatalytical nanoparticles tend to form aggregates which severely impedes the subsequent separation and reusability of the reacted photocatalyst in engineering application (Pan et al., 2010a). Moreover, the aggregates could serve as recombination centers for the photogenerated electrons and holes (Choi et al., 2010). Meanwhile, Wu et al. (2011) has successfully fabricated a novel CuO nanotube decorated with agglomerated TiO₂ nanoparticles for enhanced photocatalytic dye removal (Wu et al., 2011). However, the CuO nanotube-TiO₂ nanoparticle photocatalyst exhibited minimal surface area for dye adsorption. This could be ascribed to the occupied surface area on the CuO nanotubes by TiO₂ nanoparticles as well as agglomeration of TiO₂ nanoparticles which have resulted in the reduced available surface area for adsorption (Wu et al., 2011). The agglomeration of TiO₂ nanoparticles in the photocatalyst has also resulted in a less uniform CuO nanotube-TiO₂ nanoparticle structure with an un-optimized contact between the TiO₂ and CuO (Wu et al., 2011). Thus, the elimination of agglomeration phenomena which could influence the properties and subsequent photocatalytic performance of the resulting photocatalyst remains a great challenge. In view of this, one-dimensional TiO₂ composite nanofibers could present a more promising alternative by the virtue of its superior properties such as (1) high porosity and large surface area enhancing adsorption ability and light utilization rate, and (2) long aspect ratio retarding the recombination of photogenerated electrons and holes (Choi et al., 2010).

Nanofibers can be synthesized via several routes such as the hydrothermal method, sol-gel method, and electrospinning (Bian et al., 2007; Lin et al., 2008; Liu et al., 2007). Comparatively, electrospinning is the simplest and most inexpensive method (Dzenis, 2004; Li et al., 2006). It offers a versatile route to tune and control the morphology and chemical composition of nanomaterials by varying electrospinning process parameters such as voltage, precursor solution concentration, flow rate, and humidity (Li et al., 2006). Zhang et al. (2010) has fabricated electrospun ZnO/SnO₂ composite nanofibers with high porosity and enhanced specific surface (Zhang et al., 2010). Following this, both Hwang et al. (2011) (Hwang et al., 2011) and Lee et al. (2012) (Lee et al., 2012) have successfully fabricated TiO₂/SnO₂ composite nanofiber via electrospinning a precursor solution with homogeneous distribution of Ti and Sn. Despite the similar synthesis method employed and same chemical composite system with similar morphology, both of the TiO₂/SnO₂ composite nanofibers differed significantly in term of porosity, surface area, and light utilization which could influence the subsequent photocatalytic performance and application. These differences were likely attributed to the different raw materials used in the precursor solution. These studies have suggested that the facile electrospinning method has high potential and vast room for innovation in fabricating highly efficient photocatalyst of different composite system.

Nevertheless, little work has been done to fabricate TiO₂ composite nanofibers via electrospinning for concurrent photocatalytic organic degradation and H₂ production from waste water. As far as TiO₂/CuO composite system is concerned, there has not been any report on the electrospinning of its nanofiber with incorporation and synergy of excellent physicochemical properties which are beneficial for photocatalytic reaction such as enhanced mesoporosity and specific surface area, enhanced solar light absorption with visible light sensitivity, good contact and high dispersion of TiO₂/CuO heterojunctions, longer lifetimes of photogenerated charge carriers and long nanofibrous structure for efficient charge transfer and recovery (Lee et al., 2012). In addition, no report was available on the feasibility of TiO₂/CuO composite nanofibers for concurrent photocatalytic organic degradation and H₂ production

from dye waste water. In view of its simplicity and advantage over other method as well as the recently developed $\text{TiO}_2/\text{SnO}_2$ composite nanofibers by our group (Lee et al., 2012), electrospinning could be exploited to fabricate new TiO_2/CuO composite nanofibers with enhanced photocatalytic organic oxidation and H_2 production from dye wastewater.

In this study, novel-structured TiO_2/CuO composite nanofibers were successfully synthesized via electrospinning an innovated precursor solution (Lee et al., 2012). For the first time, the composite nanofibers were used for simultaneous photocatalytic organic pollutant degradation and H_2 production from dye wastewater. AO7 was used as the model dye wastewater since azo dye represents the major portion of dye wastewater generated from the industry (Peternel et al., 2006). It is worthy to note that unlike the bare TiO_2 nanofibers which was only useful for organic removal, the TiO_2/CuO composite nanofibers exhibited multifunctional ability to evolve H_2 gas concomitantly with dye degradation. The H_2 generation rate over the as-synthesized TiO_2/CuO composite nanofibers was 3 times more than that reported for Pt/TiO_2 (Patsoura et al., 2006). What is more, the TiO_2/CuO composite nanofibers were shown to be reusable without significant deterioration of its photocatalytic performance. Hence, the as-synthesized new TiO_2/CuO composite nanofibers possess great potential for an economical and sustainable dye wastewater remediation with clean energy production capability.

2. Materials & Methodology

2.1 Materials

Analytical grade ethanol, acetic acid, tetra n-butyl titanate ($\text{Ti}(\text{oBu})_4$), polyvinylpyrrolidone (PVP; $M_w=1\ 300\ 000$) and copper-2-ethylhexanoate ($\text{Cu}[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2]_2$) were obtained from Sigma Aldrich. All the materials were used without any further purification.

2.2 Preparation of bare TiO_2 and TiO_2/CuO nanofibers

A solution containing 53 wt% ethanol, 18 wt% acetic acid, 7 wt% PVP, 20 wt% $\text{Ti}(\text{oBu})_4$ and 2 wt% $\text{Cu}[\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CO}_2]_2$ was mixed for 6 hours using a magnetic stirrer in order to obtain a homogenous and clear mixture of precursor solution containing 10% mol Cu. This Cu amount was selected based on our previous study which demonstrated that 10% mol Cu was the optimum loading for photocatalytic H_2 generation (Xu and Sun, 2009). For the preparation of bare TiO_2 nanofiber, only $\text{Ti}(\text{oBu})_4$ was added to the precursor solution. Subsequently, the precursor solution was passed through a hypodermic syringe with a 1.1 mm diameter stainless steel nozzle (Li and Xia, 2003). An electrical potential of 19 kV was applied using a high voltage DC supply (Dongwen High Voltage Power Supply, China). A distance of 18 cm was maintained between the needle tip and the grounded aluminium foil collector. During electrospinning process, the humidity was maintained at $< 40\%$ using N_2 gas to prevent pre-mature hydrolysis of the precursor solution (Li et al., 2006). The precursor solution was ejected at a rate of 0.3mL/hr via a syringe pump (NE-1000, USA). Non-woven nanofiber webs were consequently obtained at the collector and left in the air for 2 hours for complete hydrolysis. The electrospun nanofibers were calcined in the air at 450°C for 45 min to obtain TiO_2/CuO and bare TiO_2 nanofibers.

2.3 Characterization

The morphology of the electrospun nanofibers was studied using a field-emission scanning electron microscope (FESEM, JEOL JSM-7600F). The microstructure of the electrospun TiO_2/CuO composite nanofibers were observed by scanning transmission electron microscopy (STEM) attached to the FESEM, JEOL, JSM-7600F, working at an accelerated voltage of 30 kV, and the high resolution transmission electron microscopy (HRTEM, JEOL JEM-2010) working at an accelerated voltage of 200 kV. The selected area electron diffraction (SAED) pattern was indexed using Jems, a HRTEM SAED indexing software. The crystalline structure was obtained using a Bruker D8 Advance X-ray diffractometer (XRD) with monochromated high-intensity $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Scherrer equation which is well-used to measure the crystal size according to the XRD pattern was adopted for

the estimation of nanocrystalline size. The Scherrer Equation is $L = K\lambda / \beta \cos \theta$ where L , K , λ , β , and θ are size of particles in nm, a constant of 0.891, wavelength of X-ray, full width at half maximum (FWHM) of the XRD peak, and angle of diffraction, respectively (Chen and Mao, 2007). X-ray photoelectron spectroscopy (XPS) was carried out to determine the chemical states of all the elements present using a Kratos Axis Ultra Spectrometer with a monochromic Al K α excitation source at 1486.7 eV, with a voltage of 15 kV and an emission current of 10 mA. All binding energies were referenced to C 1s at 284.6 eV. Elemental composition of the photocatalyst was analyzed using an energy dispersive X-ray spectrometer (EDX) (Oxford Instrument, X-Max, 80 mm²) attached to the FESEM (JEOL, JSM-7600F). The FESEM-STEM sample was used for EDX analysis in order to obtain elemental mapping for a single nanofiber under high magnification. The Brunauer, Emmett, and Teller (BET) specific surface area were determined at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2040 system. The samples were degassed at 200°C for 3 hours prior to measurement. The Barret-Joyner-Halenda (BJH) method was employed to obtain the pore size distribution of the photocatalysts. The absorption spectra of the photocatalysts were recorded using the Thermo Scientific Evolution 300 UV-Vis spectrometer (Thermo Fisher Scientific, Massachusetts, USA) equipped with the integrating sphere and a xenon lamp source. The indirect bandgap energy (E_g) of the photocatalysts was approximated by employing the Kubelka-Munk function which converts diffusive reflectance measurements into the equivalent absorption coefficients (Liu et al., 2011). It is the photon energy ($h\nu$) value when $[F(R_\infty)]^{0.5}=0$, obtainable when the vertical segment of the plot of $[F(R_\infty)]^{0.5}$ against $h\nu$ is extended to intersect the X-axis ($h\nu$) (Ng et al., 2010). Photoluminescence (PL) analysis was carried out using a Fluorolog-3 spectrofluorometer (Horiba Scientific, New Jersey, USA) with an excitation wavelength at 300 nm (Ng et al., 2010).

2.4 Photocatalytic H₂ generation and organic degradation

Concurrent photocatalytic H₂ generation and organic degradation test was carried out in an inner irradiation type Pyrex reactor with a volume of 270 mL with a 400W high pressure Hg lamp (Riko,

UVL-400HA) as the light source. The TiO_2/CuO composite nanofibers were suspended at a concentration of 0.4 g/L into 20 mg/L of Acid Orange II (AO7) solution which is used as the model organic pollutant. Solution pH of 6.02 was not adjusted. The reactor was maintained at a temperature of 298K (25°C) throughout the photocatalytic reaction. Scheme 1 illustrates the schematic diagram of the photoreactor setup. Prior to UV-visible light irradiation, the suspension was stirred for 30 min in the dark to reach adsorption-desorption equilibrium between organic substrates and the photocatalysts. The reactor was subsequently purged with nitrogen gas for 30 min to de-aerate the reactor. Gas produced from the photocatalytic reaction was analyzed using a TCD-type gas chromatography (Agilent 7890A, HP-PLOT MoleSieve/5A) (Xu et al., 2011a; Xu and Sun, 2009). An aliquot of 3 mL was sampled at $t=3$ min during the UV-visible irradiation. It was filtered through a Millipore filter (0.45 μm) following which the dye concentration of the filtrate was measured using the UV-visible spectrophotometer at the characteristic absorbance wavelength of 485 nm. This experiment was carried out in triplicate. At the end of the reaction, the suspension was filtered through a Milipore filter of 0.45 μm . The reacted photocatalysts which was collected on the filter was dried overnight at 350 °C in a furnace to regenerate the photocatalysts (Xu and Sun, 2009). In order to investigate the stability and recyclability of the TiO_2/CuO composite nanofibers, the dried composite nanofibers were re-used in the similar reaction for 3 cycles. The as-prepared bare TiO_2 nanofibers were also tested for concurrent H_2 generation and organic degradation for comparison. Photolysis of the dye and H_2 generation under UV-vis irradiation without photocatalyst was conducted under the same condition as control.

3. Results and Discussion

3.1 Characterization of TiO_2/CuO composite nanofibers

3.1.1 Morphological observation by FESEM and TEM

The surface morphology of the electrospun TiO_2/CuO composite nanofibers measured by FESEM is shown in Figs. 1(a)-(d). The uncalcined fibrous structure of an as-spun individual composite nanofiber

is illustrated in Fig. 1(a). Prior to calcinations, the surface appeared smooth, without any obvious pores. As shown in Fig. 1(b), after calcinations at 450 °C, the length of the nanofibers remained more than 10 μm long with a typical aspect ratio of around 30-50 and bead-less. The composite nanofibers were shown to be very consistent in diameter, approximated to be less than 100 nm (Fig. 1(c)). The uniformity and elimination of beads provides corroborating evidence that the viscoelastic force and electrostatic repulsion between charges in the precursor solution were sufficiently maintained through humidity control, and hence was able to suppress the influence of surface tension which drives the formation of beads (Li and Xia, 2004). The diameter of the calcined nanofibers decreased and the surface became rough and highly porous (Fig. 1(d)) due to the loss of PVP and other organic substances used in the preparation of the precursor solution and crystallization of anatase TiO_2 during calcinations (Li and Xia, 2003). The pores were measured to be approximately between 5 – 10 nm. This porous structure is highly advantageous for photocatalysis because it renders more active sites for adsorption and enhanced residence time and utilization of absorbed light as well as good separation characteristic (Pan et al., 2010a).

Fig. 2(a) shows the dark-field mode FESEM-STEM images of the TiO_2/CuO composite nanofibers. The nanofibers were further affirmed to be very consistent and uniform. Under the dark field mode of the STEM, heavy element such as Cu should appear brighter while lighter element such as Ti should appear darker. Therefore, the white spots on the composite nanofibers could be attributed to the Cu element on and within the composite nanofibers. Fig. 2(b) shows the microstructure of the as-synthesized TiO_2/CuO composite nanofibers observed under the bright field mode of TEM. It vividly depicts that the composite nanofibers were made up of well-grown granular nanocrystals. Good crystallinity is one of the pre-requisites for an efficient photocatalytic activity because it facilitates charge transfer (Pan et al., 2010a). The selected area electron diffraction (SAED) as shown in Fig. 2(c) was indexed for anatase TiO_2 (Kumar et al., 2007; Nonoyama et al., 2012). The diffuse ring pattern indicates that the TiO_2/CuO composite nanofibers were made up of polycrystalline structure of TiO_2 ; thus confirming that there were

more than one crystal which have made up the nanofibers (Ng et al., 2010). HRTEM was employed to further elucidate the crystal structures of the TiO_2/CuO composite nanofibers. As presented in Fig. 2(d), the high magnification HRTEM image clearly indicates two distinctive lattice fringes of 0.325 nm and 0.253 nm; which correspond well to the (101) plane of anatase TiO_2 (Ng et al., 2010) and the (111) plane of CuO , respectively (Cao et al., 2003; Gouma and Lee, 2011).

3.1.2 Elemental analysis by EDX

The EDX analysis was carried out on a STEM-FESEM sample under high magnification as depicted in Fig.3(a). Figure 3(b) illustrates the EDX spectrum for a selected point (in yellow) outside the TiO_2/CuO composite nanofibers. While no peaks for Ti and O were observed, weak peaks of Cu as shown in Fig. 3(b) suggested possible detection of Cu element from the Cu-grid which was used to hold the STEM sample, possibly due to the interaction of the scattered electron beam within the FESEM equipment with the Cu-grid. On the other hand, the EDX spectrum from a selected point (in red) on the TiO_2/CuO composite nanofibers (Fig.3(c)) depicts prominent peaks of Ti and Cu. It is worthy to note that the Cu peaks in Fig.3(c) was significantly more intensified than that in Fig.3(b), thus implying that besides the Cu-grid, the detected Cu element could be contributed by that present within the TiO_2/CuO composite nanofibers as well. Elemental mapping was carried out for the selected area (in white) on the TiO_2/CuO composite nanofibers in Fig.3(a) to further verify the presence of Ti, Cu and O in the composite nanofibers. As shown in Figs.3(d)-(f), all elemental maps notably correspond and match well with the shape of the nanofibers in Fig.3(a) hence signaling the presence of Ti, Cu and O in the TiO_2/CuO composite nanofibers. Meanwhile, in consistent with the EDX spectrum in Fig.3(b), some Cu was also detected outside the nanofibers as illustrated in Fig.3(f) thus further affirming the possible cross-analysis from the Cu-grid. Nonetheless, the significant density difference of the Cu mapping between the nanofibers and their surrounding, coupled with the distinctive nanofibers shape of the mapping as well as the amplified Cu peaks in the EDX spectrum in Fig.3(c) have reasonably evidenced that Cu in the TiO_2/CuO composite nanofibers was well-witnessed by the EDX analysis albeit the inevitable Cu signal

from the Cu-grid. Figs.3(d)-(f) were also evidence of the well-dispersed Ti, Cu, and O elements with negligible agglomeration throughout the TiO₂/CuO composite nanofibers. This implies that a good distribution of elements has been achieved from the mixing of the precursor solution with mere magnetic stirrer for 6 hours (Xu and Sun, 2009). From synthesis point of view, this is an additional advantage since high temperature and high speed mixing using a dispersive equipment as reported by others were not necessary to achieve a good dispersion (Hwang et al., 2011; Zhang et al., 2009). Uniform dispersion of CuO is advantageous by ensuring strong interaction between TiO₂ and CuO for migration of electrons between conduction bands thereby enhancing its charge transfer and separation for photocatalytic reaction (Yoong et al., 2009).

3.1.3 Crystal phase determination of TiO₂/CuO composite nanofibers by XRD

The XRD was used to examine the crystal phases of TiO₂/CuO composite nanofibers. As shown in Fig. 4(a), the TiO₂/CuO composite nanofibers have been well-crystallized into anatase TiO₂ phase (JCPDS file No. 21-1272) (Liu et al., 2012). A close-up XRD pattern in the region of $2\theta=30^{\circ}$ - 45° was plotted to provide a clearer visualization on the phase existence in the TiO₂/CuO composite nanofibers (Fig. 4(b)). A relatively weak peaks were observed at $2\theta=36.5^{\circ}$ and $2\theta=38.8^{\circ}$ which could be corresponded to the (111) and (002) reflections of CuO (Mor et al., 2008). A few reports have attributed the non-existence or weak peak of CuO to the low Cu content and high dispersion of the Cu species within the photocatalysts (Amores et al., 1994; Gombac et al., 2010; Xu et al., 2011b). Meanwhile, research have found that the intensity of the XRD peak is also dictated by the degree of crystallization which is influenced by the calcination temperature (Jiang et al., 2012; Pan et al., 2010b). Thus, in order to observe the change in the crystallinity and corresponding XRD peak as well as to further verify the existence of CuO peak, we have employed different calcination temperature (450°C , 550°C , and 750°C) for the as-spun composite nanofibers with the same Cu content of 10% mol. As depicted in Fig. 4(b), significantly sharper and more intense diffraction peaks were observed for both anatase TiO₂ and CuO even at the same low Cu content. The peaks at $2\theta=36.5^{\circ}$ and $2\theta=38.8^{\circ}$ were clearly given by the (111)

and (002) phases of CuO (Mor et al., 2008). This observation implies that a higher degree of crystallization has been attained for both phases with increase in the calcination temperature; and that the synthesis method employed in this study has produced both TiO₂ and CuO crystals in the composite nanofibers. Table 1 summarizes and compares the calculated crystalline size of anatase TiO₂ phase between the bare TiO₂ nanofibers and the TiO₂/CuO composite nanofibers. There was a decrease in the crystalline size which suggests that the crystallization of anatase TiO₂ was affected following the incorporation of Cu (López-Ayala and Rincón, 2011). With the reduced crystal size of the anatase TiO₂, the distance which the photogenerated electrons and holes need to travel to arrive at the reaction sites on the surface of the photocatalyst becomes shorter (Kudo and Miseki, 2009). In principle, the faster the photogenerated charges reach the reaction sites, the lower the recombination rate because the availability of the photogenerated charges for reduction and oxidation process has been increased. Thus, reduction in the crystal size should enhance the photocatalytic performance of the TiO₂/CuO composite nanofibers.

3.1.4 Chemical state analysis by XPS

The chemical state of each element in the TiO₂/CuO composite nanofibers was studied by XPS analysis. The results were observed in Figs. 5(a) – (d). The binding energy for C1s peak at 284.6 eV was used as the reference for calibration. The survey spectrum as presented in Fig. 5(a) confirms that only Ti, Cu, and O were present in the TiO₂/CuO composite nanofibers, which are in consistent with the EDS spectrum. High resolution XPS spectrum of Ti 2p, Cu 2p, and O 1s were observed in Fig. 5(b) – (d), respectively. The peaks in the Ti 2p spectra (Fig. 5(b)) were indicative of Ti 2p_{3/2} and Ti 2p_{1/2} of Ti⁴⁺ (Xu et al., 2011a), located at the binding energy of 458.0 eV and 464.0 eV, respectively. As shown in Fig. 5(c), the binding energy of 933.9 eV and 953.9 eV were ascribed to the Cu 2p_{3/2} and Cu 2p_{1/2} of Cu²⁺ in CuO (Wu and Lee, 2004), respectively. The characteristic shakeup satellite peak around 942.0 eV and 962.0 eV further confirmed the oxidation state of Cu to be +2 (Li et al., 2008). The peak of O 1s spectrum (Fig. 5(d)) at binding energy of 529.5 eV was attributed to the O in TiO₂ and CuO (Xu et al.,

2011a), whereas the peaks at higher binding energy of 531.2 eV was indicative of surface contamination by hydroxides, from the atmosphere (Xu et al., 2011a). On the basis of the EDX spectrums and elemental mappings (Figs.3(b)-(f)), high-magnification HRTEM image (Fig. 2(d)), close-up XRD pattern in the region of $2\theta=30^{\circ}$ - 45° (Fig.4(b)) and XPS spectrum for CuO (Fig. 5(c)), it is reasonable to suggest that TiO_2/CuO heterojunctions were present in the as-synthesized TiO_2/CuO composite nanofibers.

3.1.5 Porous structure determination by N_2 adsorption-desorption

The porous structure of the TiO_2/CuO composite nanofibers was determined by N_2 sorption-desorption isotherm method. As illustrated in Fig. 6(a), a type IV isotherm curve with obvious H3-type hysteresis behavior was observed according to IUPAC classification, which characterized both the bare TiO_2 and TiO_2/CuO composite nanofibers to be mainly mesoporous (Sing, 1995). This mesoporous structure is good to promote efficient mass transfer for photocatalysis owing to the enhanced accessibility to the inner reactive sites of the photocatalyst (Pan et al., 2010a). However, the TiO_2/CuO composite nanofibers possess higher pore volume than bare TiO_2 nanofibers implying a more complex mesoporosity structure of the composite nanofibers. As shown in Table 2, the BET specific surface area of the TiO_2/CuO composite nanofibers was significantly higher than that of the bare TiO_2 nanofibers. This observation could be addressed by the decreasing crystal size of anatase TiO_2 owing to the addition of Cu element (Table 1) which has endowed the composite nanofibers with higher surface area. The increased specific surface area could benefits the heterogeneous photocatalysis by facilitating surface adsorption of reactants and thus promoting the interfacial charge transfer. Meanwhile, the BJH analysis outcome has depicted a narrow pore size distribution between 2-20 nm with peaking position at 3 nm and 6 nm (Fig. 6(b)). This is in close agreement with that approximated from the FESEM image in Fig. 1.

3.1.6 UV-visible spectrum of TiO_2/CuO composite nanofibers

The TiO₂/CuO composite nanofibers have demonstrated significantly increased absorption edge in the UV region and visible light region, between 350-800 nm (Fig. 7(a)). A narrower bandgap of approximately 2.60 eV was recorded using Kubelka-Munk equation (Fig. 7(b)). This smaller bandgap could be formed due to the transition from the valence band of CuO to the conduction band of TiO₂, which are both in good contact (Bokhimi et al., 1997) as well-witnessed by the HRTEM image in Fig.2(d) and the elemental mapping in Figs.3(d)-(f). The increased surface area and porosity as evidenced by the BET specific surface area (Table 2) and N₂ adsorption-desorption isotherm method (Fig. 6(a)) could address the enhanced light absorption ability of the TiO₂/CuO composite nanofibers thus increasing the absorbance in the UV region of around 350 nm. In principle, the enhanced sensitivity in the visible light range and light absorption will favor greater photon absorption which increases the likelihood of photo-induced electrons-holes generation for improved photocatalytic activity.

3.1.7 Photoluminescence emission of TiO₂/CuO composite nanofibers

The photoluminescence (PL) emission was used to evaluate the separation and recombination tendency of the photogenerated electrons and holes within the activated TiO₂/CuO composite nanofibers (Liu et al., 2007). The emission signal of the PL spectra is given by the recombination phenomenon of the free electrons and holes (Ng et al., 2010). A high PL spectra intensity implies a high recombination tendency of the photogenerated charge carriers which could weaken the photocatalytic performance. Hence, this method provides a good indication of the electrons and holes lifetime within a semiconductor (Yu et al., 2011). Figure 8 depicts the PL spectra of the TiO₂/CuO composite nanofibers as well as the bare TiO₂ nanofibers. Both nanofibers exhibited significant PL signals upon irradiation at 300 nm. However, the addition of CuO to TiO₂ has resulted in a weaker PL intensity than that of bare TiO₂ nanofibers. This is because of the formation of TiO₂/CuO heterojunctions between the TiO₂ and CuO in the TiO₂/CuO composite nanofibers (Shifu et al., 2009) as well-evidenced in the HRTEM image (Fig. 2(d)). The recombination rate of electrons and holes in the TiO₂/CuO composite nanofibers is greatly suppressed as

there is a tendency of electron transfer from the conduction band (CB) of TiO_2 to the CB of CuO due to the potential difference between the CBs (Wu et al., 2011) as depicted in Scheme 2. The high dispersion of Ti and Cu as witnessed by the EDX elemental mapping in Figs.3(d)-(f) further facilitate the efficient and fast electron transfer between the CBs because of the close contact between TiO_2 and CuO junctions. In addition, the long structure of the TiO_2/CuO composite nanofibers as shown in Fig.1 has also contributed to the enhanced charge transfer thus lowering the charge recombination rate. It is therefore postulated that the photocatalytic activity of the composite nanofibers will be greatly enhanced due to the efficient charge separation.

3.2 Concurrent photocatalytic organic degradation and H_2 production over TiO_2/CuO composite nanofibers

3.2.1 Adsorption of AO7

The dark adsorption process was carried out to achieve the adsorption-desorption equilibrium between organic substrates and the photocatalysts prior to the photocatalytic experiment. At the end of the dark adsorption, the concentration of AO7 was measured to determine the adsorption capability of the photocatalysts. As shown in Fig. 9(b), the TiO_2/CuO composite nanofibers exhibited a much higher adsorption capability, which promotes the organic removal process from the waste water. The concentration of AO7 decreased approximately 46 % following the dark adsorption process using the TiO_2/CuO composite nanofibers. No further reduction of AO7 was observed after 30 min in the dark condition as the experiment was carried out in a black box which is completely free from the influence of light. On the other hand, bare TiO_2 nanofibers demonstrated only adsorption of approximately 25 %. As corroborated by the BJH (Fig. 6) and BET (Table 2) analysis, the enhanced pore structure and volume as well as larger surface area of the TiO_2/CuO composite nanofibers have increased the reaction sites availability and accessibility thus facilitating reactants adsorption on the composite nanofibers. Ultimately, this would facilitate a more efficient interfacial charge transfer to the adsorbed substrates which is needed for organic oxidation. Similar observation was reported by Doh et al. (2008) where

electrospun TiO₂ nanofibers, owing to its mesoporosity, adsorbed more dye than TiO₂ P25 (Doh et al., 2008). While it has been reported before that dye degradation was not dependent on its adsorption on the photocatalyst (Chen et al., 2005; Wu et al., 2011), the morphology and structure of the photocatalyst used may influence the importance of adsorption in facilitating photodegradation of AO7. Unlike the TiO₂ P25 (Chen et al., 2005) and the CuO nanotube-TiO₂ nanoparticles photocatalysts (Wu et al., 2011), the long nanofibrous and mesoporous structure of the as-synthesized TiO₂/CuO composite nanofibers in this study has intrinsic advantageous of facilitating interparticle charge transfer and low aggregation tendency which contribute to effective surface reaction (Choi et al., 2010). Thus, as far as surface reaction is concerned, the possibility of AO7 oxidation by the photogenerated holes may be enhanced and even more with the high adsorption capability of the one-dimensional TiO₂/CuO composite nanofibers (Xu et al., 2011c). This is because compared to the AO7 molecule in the solution, the adsorbed AO7 molecules or its intermediates will be more readily and easily accessible thus scavenged by the reactive oxidative species (ROS) generated on the surface of the photocatalyst upon the UV-vis light irradiation (Xu et al., 2011c).

3.2.2 Photocatalytic oxidation of AO7

Photocatalytic organic degradation by the TiO₂/CuO composite nanofibers was evaluated by means of its discoloration efficiency in a 20 mg/L AO7 solution irradiated with UV-visible light and thereafter compared with that of the as-prepared bare TiO₂ nanofibers under the same experimental condition. Following a 30-min dark adsorption process, the suspension was subjected to photocatalytic reaction for 3 hours. Figure 9(a) illustrates the changes in concentration of AO7 when $t=3$ min during the UV-visible irradiation. Discoloration of AO7 as illustrated in Fig.9(b) was significantly enhanced by photocatalysis in the presence of TiO₂/CuO composite nanofibers, hence indicating that the photocatalyst played a prominent role in promoting the degradation rate of the organic pollutant from waste water. Complete discoloration of the dye solution due to photocatalysis was observed in less than 20 min in the presence of photocatalyst, whereas under photolysis (without photocatalyst) a longer

duration of approximately 40 min was required to remove the colour of the dye solution with the same concentration. Discoloration of the AO7 solution was ascribed to the breaking of azo-bond of AO7 into smaller colorless molecules upon oxidation by the photogenerated holes and holes-induced ROS such as $\text{OH}\cdot$ on the surface reactive sites and bulk solution, respectively (Stylidi et al., 2004).

Among the two photocatalysts used, TiO_2/CuO composite nanofibers demonstrated the highest discoloration of 35.3 % at $t=3$ min during the irradiation. The enhanced photocatalytic organic degradation over TiO_2/CuO composite nanofibers compared to bare TiO_2 nanofibers was ascribed to: (1) the TiO_2/CuO heterojunctions which have retarded the recombination of the photogenerated holes and electrons, as verified by the PL emission in Fig.8 and (2) the red-shift of absorbance spectra as witnessed by the UV-vis spectra in Fig. 7 thus increasing the light utilization ability. The highly dispersed Cu in the composite nanofibers as well-witnessed in the elemental mapping in Fig. 3 also suggested that good contact between TiO_2 and CuO, has been achieved to further enhance the photogenerated electrons and holes separation between the heterojunctions. In addition, smaller anatase TiO_2 crystal size as shown in Table 1 was advantageous because it offered shorter migration distance for photogenerated charge transfer to the surface reaction sites and thus lowered the recombination rate. As discussed in section 3.2.1, high adsorption capability of the TiO_2/CuO composite nanofibers could have contributed to the enhanced photodegradation of the AO7 as well.

Meanwhile, the enhancement of photocatalytic organic degradation by dye-sensitization phenomenon of TiO_2 by the adsorbed AO7 has been well-studied and can be found elsewhere (Stylidi et al., 2004; Tanaka et al., 2000). Dye-sensitization of TiO_2 leads to utilization of the visible light and thus more formation of ROS which eventually enhance the total photocatalytic degradation of dye. However, dye-sensitization is very much dependent on the continuous supply of colored dye wastewater because the colorless by-products from the degradation of AO7 was not sensitive towards visible light (Stylidi et al., 2004). Since a batch reactor was employed in this study, it is therefore reasonable to conclude that the

contribution by dye-sensitization was only valid in the first half an hour of the degradation process. Thus, the physicochemical properties of TiO_2/CuO composite nanofibers still play a big role in enhancing the overall photocatalytic organic degradation and H_2 generation process, which is discussed in the following section.

3.2.3 Photocatalytic H_2 generation

In addition to organic pollutants removal, significant simultaneous photocatalytic H_2 generation was also observed over the TiO_2/CuO composite nanofibers. As presented in Fig. 10(a), H_2 evolution over TiO_2/CuO composite nanofibers was significantly higher than that of the bare TiO_2 nanofibers throughout the 3 hours of UV-visible irradiation. Negligible H_2 was generated in the absence of either photocatalyst or light. Despite the complete discoloration of AO7 solution in less than 20 min, H_2 was continuously generated during the 3-hour reaction because complete mineralization of AO7's intermediate by-products into H_2O and CO_2 required a much longer time (Patsoura et al., 2006). This verifies the theory that H_2 will be generated via H_2O reduction by photogenerated electrons as long as the recombination of the electron-hole pairs and the back reaction of H_2 and O_2 were retarded by photo-oxidation of organic molecule by the photogenerated holes (Kudo and Miseki, 2009). The enhanced generation of H_2 throughout the 3 hours over the TiO_2/CuO composite nanofibers compared to that of the bare TiO_2 nanofibers was attributed mainly to the synergy effect of the excellent physicochemical properties such as (1) enhanced mesoporosity and specific surface area, (2) red-shift of the solar light absorbance (3) long nanofibrous structure and (4) TiO_2/CuO heterojunctions, which ultimately promote charge transfer and separation as well as enhance light utilization. Furthermore, in the TiO_2/CuO composite nanofibers, the CB of CuO is located not only below the CB of TiO_2 ; it is also more electronegative than H_2O reduction potential (Xu and Sun, 2009). Consequently, the CB of CuO serves as an interim location which accepts photogenerated electrons from TiO_2 and subsequently lose these electrons rapidly for H_2 production. Hence, CuO in this composite nanofiber serves dual roles to enhance photocatalytic H_2 production: (1) promote electron transfer from TiO_2 to CuO in the

heterojunctions enhancing the charge separation and (2) as co-catalyst by rendering reduction sites for H₂ production (Ashokkumar, 1998). The composite's new physicochemical properties become even more significant by the diminishing effect of dye-sensitization following the complete discoloration of AO7 solution in the first half an hour of the reaction since H₂ generation continued to rise thereafter. Meanwhile, as shown in Fig. 10(b), the TiO₂/CuO composite nanofibers demonstrated a H₂ evolution rate of 62.7 μmol/hr which is nearly five and three times higher than the rate obtained with the bare TiO₂ nanofibers and Pt/TiO₂ nanoparticles (Patsoura et al., 2006), respectively. This implies that Cu can be a potential substitute to Pt in the modification of TiO₂ properties for concurrent photocatalytic organic degradation and H₂ production from dye wastewater.

3.2.3 Stability of TiO₂/CuO composite nanofibers for reuse

The TiO₂/CuO composite photocatalyst was also investigated for its reusability to address the importance of highly stable and reusable photocatalyst for long-term photocatalytic application. At the end of the reaction when the mixing was stopped, the photocatalyst was observed to settle instantly at the bottom of the photoreactor thus indicating it has good separation characteristic. Fig. 11 shows a sustainable photocatalytic performance in H₂ generation after 3 cycles. There was insignificant loss of H₂ evolution rate, which indicates that the TiO₂/CuO composite nanofibers were highly stable and reusable. The heating of the reacted TiO₂/CuO composite nanofibers served to regenerate the photocatalyst by removing adsorbed organics by-products on the photocatalyst (Xu and Sun, 2009). The opportunity to reuse the TiO₂/CuO composite nanofibers has rendered it a highly potential material for economical and sustainable engineering applications.

3.2.4 Proposed mechanism summary for concurrent photocatalytic organic degradation and H₂ production from dye wastewater

Scheme 2 elucidates the electrons and holes transfer pathway within the TiO₂/CuO composite nanofibers. The TiO₂/CuO composite nanofibers were envisaged to mimic the artificial photosynthesis

inspired by the nature (Kudo and Miseki, 2009). Upon photon absorption, holes and electrons were produced in both TiO_2 and CuO . Due to the potential difference, the electrons were transferred from CB of TiO_2 into the CB of CuO in the heterojunctions (Xu et al., 2011a). Consequently, the excess electrons which have accumulated in the CB of CuO would cause a negative shift in its Fermi level; rendering higher electron availability for interfacial transfer to H^+ in solution to produce H_2 (Xu et al., 2011a). Meanwhile, the photogenerated holes on the valence band (VB) which escaped recombination with the photogenerated electrons were used to oxidize AO7 (Stylidi et al., 2004). The oxidation of AO7 could take place on the surface of the photocatalysts and in the bulk solution by photogenerated holes and ROS, respectively (Chen et al., 2005). Unlike the adsorption process in the dark, during the photocatalysis process, adsorption of AO7 molecule and its intermediates from the solution becomes a dynamic or an active process. Any free sites on the photocatalyst will be immediately occupied by AO7 molecule or its intermediates from the solution and subsequently photo-degraded on the active surface sites, as soon as the previously adsorbed AO7 molecule or intermediates were degraded either completely or into a smaller molecule. Meanwhile photo-degradation of AO7 molecule and its intermediates remaining in the solution continue to take place concurrently. As shown in Table 2, the BET specific surface area of the spent photocatalyst was significantly low even after 3-hours of photoreaction; thus implying that the specific surface area remained occupied by the AO7 intermediate by-products. The recovery of the specific surface area upon an overnight heat treatment at 350°C on the spent TiO_2/CuO composite photocatalyst (Table 2) indicates that the specific surface area were previously occupied by organic products; thus further verifying the dynamic adsorption-photocatalysis-adsorption process of the remaining AO7 intermediate by-products which occurs throughout the photocatalysis reaction. The continuously rising H_2 generation as shown in Fig. 10(a) strongly supports the hypothesis that the intermediate by-products were still present after 3 hours.

Adsorbed AO7 could also be sensitized by the visible light of the irradiation (Stylidi et al., 2004). Thus, it could generate electrons which will then be transferred to the CB of TiO_2 and used to form ROS

useful for organic oxidation, or the electrons may be further transferred to the CB of CuO useful for H₂ generation. However, the effect of dye-sensitization happened only during the first half an hour of the of the degradation process. During the photocatalytic reaction, AO7 and its intermediate by-products played the role of the sacrificial reagent or electron donor that consumed the photogenerated holes or holes-induced ROS such as OH[•] (Hernández-Alonso et al., 2009). Moreover, the formation of O₂ from H₂O could be retarded owing to the consumption of photogenerated holes by AO7 and its intermediate by-products thus suppressing the back reaction between H₂ and O₂ which can impede the H₂ generation. Therefore, the recombination of photogenerated holes and electrons was also retarded thus increasing the available electrons needed to reduce H⁺ into H₂. Compared to the conventionally used methanol (Hernández-Alonso et al., 2009), AO7 is a more viable sacrificial reagent for enhancing photocatalytic H₂ evolution because AO7 is readily available from the industry. Methanol, on the other hand, is a useful fuel source by itself (Lalitha et al., 2010) and thus its usage would incur additional operational cost.

4. Conclusion

In summary, a novel-structured TiO₂/CuO composite nanofibers was successfully fabricated via facile electrospinning. The TiO₂/CuO composite nanofibers exhibited an additional ability to concurrently evolve H₂ and degrade organic pollutants. The enhanced photocatalytic performance of TiO₂/CuO composite nanofibers was attributed to its merits of having (1) long nanofibrous structure with enhanced mesoporosity and specific surface area hence enabling efficient reactants adsorption and mass transfer, light absorbance and interparticle charge transfer, (2) lower band gap energy thus promoting absorbance and utilization of photon energy from a broader light spectrum, (3) TiO₂/CuO heterojunctions with good dispersion and contact thus facilitating an efficient separation of photogenerated electrons and holes and (4) CuO which served as the co-catalyst by providing H⁺ reduction site for H₂ production. Coupled with its uncompromising reusability, the excellent synergy of the new physicochemical properties

affirms the huge potential of the as-synthesized TiO_2/CuO composite nanofibers for use in a sustainable and an economical concurrent photocatalytic dye wastewater treatment and clean energy production.

ACKNOWLEDGEMENT. The authors thank the Clean Energy Research Programme under National Research Foundation of Singapore for their research grant (Grant No. NRF2007EWT-CERP01-0420) support for this work and the support received from Public Utilities Board (PUB) of Singapore. The Scholarship provided by NTU is appreciated.

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Captions of Figures

Figure 1. (a) FESEM image of an as-spun individual composite nanofiber (uncalcined), (b) Low magnification FESEM image of TiO_2/CuO composite nanofibers after calcinations at 450 °C, (c)-(d) High magnification FESEM images of TiO_2/CuO composite nanofibers showing the porous structure

Figure 2. (a) Dark field FESEM-STEM image of TiO_2/CuO composite nanofibers sample, (b) Bright field TEM image of calcined TiO_2/CuO composite nanofibers, (c) SAED pattern of calcined TiO_2/CuO composite nanofibers in which the individual crystal plane was indicated by a Jems software, and (d) High magnification HRTEM image showing the corresponding crystal lattice of anatase TiO_2 and CuO from the delineated area in (b)

Figure 3. (a) High magnification dark field FESEM-STEM image of TiO_2/CuO composite nanofibers, (b) EDX spectrum of the indicated point in yellow outside the nanofibers in (a), (c) EDX spectrum of the indicated point in red on a single nanofibers in (a), Elemental mapping of the selected area (white box as in Figure 3(a)) for (d) O element, (e) Ti element, and (f) Cu element (although this could be affected by the Cu signal from the interaction between the scattered electron beam and the Cu-grid)

Figure 4. (a) Full range XRD patterns of electrospun TiO_2/CuO composite nanofibers and bare TiO_2 nanofibers, and (b) Close-up XRD patterns for bare TiO_2 nanofibers, and TiO_2/CuO composite nanofibers with 10% mol Cu calcined at different temperature ($2\theta=30^\circ$ - 45°)

Figure 5. (a) XPS survey spectrum for TiO_2/CuO composite nanofibers; High resolution XPS spectrum for (b) Ti 2p, (c) Cu 2p, and (d) O 1s

Figure 6. (a) N_2 adsorption/desorption isotherm curve of TiO_2/CuO composite nanofibers , and (b) BJH pore size distribution of bare TiO_2 and TiO_2/CuO composite nanofibers

Figure 7. (a) The UV-visible spectra of the TiO_2/CuO composite nanofibers and bare TiO_2 nanofibers, and (b) the corresponding Kubelka-Munk transformed reflectance spectra to determine indirect new bandgap value for the TiO_2/CuO composite nanofibers and bare TiO_2 nanofibers

Figure 8. Photoluminense spectra of the TiO_2/CuO composite nanofibers and bar TiO_2 nanofibers

Figure 9. (a) Removal of AO7 by adsorption on TiO₂/CuO composite nanofibers and bare TiO₂ composite nanofibers during dark adsorption process and (b) Removal of AO7 by PCO at $t=3$ minutes during the UV-visible irradiation on the photocatalysts suspension

Figure 10. (a) Accumulation of photocatalytic H₂ evolution over the irradiation time of 3 hours on TiO₂/CuO composite nanofibers, bare TiO₂ nanofibers as well as during photolysis in the absence of photocatalyst and (b) Comparison of H₂ evolution rate between TiO₂/CuO composite nanofibers and bare TiO₂ nanofibers

Figure 11. Reusability experiment for photocatalytic H₂ generation by TiO₂/CuO composite nanofibers.

Captions of Schemes

Scheme 1. Schematic diagram of the photo reactor setup

Scheme 2. Schematic diagram of the photo-generated electrons and holes transfer between the TiO₂/CuO heterojunctions

Captions of Tables

Table 1. Summary of physical properties of calcined TiO₂/CuO composite nanofibers

Table 2. BET specific surface area of TiO₂/CuO composite nanofibers

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Scheme 1

Scheme 2

Table 1 – Summary of physical properties of calcined bare TiO₂ nanofibers and TiO₂/CuO composite nanofiber

Materials	FHWM (degree)	Size of anatase crystal ^a (nm)
Bare TiO ₂ nanofibers	0.443	18
TiO ₂ /CuO composite nanofibers	0.493	16

^a Calculated by the Scherrer equation (Chen and Mao, 2007).

Table 2 – BET specific surface area of bare TiO₂ nanofibers and TiO₂/CuO composite nanofibers

Materials	BET surface area (m ² /g)
Bare TiO ₂ nanofibers	34.3
TiO ₂ /CuO composite nanofibers	108.1
Spent TiO ₂ /CuO composite nanofibers	4.5
Regenerated TiO ₂ /CuO composite nanofibers	102.0