



Degradation of Rhodamine B using a Visible-light driven Photocatalytic Fuel Cell



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ABSTRACT

A visible-light driven Photocatalytic Fuel Cell (PFC) system comprising WO₃/TiO₂ and CuO/TiO₂ nanotube array materials as photoanode and photocathode, was established with a dual objective of degrading an organic water pollutant and generating electric power as well. Under illumination, the Fermi level of WO₃/TiO₂ nanotube arrays photoanode was higher than that of CuO/TiO₂ nanotube arrays photocathode. Arising an interior bias (0.18 V) induced the transfer of electrons from the photoanode across the external circuit to the photocathode and combination with the holes produced therein with electric power generation. In this manner, the separation of electron/hole pair was achieved in the photoelectrodes by releasing the holes of WO₃/TiO₂ nanotube arrays photoanode and electrons of CuO/TiO₂ nanotube arrays photocathode. Using this PFC based system, the degradation of an organic water pollutant, Rhodamine B, was successfully accomplished with determining its decolorization and the variation in total organic carbon (TOC) content. The decolorization and TOC removal were obtained to the extent of 100% and 57%, respectively at 4 h reaction time. The stability of the photoelectrodes for scaling up applications could also be confirmed by the repeated several experimental runs using the electrodes. The proposed photoelectrocatalytic system provides a self-sustained and energy-saving methodology for wastewater treatment with a parallel energy production.

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1. Introduction

Photocatalytic oxidation technique based on TiO₂ has been proven to be a promising method, which is widely being used to degrade various persistent and hazardous organic pollutants [1–3]. Upon illumination, photogenerated electrons are excited from the valence band to the conduction band, which lead to the generation of electron-hole pairs. The holes are powerful oxidants for degrading the organic pollutants, which get adsorbed on the TiO₂ surface during the treatment, into CO₂ and H₂O [4,5]. However, due to a high degree of recombination between the photogenerated electrons and holes, the concentration of available holes is usually of a low level, which decreases the photocatalytic efficiency of the material [6]. A positive bias potential applied to the TiO₂ favors the driving of photo-generated electrons to the counter electrode, by which the recombination of photogenerated electrons and holes could be prevented. Consequently, the electrons and the holes have

maximum possibility of involving in the degradation reaction [7,8]. However, such an approach requires additional power supply that inevitably increases the cost of wastewater treatment technique.

A photoelectrocatalytic (PEC) system based on TiO₂ nanotube arrays (TiO₂-NTs) has been recently reported, which shows the significant enhanced performance [9–11]. The TiO₂ photocatalytic process may degrade organic pollutant and produce photogenerated electrons, which pass through the conductive substrate to the cathode with the transformation of the chemical energy of organic pollutants into electric power. The generation of electrons in the PEC system originates from photoexcitation, which is a rapid and direct process [12]. However, there are yet two major problems: firstly, the maximum usage of Pt cathode makes it too expensive, which would obviously restrict its large-scale application; secondly, the light efficiency of PEC would be relatively low as there is a single electrode, viz. TiO₂ photoanode, which is solely responsible for UV illumination.

To overcome the above-mentioned drawbacks, the combination of photoanode and photocathode that have different Fermi level seems to be promising and effective approach. The replacement of Pt cathode by a photoresponsive material may be reducing the cost and improving the utilization of solar light effectively and

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remarkably. In the present approach, both the photoanode and the photocathode need to be illuminated simultaneously. The photoanode should be a n-type semiconductor that usually has a positive located valence band (VB) edge for oxidation of water molecule. The Fermi level of photoanode should be more negative than that of photocathode. Based on the idea, a novel PFC system using WO_3/TiO_2 -NTs photoanode and CuO/TiO_2 -NTs photocathode, is demonstrated in this work which can be operated under visible light illumination for dual applications of wastewater treatment and electric power generation as well. WO_3 has been identified as a prototype photoanode material with smaller bandgap of 2.3–2.8 eV for visible light response [13–15]. CuO can also be activated by visible light because its optical bandgap is ~ 2.0 eV, which has already been proven to be an efficient photocathode [16,17]. CuO is relatively stable as photocatalyst, which is important in practical applications [18]. The CuO/TiO_2 -NTs would be more stable with prolonged use on the basis of rapid charge transfer and separation. Since the Fermi level of WO_3/TiO_2 -NTs photoanode is more negative than that of CuO/TiO_2 -NTs photocathode under light illumination, the latter could offer a positive bias to the former. Thus, both the degradation of organic pollutant and the electric power generation could be achieved simultaneously by the PFC system under visible light illumination.

2. Experimental

2.1. Chemicals and materials

A 1 mm thick titanium sheet (99.9%, Strem Chemicals) with a dimension of 3 cm \times 2 cm was obtained. The chemicals viz. glycerine, ammonia fluoride (NH_4F), sodium tungstate dihydrate (Na_2WO_4), isopropyl alcohol, perchloric acid (HClO_4), hydrogen peroxide (H_2O_2), cupric acetate, sodium acetate, sodium hydroxide (NaOH), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) and sodium sulfate (Na_2SO_4), were purchased from Acros Organics and used as received. The aqueous solutions used in the experiments were prepared by deionized (DI) water with a resistivity of 18.2 $\text{M}\Omega\cdot\text{cm}$ collected from a Millipore system.

2.2. Preparation of WO_3/TiO_2 -NTs Photoanode

The highly ordered TiO_2 -NTs was fabricated by anodic oxidation of the Ti substrate in NH_4F electrolyte, adopting a method described in the earlier work [7,19]. The photoanode preparation was carried out in aqueous electrolyte that contains 20 mmol dm^{-3} of H_2O_2 (Prolabo, 30%), 5 mmol dm^{-3} of Na_2WO_4 and 70 mL of isopropyl alcohol (40%). The pH of the resulting solution was between 10.3 and 10.5. The pH was adjusted to 1.2 by a subsequent addition of perchloric acid. Then a square-wave potential between -0.5 V (100 ms) and 0 V (1000 ms) versus saturated calomel electrode (SCE) was applied repeatedly. Cathode square wave lasted up to 600 cycles, followed by rinsing with DI water and drying at 373 K for 12 h. This treatment would facilitate the strong interconnection between WO_3 and TiO_2 , which could bring out the effective degradation of the organic compound under visible light illumination [20].

2.3. Preparation CuO/TiO_2 -NTs Photocathode

CuO nanoparticles were electrodeposited on Ti substrates by a three-electrode electrochemical cell containing aqueous solutions of 0.05 mol dm^{-3} sodium acetate and 0.05 mol dm^{-3} cupric acetate. The counter and reference electrodes used were Pt wire and SCE, respectively. The electrodeposition was carried out under potentiostatic control at -0.1 V vs. SCE for 30 min, and its cycle

repeated thrice to change the phase interface between the electrode and solution environment and avoid interference in next polarization process. After the polarization, the as-prepared samples were washed with DI water, and immersed in aqueous solution containing 2.5 mol dm^{-3} NaOH and 0.125 mol dm^{-3} $(\text{NH}_4)_2\text{S}_2\text{O}_8$ for 30 min. Then, it was rinsed with DI water and dried in the air, and finally annealed at 723 K for 1 h in the muffle furnace.

2.4. Characterization studies

The morphology characterization was performed on a field emission scanning electron microscope (FE-SEM, NANOSEM 450, FEI) operating at an accelerating voltage of 30 kV. Transmission electron microscope (TEM) analyses were conducted with a JEM-2100F electron microscope (JEOL, Japan), using a 200 kV accelerating voltage. The phase purity and crystal structure of the obtained samples were examined by X-ray diffraction (XRD) technique using a Rigaku Ultima IV X-ray diffraction (Rigaku Corporation, Japan) instrument equipped with $\text{Cu-K}\alpha$ radiation (40 kV, $\lambda=1.5406$ Å), and the 2θ scanning angle range was fixed 20° – 80° with a step of 0.05°s^{-1} . UV-visible diffuse reflectance spectra (DRS) were obtained on a UV-visible spectrophotometer (UV-2550, Japan). The spectrum range analyzed was 250–800 nm, in which the reflectance standard was BaSO_4 .

2.5. Photoelectrochemical Measurements

The photoelectrochemical response of the photoelectrodes were studied with a three-electrode system by using an electrochemical workstation (CS310, CorrTest, China) in which the reference and the auxiliary electrodes were SCE and Pt foil, respectively. Mott-Schottky plots were measured at a frequency of 1 kHz and 5 kHz. The linear sweep was evaluated under chopped light irradiation (light on-off cycles: 20 s) with a scan rate of 5 mV s^{-1} in 0.1 mol dm^{-3} Na_2SO_4 aqueous solution after N_2 bubbled for 30 min. A 60 W incandescent lamps (PHILIPS, Netherlands) was used as light source and the light was allowed to fall on the surface of the samples with an intensity of 86610 Lux measured by a visible-light radiometer (Testo 540, Germany). The photoelectrocatalytic fuel cell was designed by fixing two electrode configuration set up in which the photoelectrodes were immersed in the electrolyte and illuminated separately with the same light intensity. The reproducibility of the obtained results was confirmed by repeated experimental run.

2.6. Photoelectrocatalytic degradation of organic contaminants under visible light irradiation

Photoelectrocatalytic oxidation experiments were carried out with a two-electrode configuration in a quartz container with a volume capacity of 70 mL. The two pieces of the electrodes were connected by wires directly. The degradation of the model organic compound viz. Rhodamine B (1×10^{-5} mol dm^{-3}), was carried out with working solution volume of 45 mL that contains 0.1 mol dm^{-3} Na_2SO_4 as supporting electrolyte. The temperature of the sample was constantly maintained at 298 K by a water bath thermostat. The cylindrical container with the thermostat system was kept on a magnetic stirrer and the stirring rate was constantly maintained at 350 rpm. The effective illumination area of the WO_3/TiO_2 -NTs photoanode and CuO/TiO_2 -NTs photocathode were 2×2 cm^2 . The decolorization rate of Rhodamine B was detected by a UV-vis spectrophotometer (UV2102 PCS, UNICO, Shanghai) fixing the wavelength at 554 nm. The mineralization of Rhodamine B was further confirmed by total organic carbon (TOC) analysis using a TOC analyzer (Multi N/C, 2100, Jena, Germany).

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