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Photoreduction preparation of Cu_2O@polydopamine nanospheres with enhanced photocatalytic activity under visible light irradiation

Xiaosong Zhou[a,b,*], Bei Jin[a], Jin Luo[a], Xingxing Gu[b], Shanqing Zhang[b]

[a] School of Chemistry and Chemical Engineering, and Institute of Physical Chemistry, Lingnan Normal University, Zhanjiang 524048, PR China
[b] Centre for Clean Environment and Energy, Griffith School of Environment, Griffith University, Gold Coast, QLD 4222, Australia

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ABSTRACT

Cuprous oxide (Cu_2O) suffers from severe electron-hole pairs recombination, instability and low photocatalytic degradation efficiency, though it has been considered as an excellent visible light photocatalyst. The incorporation of the Cu_2O with other photocatalysts can address these problems. Herein, unique Cu_2O@polydopamine (PDA) nanospheres are prepared by a simple photo-reduction approach. Due to the synergistic effects of the Cu_2O and PDA semiconductors, the Cu_2O@PDA nanospheres composite possesses enhanced photocatalytic activity and extended life time for the degradation of the methyl orange under visible light irradiation.

1. Introduction

Semiconductor photocatalysts have attracted considerable attention for both fundamental research and practical application in energy and environment fields. Recently, cuprous oxide (Cu_2O), a well-known p-type semiconductor with low toxicity, good environmental acceptability, and low cost [1–11], has appealed worldwide interest due to its potential applications in many fields, such as gas sensing [12], solar energy conversion [13], the photoactivated splitting of water into H_2 and O_2 [14], lubricants [15], magnetic memory [16] and Li/Na-ion batteries [11]. However, the photocatalytic efficiency of the Cu_2O nanoparticles still need to be further improved because of low light absorption efficiency, the fast recombination of the photogenerated electron-hole pairs and slow mass transport [17–24]. In order to address these problems, researchers have proposed numerous strategies to synthesize Cu_2O nanoparticulate composite in combination with other semiconductors. Gao et al. [25–27] proposed a one-pot hydrothermal method to synthesize Cu_2O/TiO_2 that exhibits superior catalytic activity towards water splitting. The photocatalytic efficiency was even higher than that of TiO_2 loaded with noble metal Au nanoparticles. Ievskaya et al. [28] reported $Zn_{1-x}Mg_xO/Cu_2O$ heterojunctions were successfully fabricated in open-air at low temperatures via atmospheric atomic layer deposition of $Zn_{1-x}Mg_xO$ on thermally oxidized cuprous oxide. The solar cells employing these heterojunctions demonstrated a power conversion efficiency exceeding 2.2%. Cuo et al. [29] developed a one-pot in-situ reduction method to synthesize Cu_2O/C_3N_4 heterojunctions. The visible light photocatalytic hydrogen production activity over g-C_3N_4 was enhanced by more than 70% with Cu_2O nanoparticles modification. Sunkara et al. [30] prepared 3D hierarchical heterostructures of p-type Cu_2O/n-type SnO_2 by impregnating porous SnO_2 nanospheres with different weight percentages of Cu_2O by a simple hydrothermal route. Photocatalytic activity of the Cu_2O/SnO_2 nanocomposite for the degradation of RhB was much higher than that of individual nanoparticles; Feng et al. [31] designed a novel visible-light-responding $InVO_4$-Cu_2O-TiO_2 ternary nanoheterostructure, and prepared through a typical wet chemistry method. The as-prepared ternary photocatalysts show significant enhancement in the photocatalytic performance for the degradation of methyl orange (MO) under visible-light irradiation. However, these synthesis processes are complicated for manufacturing and there are a lot of room to be improved in terms of the photocatalytic efficiency. It can be concluded that a strategy incorporating Cu_2O with other nanoscale semiconductor catalyst could resolve the problems of current Cu_2O catalyst.

Polydopamine (PDA), due to its unique electron and hole transporting properties, good chemical stability and simple doping chemistry, has been one of the most widely used conducting polymers in the nanomaterials synthesis. Recently, it has presented great potential in photocatalysis applications [32–34]. Because PDA has an extended π-conjugated electron system, it offers a high mobility of charge carriers and high absorption in the visible-light range. In addition, PDA of either undoped or partially doped states is an electron donor upon photoexcitation, and is known as a good hole conductor. Very recently, our group [35] has synthesized PDA@TiO_2 nanospheres composite photocatalysts, and exhibited the enhanced photocatalytic activities in

* Corresponding author at: School of Chemistry and Chemical Engineering, and Institute of Physical Chemistry, Lingnan Normal University, Zhanjiang 524048, PR China.
E-mail address: zxs801213@163.com (X. Zhou).

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the degradation of MO dye compared to the pure TiO_2 photocatalyst. Inspired by this finding, we propose that the combination of the Cu_2O photocatalyst with PDA, i.e., Cu_2O@PDA, could result in excellent photocatalytic activity under visible light.

In this work, PDA nanospheres are firstly prepared via polymerization of dopamine under alkaline conditions. A simple photo-reduction approach is designed to decorate the Cu_2O nanoparticles onto the as-prepared PDA nanospheres, The Cu_2O@PDA nanospheres composite is used to degrade in the MO dye under visible light irradiation, showing significantly enhanced photocatalytic performance and stability compared to the pure Cu_2O and PDA photocatalyst. It is suggested that the improved photocatalytic activity stems from the synergistic effect between PDA and Cu_2O that enhances the light absorption and promote electron-hole separation.

2. Experimental section

2.1. Preparation of PDA nanospheres

The PDA nanospheres are prepared based on our previous reports [35]. At first, 1.0 mL ammonia aqueous solution (NH_4OH, 28%) was mixed with ethanol (40 mL) and deionized water (90 mL) under mild stirring at 30 °C in a water bath for 30 min 10 mL 5% (w/w) Dopamine hydrochloride aqueous solution was slowly injected into the above mixture solution in 10 min. The reaction was kept stirring at 30 °C for 24 h. The PDA nanospheres were formed and obtained after centrifugation, washing with water and absolute ethanol for three times, and dried at 60 °C in air over night. The dry PDA in powder form were calcined at 600 °C for 2 h in a N_2 atmosphere in order to remove impurity and improve crystallinity of the PDA.

2.2. Preparation of Cu_2O@PDA nanocomposites

A 50 mL aqueous solution containing $CuSO_4{\cdot}5H_2O$ (0.0971 g), polyvinyl alcohol (PVA, 0.1 g), and methanol (10 mL) was stirred ultrasonically for 20 min. Meanwhile, nitrogen gas was sparged into the solution continuously for the sake of eliminating a small amount of dissolved oxygen in the solution. The pH of the solution was adjusted to pH = 8 by ammonia solution. And then, 0.5 g of the as-prepared PDA nanospheres were added. After stirring for about 30 min, the mixture was irradiated under a 300 W Xe lamp for 4 h. After that, the products were collected and washed three times with deionized water and absolute ethanol, and then the powders were dried for 24 h under vacuum at 60 °C. The as-prepared samples were denoted as Cu_2O@PDA-10%. According to the precursor (Cu^{2+}) concentrations, the obtained samples are denoted as Cu_2O@PDA-1% (CP-1), Cu_2O@PDA-2% (CP-2), Cu_2O@PDA-5% (CP-5), Cu_2O@PDA-10% (CP-10) and Cu_2O@PDA-20% (CP-20), respectively (show in Table 1).

2.3. Materials characterization

X-ray diffraction (XRD) patterns of the as-prepared samples were recorded on an X-ray diffractometer (D/max-IIIA, Japan) using Cu *K*-alpha radiation. The surface morphology of the as-prepared samples was examined by a scanning electron microscopy (SEM) (LEO1530VP, LEO Company). The UV–vis diffuse reflectance spectroscopy (DRS) of as-prepared samples were obtained from a Hitachi UV-3010 spectrophotometer equipped with an integrating sphere assembly and using the diffuse reflection method and $BaSO_4$ as a reference. The chemical states of the each element in the Cu_2O@PDA-5% nanocomposite was studied using X-ray photoelectron spectroscopy (XPS) in Krato Axis Ultra DLD spectrometer. The binding energy was referenced to C *1 s* line at 284.6 eV for calibration. Photoluminescence (PL) spectra were measured on an F-7000 Fluorescence spectrohpotometer (Hitachi, Japan). The BET surface area was determined using adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. The desorption data were used to determine the pore size distribution via the Barret-Joyner-Halender (BJH) method.

Table 1
The Cu_2O content, specific surface area and Kapp value of the as-prepared samples.

Samples	Cu_2O (wt%)	S_{BET} ($m^2{\cdot}g^{-1}$)	K_{app} (min^{-1})
PDA	0	30.8	0.00236
Cu_2O	100	85.3	0.00318
CP–1	1.0	31.2	0.00582
CP–2	2.0	35.7	0.01212
CP–5	5.0	38.8	0.02484
CP–10	10	41.6	0.01524
CP–20	20	43.8	0.01330

2.4. Evaluation of photocatalytic activities

The photocatalytic reaction was conducted in a 200 mL cylindrical glass vessel fixed in the XPA-II photochemical reactor. A 1000 W Xe lamp was used as the simulated solar light source (UV–visible light), and a house-made filter was mounted in front of the lamp to eliminate UV portion of the light. The visible-light was obtained by using a cur-off filter that was made up of 1 M sodium nitrite solution which can absorb the light with wavelength under 400 nm. Methyl orange (MO, 20 $mg{\cdot}L^{-1}$) was used as a substrate for photocatalytic degradation tests. In order to obtain a uniformly dispersed system and reach complete adsorption/desorption equilibration, 20 mg photocatalyst powder was dispersed in 200 mL reaction solutions by supersonic for 15 min and then the suspension was magnetically stirred in dark for 1 h. During the photocatalytic reaction, air was blown into the reaction medium at a flow rate of 200 mL min^{-1}. At each regular intervals of 30 min, 8 mL of the suspension was collected, filtered and then centrifuged. The concentration of the remaining MO was measured by its absorbance (A) at 465 nm with a Hitachi UV-3010 spectrophotometer (The initial concentration of MO is A_0). The degradation ratio of MO can be calculated by Eq. (1):

$$X\% = (A_0 - A)/A_0 \times 100\% \quad (1)$$

3. Results and discussion

The synthesis of the precursors for the Cu_2O@PDA nanospheres composite are prepared can be classified into two steps as shown in Fig. 1. Firstly, in the ethanol and ammonia solution, the dopamine solution is added into drop by drop, the dopamine molecules undergo oxidation, cyclization, and polymerization process, and the formation of PDA nanospheres (Scheme 1).

It is observed that the addition speed of the dopamine solution needs to be carefully controlled at less than 0.5 mL min^{-1} in order to smooth PDA nanoparticles with uniform sizes. The PDA nanospheres separated from solution is subject to the calcination at 600 °C in a N_2 atmosphere in order to increase the crystallinity and remove impurity. It is to note that the PDA nanoparticles are extremely stable under such a high temperature but inert atmosphere. The morphology of the as-prepared Cu_2O@PDA nanospheres is shown Fig. 2. The SEM image of PDA exhibits a typical smooth and homogeneous sphere structure with a diameter of ca. 200 nm (Fig. 2(a)). Secondly, the annealed PDA nanospheres were added into the $CuSO_4$ pH = 8 solution. Under the simulated solar light illumination, PDA absorbs visible light to induce π-π* transition, producing excited electrons and transferring them from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), resulting inactive intermediates PDA(e^-) (Eq. (2)). Such electrons are a powerful reducing radical that can reduce Cu^{2+} into Cu^+ (Eq. (3)), that quickly form a unstable intermediate CuOH in the alkaline solution and transform into a