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New photocatalyst based on graphene oxide/chitin for degradation of dyes under sunlight

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ABSTRACT

Sunlight photocatalyst was fabricated by in situ synthesis of Cu_2O in the regenerated chitin (RC)/graphene oxide (GO) composite film, where the porous chitin film was used as the microreactor for the formation of nano Cu_2O. Nano Cu_2O was immobilized and evenly distributed in the matrix and Cu_2O tended to grow on the GO sheets. Cu_2O inside the matrix excite and generate free photoelectrons and electron holes, which was responsible for the degradation of dyes, while GO transferred the yielded photoelectrons to prevent the generation of local high potential zone and induce the chain degradation at more points. So it was found that the porous chitin film could load Cu_2O and graphene at the same time, controlling the size of Cu_2O and leading to easy recycle and reuse of the photocatalyst. Moreover, the introduction of GO has dramatically improved the photocatalytic activity of Cu_2O in the Cu_2O/GO/RC film, showing great potential application in wastewater treatment utilizing solar energy.

1. Introduction

Nowadays, toxic organic dyes and their effluents have become one of the main sources of water pollution because of the greater demand in industry. Because of the high stability against light, temperature, chemicals, and microbial attack, all the dyes were difficult to remove using traditional wastewater treatment [1,2]. Among the techniques to deal with these dyes, photocatalysis has long been known to be one of the most promising techniques to degrade organic pollutants from wastewater [3]. Many semiconductors, such as TiO_2, Ti_2O, ZnO, CdS, ZnS and Ag_3PO_4 can act as photocatalyst to decompose organic pollutants in wastewater [4–6]. However, they are not applied into practice because of such disadvantages or drawbacks as toxicity or low efficiency. Additionally, taking into account that a substantial fraction (44%) of, the whole solar spectrum is visible light, while only a small percentage (<5%) of that is UV light [7], there is an urgent need to develop highly efficient and environmentally friendly visible-light-active photocatalyst that could utilize sunlight directly to degrade organic pollutants.

As a p-type semiconductor with a narrow band gap of 2.0 eV, Cu_2O has been extensively studied in recent years due to its easy fabrication, abundance, high photostability and low toxicity [8]. More importantly, this stable photocatalyst exhibited excellent activities such as decomposition of water into O_2 and H_2, degradation of organic pollutants and sensing gas under visible light ($\lambda < 620$ nm) irradiation [9]. Moreover, these semiconductors are usually combined with such novel materials as graphene to enhance the photocatalysis efficiency because of its large surface area and high intrinsic electron mobility, which could promote the transfer of electrons in electrochemistry [10]. To date, several kinds of graphene-based composite materials containing metal oxides, metal sulfides and metal nanoparticles have been reported for the improved photocatalytic efficiency [11,12]. Lately, it was reported that the incorporation of graphene oxide with WO_3 lead to a 1.6 times improvement in the generation of photocurrent. Additionally, the introduction of graphene-oxide led to significant increasing of efficiency in the degradation of dyes under visible light for the Ag_3PO_4/graphene-oxide (Ag_3PO_4/GO) composite [1]. So it is expected that the combination of Cu_2O and graphene would lead to the formation of highly efficient catalyst for the degradation of dyes.

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Usually, nanoparticles are difficult to recycle and reuse because they are too small and easy to aggregate [13]. So searching for another appropriate material that could load Cu_2O and graphene at the same time is vital for fabricating highly efficient catalyst with excellent reusability. Chitin is the second most abundant natural polymer with good properties such as biodegradability and biocompatibility [14], and various kinds of chitin related materials have been fabricated for the removal of dyes in the water in the past [15,16]. Moreover, a simple and "green" route of alkali/urea/H_2O system has been already developed by Zhang to fabricate various regenerated chitin (RC) materials such as microspheres hydrogel and films recently [17–19]. Moreover, these novel materials process unique three-dimensional porous structure which could be used for in situ synthesis of nanoparticles [1,20], which could immobilize and prevent the aggregation of nanoparticles.

So in this study, first, graphene oxide was introduced to chitin to fabricate regenerated chitin/GO film, and then Cu_2O was in situ synthesized in the chitin matrix. This simple and green fabrication route could improve the catalytic efficiency of Cu_2O by incorporation of GO and preventing aggregation of nanoparticles. Moreover, the catalyst can be easily recycled and reused.

2. Materials and methods

Chitin powder was purchased from Golden-Shell Biochemical Co. Ltd. (Zhejiang, China) with molecular weight (Mw) of 4.0×10^5 Da. Graphite was purchased from Nanjing XFNANO Materials Tech Co. Ltd. Other chemicals were of analytical grade and used without further purification.

2.1. Preparation of regenerated chitin (RC) film

To prepare chitin solution, 4.5 g purified chitin powder was dispersed into 100 g mixture of NaOH, urea and distilled water of 11:4:85 by weight with stirring to obtain a suspension. Subsequently, the suspension was frozen at −30 °C for 4 h, and then vigorously stirred at room temperature. The freezing/thawing cycle was repeated twice to obtain the chitin solution with concentration of 4.5 wt% [21]. Then the chitin solution was centrifugated at 6000 rpm for 10 min under 0 °C to eliminate bubbles. Last, the solution was casted on a glass plate, then immersed in ethanol for 2 h to obtain regenerated chitin, coded as RC film. The film thickness is 0.5 mm. Finally, the RC film was washed with distilled water to remove NaOH, urea, dried for further characterization and application [18].

2.2. Preparation of Cu_2O/regenerated chitin nanocomposites

The RC film was first immersed in $CuSO_4$ solution (0.2 mol/L) for 12 h and then NaOH solution for 1 h. Then, the photocatalyst was obtained after reaction with hydrazine hydrate (diluted for 500 times) under 10 °C for 3 h. To research the effect of the concentration of $CuSO_4$ on the catalytic activity of the catalyst, the prepared RC composite was immersed in $CuSO_4$ solution with concentration of 0.05, 0.1, 0.2, and 0.5 mol/L, then following the above fabrication pathway and they were coded as CR05, CR10, CR20 and CR50.

2.3. Preparation of Cu_2O/graphene oxide/regenerated chitin nanocomposites

Firstly, GO was prepared using Hummer's method. In brief, graphite powder (1 g) was dispersed in cold concentrated sulphuric acid (25 mL, 98 wt%, ice bath) containing 1 g $NaNO_3$, and then, potassium permanganate ($KMnO_4$, 3 g) was slowly added with continuous vigorous stirring and cooling to prevent the temperature from exceeding 20 °C. The ice bath was removed and replaced by a water bath, and the mixture was heated at 35 °C for 1 h under continuous stirring, followed by slow addition of deionized water (50 mL) and rapid increase of temperature to 98 °C. The reaction was maintained for 12 h in order to increase the oxidation degree of the GO; then the resultant bright-yellow suspension was terminated by addition of more distilled water (140 mL), followed by hydrogen peroxide solution (H_2O_2, 30%, 3 mL). The solid product was separated by centrifugation and washed with 200 mL of 1:10 HCl solution, and then water until pH 7. Finally, the powder was vacuum-dried at room temperature [22].

Here, Cu_2O nanoparticles were in situ synthesized in GO/RC composite film. GO and chitin solution was first mixed to obtain GO/RC composite film with different content of GO. The resultant GO/RC composites with 20, 40, 80 mg of GO and 4.5 g of chitin were named as GO20/RC, GO40/RC and GO80/RC, respectively. The Cu_2O/GO/RC nanocomposite film were prepared via the same way with that of the preparation of Cu_2O/RC Nanocomposite (0.2 mol/L $CuSO_4$) and coded as CGR. The CGR nanocomposite film prepared from GO20/RC, GO40/RC, GO80/RC were named as CGR20, CGR40, CGR80, respectively, among which 20, 40, 80 corresponded to the GO content (20, 40, 80 mg of GO versus 4.5 g of chitin).

2.4. Characterization

X-ray diffraction patterns for 2θ from 5° to 85° were recorded using Rigaku RINT 2000 with Ni-filtered Cu KR radiation ($\lambda = 0.1548$ nm) at 40 kV and 40 mA. The surface and cross sectional images of nanocomposite film were observed using a scanning electron microscope (SEM, Hita-chi X-650 microscope, Japan) with an accelerating voltage of 10 kV. For TEM measurements, the freeze-dried nanocomposites were first embedded in epoxy resin, and then sectioned with an LKB-8800 ultratome to obtain ultrathin slices. Last, the ultrathin slices were observed on TEM (JEOL JEM-1230) at 200 kV.

2.5. Rheological measurements

The effect of GO on the gel process of chitin in the aqueous NaOH/urea solution was investigated by a MAR II dynamic rheometer (Thermo Fisher Scientific, USA) equipped with two parallel plates. The diameter of the plates was 40 mm and the measurement gap between the plates was 2 mm. The value of the strain amplitude was fixed at 1%, which is within the linear visco elastic region, and the sweep of frequency was set at 1 Hz. The storage modulus (G') and loss modulus (G'') were determined as a function of temperature from 33 °C to 40 °C at a heating rate of 1 °C min^{-1}.

2.6. Evaluation of the photo catalytic property

MO was degraded under sunlight to evaluate the photocatalytic property of the catalyst. The concentration of methyl orange (MO) was determined with an UV–visible (UV–vis) spectroscope at the wavelength of 468 nm. For the degradation of MO, the prepared catalyst (2 cm × 2 cm) was first put in 25 mL of MO solution. Then, the solution was put under sunlight to start the degradation. The concentration of MO was determined at desired time intervals.

3. Results and discussion

It has long been established that chitin could cheat metal ions with high capacity, moreover, regenerated chitin possess unique porous structure, which could be used for in situ synthesis of nanoparticles. Additionally, it was found in our early study that the incorporation of GO into Cu_2O/RC could greatly improve the