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Cu$_2$O immobilized on reduced graphene oxide for the photocatalytic treatment of red water produced from the manufacture of TNT

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ABSTRACT

In this paper, we report on the synthesis of nanocomposite catalysts composed of cuprous oxide (Cu$_2$O) and reduced graphene oxide (rGO) formed at room temperature. The nanocomposites were characterized by X-ray diffraction, transmission electron microscopic analysis, ultraviolet-visible diffuse reflection absorptive spectroscopy, etc. The results show that the cuprous oxide particles can be immobilized on the surface of rGO and that the rGO improves the optical properties of Cu$_2$O thereby enhancing the utilization of visible light. Compared with Cu$_2$O under similar synthesis condition, the Cu$_2$O/rGO composites demonstrate improved photodegradative activity of red water. This study verifies the viability of the use of Cu$_2$O/rGO composites in the treatment of red water.

Keywords: Cuprous oxide; Reduced graphene oxide; Composites; Red water; Photocatalysis

1. Introduction

Since it was first synthesized by Joseph Wilbrand in 1863, trinitrotoluene (TNT; 2,4,6-trinitrotoluene) has been widely used as an explosive in many applications because of its superior properties such as the low manufacturing cost, high explosive power, and low melting point [1]. Large-scale production of TNT results in the generation of large quantities of wastewater which has historically been an environmental hazard due to the toxic and mutagenic effects of TNT [2,3]. Red water is the wastewater produced when crude TNT is purified using sodium sulfite. This product is dark red and contains hazardous materials such as trinitrotoluene, nitrotoluene, dissolved dinitrotoluene sulfonates (mainly 4-dinitrotoluene-3-sulfonate and 2,4-dinitrotoluene-5-sulfonate), dinitrotoluene, and other materials [4]. Currently, adsorption is the most widely used method to treat red water [5,6]. Other treatment methods include incineration, degradation utilizing microorganisms [7], advanced oxidation using UV, hydrogen peroxide/ozone [8] and supercritical water treatment [9]. However, it has been found that the decomposition products of the oxidation processes may be even more hazardous than the original pollutant. Photocatalytic technology has attracted much attention due to its ability to completely remove organic pollutants in process effluent. Unlike conventional biodegradation or adsorption methods, photocatalytic technology offers a powerful way to treat bio-resistant organic contaminants by converting them into smaller molecules such as CO$_2$ [10].

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As a versatile semiconductor, Cu₂O has attracted increasing attention by researchers, because of its promising applications in hydrogen production [11], lithium ion batteries [12], solar energy [13], biosensors [14], magnetic storage devices [15], catalysis [16], and gas sensor [17]. Due to the narrow direct band gap of this material (2.0–2.2 eV) and its suitable energy level position [18], Cu₂O can be activated by visible light irradiation which constitutes about 50% of sunlight. This feature makes Cu₂O more desirable for visible light applications than conventional photocatalysts such as TiO₂ and ZnO. Additionally, compared with other narrow band gap semiconductors such as metal sulfides, Cu₂O exhibits low toxicity and low cost making it environmentally friendly and attractive for large-scale applications. Because of these properties, there has been considerable work in recent years examining the photocatalytic treatment of organic pollutants using cuprous oxide as the catalyst. To promote the photocatalytic performance of this material, porous matter, such as silicon oxide [19], aluminum oxide [20], and activated carbon [21], has been used as high-surface-area supports for cuprous oxide. In our previous study [22], we chose to immobilize Cu₂O on sepiolite and reported that the photocatalytic activity of this composite for the degradation of red water was better than unsupported Cu₂O.

Graphene is a novel two-dimensional material that has attracted much attention since its experimental discovery in 2004, because of its excellent physical and chemical properties [23,24]. Graphene and graphene oxide (GO) have potential application as a catalyst support in the field of catalysis. Compared to conventional porous carbon materials, graphene offers a higher surface area to support metal nanoparticles, which could lead to higher catalyst utility. For example, cuprous oxide/graphene nanocomposites had been synthesized as an efficient electrocatalyst for oxygen reduction reaction [25] and its application in an electrochemical sensor for dopamine had been reported [26]. In this study, we immobilized Cu₂O onto rGO, and used the composite material as photocatalyst for the decomposition of red water. The Cu₂O–rGO composite materials were characterized in detail and the photocatalytic activity for the treatment of the red water was discussed thoroughly in relation to the morphologies and the preparative conditions of the catalyst. The activity of the photocatalyst prepared under optimized conditions was significantly improved over the two singular components in the composite, (i.e. Cu₂O or rGO) when they were used individually. Our experimental results suggest that rGO plays an important role in enhancing the photocatalytic activity of Cu₂O and the Cu₂O/rGO composite appears to be an effective photocatalyst for the treatment of the red water.

2. Experimental

2.1. Preparation of GO

Natural graphite powder (particle size 60 μm) was oxidized using the modified Hummer’s method to produce GO [27]. In this method, graphite (5 g) and concentrated H₂SO₄ (120 mL) were added to a 1,000 mL erlenmeyer flask with stirring in an ice bath. KMnO₄ (15 g) was added slowly in portions to keep the reaction temperature below 5°C and the mixture was stirred for 60 min in an ice bath. Following this, the ice bath was removed and the dark green solution was continuously stirred at 35°C for 60 min. Subsequently, 200 mL of DI water was added slowly to the reaction mixture and the erlenmeyer flask was warmed in an oil bath to 98°C and held at this temperature for another 60 min. Finally, 360 mL of deionized water and 10 mL of 80% H₂O₂ were added to the reaction mixture to stop the reaction. The precipitate was centrifuged and washed repeatedly with 5% HCl and ethanol and then vacuum dried by lyophilization.

2.2. Preparation of Cu₂O/rGO

Cu₂O nanoparticles were deposited on graphene by chemical reduction of CuSO₄ in the presence of GO. Various amounts of rGO were added to the Cu₂O synthesis system to produce Cu₂O/rGO composites with various Cu₂O loadings. The quantities of reduced GO (0, 100, 200, 300, 400, or 500 mg) were ultrasonically dissolved in 150 mL of water. Then, 10 mmol CuSO₄ was dissolved in 50 mL of water and added into each of the rGO solutions under ultrasound conditions to form a uniform dispersion. Following this, 20 mmol NaOH was dissolved in each of the above solutions. The resultant mixtures were stirred for 60 min to produce a blue flocy precipitate. Next, 10 mmol L-ascorbic acid was then added into each separate solution and each was stirred for another 60 min, this produced a color change in the precipitate from blue to light yellow. The resulting precipitates were collected and washed repeatedly with ethanol and then lyophilized. This procedure produced six samples which were denoted as A1–A6. The entire preparation process is shown in Fig. 1.
2.3. Characterization and properties

The crystal structure of the synthesized particles was determined using X-ray diffraction (XRD, Rigaku D/Max-Ra). The samples were scanned at 8°/min from 5° to 80° using Cu-Kα radiation (λ = 0.154056 nm) at a filament voltage of 40 kV and current of 100 mA. The morphologies and compositions of the resulting products were studied by transmission electron microscopy (TEM) and Fourier transformation infra-red spectroscopy (FT-IR). TEM images were obtained on a JEM2010 microscope at 200 kV. The samples were prepared by drying a droplet of each suspension (5 × 10^{-4} g/mL) on 400-mesh carbon-coated copper grids. The FT-IR spectra of the samples were acquired on a Perkin–Elmer Spectrum 100 FT-IR spectrophotometer in the range of 4,000–400 cm^{-1}. Test samples were prepared using potassium bromide to form a test pellet. The ultraviolet–visible diffuse reflection absorptive spectra (UV–vis/DRS) were obtained at room temperature on a Lambda-900 UV/vis/NIR spectrometer (Perkin–Elmer, USA) equipped with an integration sphere.

2.4. Photocatalysis measurement

The red water produced from TNT manufacturing was obtained from Dongfang Chemical Corporation (Hubei Province, China). The red water was diluted 200 times with deionized water, because the original red water is too dense to be treated efficiently photocatalytically. The chemical oxygen demand (COD) of the diluted red water used in this study was found to be 1,025 mg/L. To achieve adsorption equilibrium, 20 mg of each Cu_{2}O/rGO sample (A1–A6) was ultrasonically dispersed in 100 mL of diluted red water which was loaded into a water-cooled double-walled-beaker and the mixture was stirred in the dark for 30 min. The photocatalytic experiments were carried out in a reactor equipped with magnetic stirring and a mercury tungsten blended lamp (500 W) positioned about 12.5 cm above the solution surface. At an interval of 60 min from the start of the photoreaction, 10 mL of the suspension was sampled and filtrated. The clarified filtrates were analyzed by a COD rapid detector (5B-6, Lian-Hua Tech. Co., China) with a precision of ± 5% to determine the photocatalytic efficiency of the samples.

3. Results and discussion

Fig. 2 shows the FTIR spectra of the GO, Cu_{2}O, and Cu_{2}O/rGO composites. The results indicate that Cu_{2}O nanoparticles were successfully immobilized onto rGO. Reduced GO exhibits abundant oxygen containing groups. The strong band at 3,410 cm^{-1} results from the stretching vibration of the hydroxyl (–OH) group. The band at 1,730 cm^{-1} is caused by the C=O vibration of –COOH. The peak at 1,620 cm^{-1} may result from skeletal vibrations of the graphitic backbone. The band at 1,387 cm^{-1} can be assigned to the tertiary C–OH group stretching vibration, and the peak at 1,060 cm^{-1} is attributed to C–O stretching vibrations. These characteristic vibrational bands are
indicative that the graphene contains epoxide groups, hydroxyls, and carboxyls. With respect to the Cu$_2$O, the peak at 627 cm$^{-1}$ is due to Cu–O vibration, the band located at 3,350 cm$^{-1}$ and the peaks near 1,500 cm$^{-1}$ are caused by the stretching and bending vibrations of hydroxyl groups of the adsorbed water.

Referring to the spectra of the Cu$_2$O/rGO composites, the Cu–O vibration of Cu$_2$O shifts slightly to 618 cm$^{-1}$, which might be due to the interaction between Cu$_2$O and graphene, which perturbs the Cu–O bonds. The characteristic absorbance bands of GO disappear, while the C–O stretching vibrations are still present at 1,060 cm$^{-1}$. These results indicate that L-ascorbic acid can reduce Cu(OH)$_2$ and partially reduce GO to produce Cu$_2$O/rGO composites.

XRD spectra confirm the conclusions derived from FTIR spectra. Fig. 3 shows the XRD patterns of GO and the as-prepared Cu$_2$O/rGO composites. The GO provided a peak centered at $2\theta = 9.12^\circ$, corresponding to the interlayer spacing of the GO of 0.97 nm, which is dramatically larger than the layered spacing of graphite (0.34 nm, $2\theta = 26^\circ$). This means that the space between the graphite sheets has been expanded by oxygen containing groups. In Fig. 3, according to the JCPDS card No.05-0667, the diffraction peaks of Cu$_2$O (A1) are observed at $2\theta$ values of 29.5, 36.5, 42.3, 61.6, and 73.5$^\circ$ corresponding to the crystal planes of (110), (111), (200), (220), and (311) of crystalline cuprous oxide. No peaks belonging to Cu or Cu(OH)$_2$ are detected, indicating the efficient conversion of Cu(OH)$_2$ to Cu$_2$O by the L-ascorbic acid reduction. With respect to the Cu$_2$O/GO composites (A2–A6), the peaks of Cu$_2$O are present in XRD patterns, but no characteristic peaks corresponding to GO or graphite are observed indicating that the immobilization of Cu$_2$O onto graphene sheets disturbs the ordered structure of GO or graphite.

The morphologies of Cu$_2$O/rGO composites were observed using TEM. Fig. 4 shows TEM images of Cu$_2$O (A1) and Cu$_2$O/rGO composites (A2–A6) are synthesized with increasing amount of GO. It can be clearly seen in Fig. 4 A1 that the Cu$_2$O spheres (A1) reduced by L-ascorbic without the presence of GO are comprised of smaller Cu$_2$O particles and the diameter of the spheres is about 100 nm. As for A2, Cu$_2$O nanoparticles with diameters of about 40 nm form a dense cover on the rGO sheet and some of these particles have subsequently aggregated. In A3, in addition to the 40 nm Cu$_2$O nanoparticles as in A2, smaller 5 nm Cu$_2$O nanoparticles are also seen on the rGO sheet. In sample A4, the smaller Cu$_2$O nanoparticles are densely scattered over the rGO sheet with larger Cu$_2$O nanoparticles aggregated, the wrinkles of rGO sheet can be clearly observed. In A5 and A6, with a further increase in the quantity of GO added to the Cu$_2$O solution, only a few aggregates appear on the rGO sheet which is composed of large Cu$_2$O nanoparticles. These TEM images revealed that the oxygen containing groups on GO sheet can act as anchoring sites for the deposition of Cu$_2$O nanoparticles. There are no Cu$_2$O nanoparticles scattered outside of the rGO sheet, indicating a strong interaction between rGO support and Cu$_2$O nanoparticles. Appropriate amounts of GO in the reaction favors the homogeneous scattering of Cu$_2$O nanoparticles on rGO sheet with smaller particle size and good dispersion. This result suggests a further improvement in the photocatalytic activity of Cu$_2$O/rGO composites.

The UV–vis DRS of Cu$_2$O and Cu$_2$O/rGO (A4) are displayed in Fig. 5(a). The absorption edge of Cu$_2$O exists at around 630 nm. The absorption edge of the Cu$_2$O/rGO appears to be somewhat blue shifted. However, the absorbance of Cu$_2$O and Cu$_2$O/rGO is similar in the ultraviolet range, while Cu$_2$O/rGO exhibits higher absorbance in the visible range light than the pure Cu$_2$O. Since rGO is a black support, it has a large absorbance in visible light range. Consequently, the absorbance of composite in the visible light range can be attributed primarily to the rGO.

To further study the optical properties of the composites, we estimated the band gap energy. The direct band gap is one of the most desirable properties of photocatalyst, because this type of material can absorb photo energy more efficiently than a material with an indirect band gap [28]. Since Cu$_2$O is a direct gap semiconductor, the relationship between the absorption coefficient ($\alpha$) and photon energy ($h\nu$) can be expressed as [29]:
\[ a\hbar v = C(h\nu - E_g)^{1/2} \]  

(1)

where \( C \) is a constant that is independent of photon energy, \( E_g \) is the band gap energy, and \( a \) is the absorbance coefficient. The band gap can be estimated from the intercepts of the tangents to the \((a\hbar v)^2\) vs. photon energy \((h\nu)\) plots. Fig. 5(b) depicts the plots of \((a\hbar v)^2\) vs. \((h\nu)\) for pure \( \text{Cu}_2\text{O} \) and \( \text{Cu}_2\text{O}/\text{rGO} \). The direct band gaps of pure \( \text{Cu}_2\text{O} \) and \( \text{Cu}_2\text{O}/\text{rGO} \) are estimated to be 2.23 and 2.07 eV, respectively. There is a slight red shift in the direct band gap occurs when cuprous oxide is immobilized on rGO. The electrical properties of the rGO improve the surface optical property of the \( \text{Cu}_2\text{O} \) nanoparticles, which lowers the activation energy of \( \text{Cu}_2\text{O} \) crystals and enhances their sensitivity to light.

The photocatalytic activity of \( \text{Cu}_2\text{O} \) and \( \text{Cu}_2\text{O}/\text{rGO} \) composites (corresponding to A1–A6 in Fig. 3) was assessed by monitoring the degradation of TNT in the processed red water when exposed to visible light. Red water from TNT manufacturing is a mixture of complex constituents and every constituent has a characteristic absorption wavelength. Therefore, it is very difficult to determine the photocatalytic degradation rate using absorption spectrophotometry. In this study, we determined the degradation of red water by measuring the COD of the red water and the relative removal rates of COD were calculated by the following equation:

Relative removal of COD (\%) = \( \frac{\text{COD}_{o} - \text{COD}_{e}}{\text{COD}_{o}} \times 100\% \)

Here, \( \text{COD}_{o} \) and \( \text{COD}_{e} \) are the original and final COD values of the TNT red water, respectively. In this equation, the relative removal of COD serves as an indicator of the photolysis rate of red water. Fig. 6 shows that the direct photolysis rate of red water is 1.54%,
when the solution was irradiated using visible light for 6 h without any photocatalysts. This is the baseline result and shows that that direct photolysis of red water does not greatly degrade the dissolved TNT.

The photocatalytic activity of Cu$_2$O in Sample A1 appears to be low as only 11.2% of organics in red water were degraded. The photodegradation activities of Cu$_2$O/rGO composites (A2–A6) are significantly enhanced compared with pure Cu$_2$O, and the largest photolysis rate of red water was 42.6%. The improvement in photocatalytic activity of Cu$_2$O/rGO composites is due to the efficient retardation in the recombination process of photo-generated electron/hole pairs. Graphene has excellent electrical properties; the work function has been calculated to be 4.42 eV [30]. In addition, the conduction band position of Cu$_2$O is ~3 eV (using vacuum level as a reference) [31]. This means that graphene can accept conduction band electrons from Cu$_2$O so that the conduction band electrons of Cu$_2$O can be transferred to graphene, instead of recombining with valence band electron holes in the Cu$_2$O. This increases the photocatalytic activity of the supported Cu$_2$O.

On the other hand, the appropriate amount of rGO in the composite catalyst is crucial in determining the photocatalytic activity of the material. Sample A4 exhibits the maximized photocatalytic activity, where about 42.6% of organics in red water was decomposed in 6 h, which is dramatically higher than Cu$_2$O catalyst. This result combined with the TEM image of A4 implies that an optimum quantity of rGO can favor the homogeneous scattering of the Cu$_2$O nanoparticles. The appropriate size and dispersion of Cu$_2$O nanoparticles on rGO sheets appear to have led to more efficient interactions between rGO and Cu$_2$O resulting in a retardation of the recombination of the electron/hole pairs. This appears to enhance the photocatalytic activity. In the case of samples A2 and A3, Cu$_2$O nanoparticles were larger or they aggregated on the rGO sheets. This appeared to decrease the efficiency of its interaction between the Cu$_2$O and the rGO, which hindered the overall activity of combined photocatalyst. In samples A5 and A6, the amount of Cu$_2$O in composites appeared to be insufficient which resulted in a decrease in the transferred electrons from excitation state of Cu$_2$O apparently reducing the photocatalytic activity of these two composite catalysts.

4. Conclusions

In summary, Cu$_2$O/rGO composites with improved photocatalytic activity for the decomposition of the red water were successfully synthesized. TEM images reveal that Cu$_2$O nanoparticles were
immobilized on rGO sheets. UV–vis DRS analysis revealed that composites improved the optical properties of cuprous oxide and red shifts the band gap, thereby improving the utilization of visible light. The results of the photocatalytic treatment of red water using these experimental materials suggest that the Cu2O/rGO composites offer excellent photocatalytic performance for degrading the contaminants in the red water that result from the manufacture of TNT.

References