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Co_3O_4 nanocrystals on graphene oxide as a synergistic catalyst for degradation of Orange II in water by advanced oxidation technology based on sulfate radicals

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ABSTRACT

Graphene oxide and cobalt oxide nanocomposites (Co_3O_4/GO) are fabricated in situ as heterogeneous catalysts by the decomposition of cobalt nitrate through heat and crystal growth of Co_3O_4 on the surface of GO sheets in 1-hexanol solvent. The Co_3O_4/GO catalyst is characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM). Results show that the Co_3O_4/GO catalysts are large GO sheets decorated homogenously with well-dispersed Co_3O_4 nanoparticles. Although Co_3O_4 or GO alone exhibit little catalytic activity, their hybrid (Co_3O_4/GO) exhibits an unexpectedly high catalytic activity in the degradation of Orange II in water by advanced oxidation technology based on sulfate radicals, and 100% decomposition can be achieved in 6 min. These phenomena suggest a synergistic catalytic activity of Co_3O_4 and GO in the hybrid.

1. Introduction

Advanced oxidation processes (AOPs) that involve in situ generation of highly reactive radicals, such as $^\bullet OH$, $^\bullet O_2^-$, $^\bullet OOH$ and $SO_4^{-\bullet}$, have emerged as a promising method for degradation of organic pollutants [1–4]. Advanced oxidation technologies based on the generation of sulfate radicals ($SO_4^{-\bullet}$) have emerged over the past years as a promising technique to degrade completely most organic pollutants [2,5,6]. The coupling of transition metal ions, such as Cu^{2+}, Mn^{2+}, Fe^{2+}, and Co^{2+} to peroxymonosulfate (PMS) leads to the accelerated generation of $SO_4^{-\bullet}$ and higher oxidation efficiencies [2,6,7]. The various combinations between the dissolved transition metal ions and oxidants have been evaluated systematically for the generation of active radicals by Anipsitakis et al. [2,5,6]. PMS coupled with Co^{2+} ions is the best combination for the generation of $SO_4^{-\bullet}$ for degrading Orange II. However, the oxidation using cobalt and PMS under a homogeneous system has profound disadvantage in terms of the cobalt leachate. The cobalt leachate is biologically toxic and recognized as a priority metal pollutant. Therefore, the activation of PMS by heterogeneous cobalt sources has recently been paid great attention. So, various cobalt precursors were loaded onto various supports to prepare heterogeneous catalyst. Dionysiou et al. [8–10] studied both the unsupported and supported Co_3O_4 on several common supports (i.e., Al_2O_3, SiO_2, and TiO_2) as heterogeneous activators for PMS to degrade 2,4-dichlorophenol (DCP). Kiwi et al. [11] used a polytetrafluoroethylene flexible film as the support for Co_3O_4 nanoparticles to decompose organic dyes under light irradiation. Chen et al. [4] evaluated the performance of unsupported Co_3O_4 nanoparticles in the degradation of Acid Orange 7. Zhang et al. [12] used cobalt oxide on MgO for the degradation of organic dyes in dilute solutions. Shukla et al. [13] studied cobalt exchanged zeolites for the heterogeneous catalytic oxidation of phenol in the presence of peroxymonosulfate.

Similar to hydrogen peroxide, PMS has been proposed as an oxidant. Cobalt ion was proven as an efficient catalyst for PMS activation to produce sulfate radicals and oxidize organic compounds. In the presence of cobalt ion, PMS breaks up to generate active sulfate radicals, which consequently aid in the oxidation of Orange II. Orange II is a widely used synthetic azo dye. It does not decompose through biological methods, and resists light irradiation and chemical oxidation. It is generally used as a model substrate for the aromatic azo dyes. Therefore, several scholars have studied its degradation. In a homogeneous system, the cobalt ion catalyzed activation of PMS and degradation of Orange II as follow reactions:

$$Co^{2+} + HSO_5^- \rightarrow Co^{3+} + SO_4^{-\bullet} + OH^- \quad (1)$$

$$Co^{3+} + HSO_5^- \rightarrow Co^{2+} + SO_5^{-\bullet} + H^+ \quad (2)$$

$$SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + {}^\bullet OH + H^+ \quad (3)$$

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$$SO_4^{\bullet -} + [\text{Orange II}] \rightarrow [\text{Orange II}]^{-}SO_4^{\bullet -} \xrightarrow{-SO_4^{2-}} {}^{\bullet}[\text{Orange II}]^{+} \xrightarrow{\text{several steps}} CO_2 + H_2O \quad (4)$$

$$^{\bullet}OH + [\text{Orange II}] \rightarrow [\text{Orange II}]^{-\bullet}OH \xrightarrow{-SO_4^{-}} {}^{\bullet}[\text{Orange II}]^{+} \xrightarrow{\text{several steps}} CO_2 + H_2O \quad (5)$$

Graphene oxide (GO), which can be easily prepared by chemical modification, consists of a hexagonal ring-based carbon network with both sp^2-and sp^3-hybridized carbon atoms [14]. This carbon material has multiple oxygen-containing functional groups, such as hydroxyls and epoxides in the basal plane, and carboxyl groups at plane edges [15–19]. Such surface functionalization leads GO swell readily and disperse in water easily [20–24]. Compared with graphene, GO is hydrophilic and can form strong physical interactions with polymers because of its various oxygen functional groups, including hydroxyls, epoxides, carbonyls, and carboxyls [25]. GO sheets can be intercalated or exfoliated by small molecules or polymers [26,27]. These exfoliated GO sheets possess large surface areas and, thus, may be potential support materials to load several nanocrystals, such as a wide range of metals and oxide, fluorescent molecules, drugs, biomolecules and inorganic nanoparticles [28–44].

The current paper reports on a cobalt oxide supported on GO as an efficient heterogeneous catalyst for activation of PMS, used in the degradation of Orange II in water by advanced oxidation technology based on sulfate radicals. It has been found that the Co_3O_4/GO catalyst is able to completely degrade Orange II in dilute solutions within a very short duration of a few minutes without light irradiation and microwave activation, which indicated that Co_3O_4 nanocrystals on GO is a synergistic catalyst. The current catalyst system is therefore expected to be highly desirable for competing with the conventional non-destructive treatment processes.

2. Experimental

2.1. Materials

Flake graphite (300 mesh, 99.99%) was supplied by Shanghai Yifan Graphite Co. Ltd., China. PMS, available as a triple salt of sulfate commercially known as oxone ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, 4.5% to 4.9% active oxygen), was obtained from Shanghai Ansin Chemical Co. Ltd. and used as an oxidant. Other reagents including $Co(NO_3)_2{\cdot}6H_2O$, H_2SO_4 (98%), $NaNO_3$, $KMnO_4$, and H_2O_2 (30%) of analytical grade were provided by Sinopharm Chemical Reagent Co. Ltd. (China).

2.2. Preparation of GO

Graphite oxide was initially prepared to obtain GO. Graphite oxide was prepared according to the method reported by Hummers and Offeman [45] from purified natural graphite with a mean particle size of 48 μm. Briefly, 230 mL of concentrated H_2SO_4 (98%) was added into a 2000 mL dry flask containing 5 g of $NaNO_3$ placed in an ice-water bath and stirred until the temperature of the mixed liquor is below 5 °C. Then, 10 g of flake graphite was added into the flask, and the mixture was stirred for 30 min. Potassium permanganate (30 g) was added slowly to the suspension under continuous vigorous stirring. The rate of addition was carefully controlled to keep the reaction temperature below 20 °C, and the process required approximately 2 h. Afterward, the ice bath was replaced by an oil bath, and the mixture was stirred at 35 °C for 2 h. The mixture gradually became pasty as the reaction progressed, and the color turned into light brownish. Then, 460 mL of H_2O was slowly added under vigorous stirring, and the reaction temperature was kept at approximately 98 °C. Then, the temperature of the oil bath was set at 90 °C, and the mixture was continuously stirred for 2 h. Finally, 25 ml of 30% H_2O_2 was slowly added to the mixture, and the high-temperature reaction progressed under continuous stirring for 1 h. The mixture color changed into bright yellow from clay black. The mixture was purified by washing with approximately 2 L HCl (5%), followed by deionized (DI) water for several times until no SO_4^{2-} (tested by $BaCl_2$ solution) and Cl^- (tested by $AgNO_3$ solution) were found in the mixture. The mixture color turned to tawny. After filtration and then drying in vacuo at 60 °C for 24 h, graphite oxide was obtained as a solid. GO was obtained through ultrasound stripping of graphite oxide in water or other dissolvent.

2.3. Preparation of Co_3O_4/GO

GO (50 mg) was dispersed into 30 mL of 1-hexanol with sonication for 3 h. The suspension was centrifuged to wipe off the sediment, and the supernate was stored for further use. Then, 1.25 mmol $Co(NO_3)_2{\cdot}6H_2O$ was dissolved into another 20 mL of 1-hexanol and added into the foregoing supernate. The mixture was magnetically stirred for 2 h and heated to 140 °C under reflux and vigorous magnetic stirring for 12 h. After the system was cooled to room temperature, the suspension was centrifuged, and washed by absolute ethanol several times. Then, all the remaining 1-hexanol solvent and other sundries were removed and dried in a vacuum oven at 60 °C for 24 h. The product was labeled as Co_3O_4/GO. Additionally, Co_3O_4 was synthesized with the same parameters for comparison [46].

2.4. Characterization technique

The structural features and the mineralogy of the graphite, GO and Co_3O_4/GO were studied using X-ray diffraction (XRD) patterns obtained on a RIGAKU XRD instrument, using filtered Cu Kα radiation with accelerating voltage of 40 kV and current of 200 mA. The sample was scanned at 2θ from 5° to 90°.

The changes in the surface chemical bonding and surface composition were characterized by Fourier transform infrared spectroscopy (FT-IR; Bruker, Tensor 27), which were obtained to prove the success of support cobalt oxide on the GO sheets. The test samples were pressed into tablets with KBr.

The atomic composition of the GO and Co_3O_4/GO were detected by X-ray photoelectron spectroscopy (XPS). The XPS spectrum was recorded on a ESCALAB 250 photoelectron spectrometer (Thermo-VG Scientific, USA) with Al Kα (1486.6 eV) as the X-ray source. All XPS spectra were corrected using the C 1s line at 284.6 eV.

The texture, morphology, and semi quantitative analyses of the GO and Co_3O_4/GO were performed using scanning electron microscopy (SEM, JEOL JSM-5600LV) with both secondary and backscatter electrons. The elemental composition was determined using the energy dispersive X-ray spectroscopy (EDS). The EDS (IE300X) analysis was performed at several points in the region and averaged to obtain the representative results.

The nanoscale structures were observed using high-resolution transmission electron microscopy (FE-HRTEM, JEOL JEM-2100F) with an accelerating voltage of 200 kV. The sample was prepared by dispersing a small amount of dry powder in ethanol or water. Then, one droplet of the suspension was dropped on a formvar-carbon-coated, 300 mesh copper TEM grids (Ted Pella) covered with thin amorphous carbon film and allowed to evaporate in air at room temperature.

The BET surface areas were measured by a BET analyzer (BK122T-B, JWGB, China) using the liquid nitrogen adsorption method.