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Photocatalytic activity of the binary composite CeO_2/SiO_2 for degradation of dye

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ABSTRACT

In this study, CeO_2 photocatalyst was modified by composite with SiO_2 to increase efficiency and improve photocatalytic activity. The as-prepared SiO_2 particles have been incorporated into the precursor mixture of CeO_2 by homogeneous precipitation and subsequent calcination process. The phase compositions of CeO_2 before and after compositing with SiO_2 were identified by X-ray diffraction (XRD). The morphology and particle size of CeO_2/SiO_2 composite was analyzed by high resolution transmission electron microscopy (HRTEM) and field emission scanning electron microscopy (FESEM). The results showed SiO_2 spheres with the particle size approximately 100–120 nm, and a uniform layer of CeO_2 nanoparticles with a diameter of about 5–7 nm that were fully composite to the surfaces of SiO_2. The X-ray photoelectron spectroscopy (XPS) technique was carried out in order to characterize the change in valence state and composite characteristic by shifted peaks of binding energies. The photocatalytic activity was studied through the degradation of Rhodamine B in aqueous solution under visible light exposure. The highest photocatalytic efficiency of CeO_2/SiO_2 composite was also obtained. To explain the high photocatalytic efficiency of CeO_2/SiO_2 composite, the proposed mechanism involves the high surface properties of the CeO_2/SiO_2 composite, as measured by Brunauer-Emmett-Teller (BET) method.

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1. Introduction

Water-related pollution has received significant attention from scientists around the world. With overuse in this age of changing climates, clean water has become more and more scarce [1]. Among the available solutions to solve this water scarcity problem, contaminated water treatment is considered to be one of the most effective methods for water resource maintenance, because of the size of the readily-available supply [2,3]. When considering water treatment methods, one would quickly note that there are many different types of organic pollutants, ranging from simple to complex organic molecules; for example, Saccharides (sucrose, glucose, and fructose), Carboxylic acids (maleic acid, oxalic acid, dichloroacetic acid, formic acid, citric acid, malonic acid, acetic acid, and *iso*-butyricacid), and aromatic organics (salicylic acid, phenol, 2,4-dichlorophenol and dyes) [4,5].

Among organic pollutant compounds, the organic AZO dyes such as Methyl orange (MO), Methylene blue (MB), and Rhodamine B (RhB) are classified as the main organic water pollutants. These dyes are normally applied in almost all industries to color products [6]. Removing color from waste water is often more important than removing other colorless organic substances, because the presence of small amounts of dyes (below 1 ppm) is clearly visible, and considerably influences the water environment. Since the chemical structure of organic dyes normally contains aromatic rings as parts of their structures, this makes them stable enough and difficult to biodegrade. Many literature reviews have indicated that the presence of organic dyes in the aqueous environment has caused several serious problems due to their toxicity, persistence, and bioaccumulation [7–10]. They can cause mouth sores, nausea, and dark urine. Meanwhile, vomiting and bloody diarrhea are more dangerous symptoms of textile dye contamination at high concentration. In addition, potential carcinogenic compounds can also be formed during disinfection and oxidation processes, with obvious poten-

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tial to damage human health [11,12]. Therefore, the removal of the organic dye from waste water is one of the higher priorities for contaminated water treatment.

In this study, Rhodamine B was selected as a target compound because of its status as the main organic pollutant released directly from textile, printing, cosmetics, pharmaceuticals, paper and ink manufacturing industries, denim industries, and food industries [13]. Several technologies for treating organic dyes have been developed in recent years. These conventional methods have shown some efficiency in organic pollutant removal. However, the standards for waste water treatment is increasingly stringent, to ensure sustainability in development and environmental protection [14]. Besides, a number of treatment techniques, such as adsorption and coagulation, can only transfer pollutants to other phases rather than eliminate them completely [15]. Meanwhile, some of other methods, such as sedimentation, filtration, chemical and membrane technologies have high operating costs and/or generate secondary toxic pollutants during the treatment process [16,17]. Hence, scientist continually seek out for alternative cost-effective methods to solve this issue.

Recently, advanced oxidation processes (AOPs) are optimum alternative methods that have received much attention among those interested in organic pollutant removal. Although AOPs include many different types of reaction systems, all AOPs are described by the same principle of oxidation processes based on using the highly oxidizing hydroxyl radicals ($OH^\bullet$). Heterogeneous photocatalysis employing a semiconductor catalyst has demonstrated its efficiency in degrading organic compounds into readily biodegradable matters. Semiconductor catalysts such as TiO_2, CeO_2, ZnO, Fe_2O_3, CdS, $BiVO_4$, WO_3 or ZnS are often used in photocatalytic treatment [18]. Among other catalysts, cerium dioxide (CeO_2) has received much attention because it is non-photocorrosive, non-toxic, and has strong oxidation ability together with high chemical stability [19].

The major processes in photocatalysis by CeO_2 are presented in the reaction below. Reaction (1) explains the formation of the charge carriers upon irradiation of CeO_2. The highly reactive hydroxyl radical ($OH^\bullet$) can be formed by reaction of the hole in the valence band VB ($h^+{}_{VB}$) with either the molecule of water (decomposition in Reaction (2)) or with the hydroxyl ion OH^- (oxidation in Reaction (3)).

$$CeO_2 + h\nu \rightarrow CeO_2\,(e^-{}_{CB} + h^+{}_{VB})\ \text{(Charge separation)} \qquad (1)$$

$$h^+{}_{VB} + H_2O \rightarrow H^+ + OH^\bullet\ \text{(Radical generation in VB)} \qquad (2)$$

$$h^+{}_{VB} + OH^- \rightarrow OH^\bullet\ \text{(Oxidation in VB)} \qquad (3)$$

The electron in the conduction band CB ($e^-{}_{CB}$) can reduce molecular oxygen to the superoxide anion ($O^\bullet{}_2{}^-$) (reduction in Reaction (4)), which results in the following Reaction (5) and provides the hydroxyl radical ($OH^\bullet$), which is the principal agent of decomposition of organic molecules. The organic pollutants in water are then adsorbed and degraded by hydroxyl radicals ($OH^\bullet$) until they are mineralized completely to carbon dioxide and water (overall reaction in Reaction (6)).

$$e^-{}_{CB} + O_2 \rightarrow O^\bullet{}_2{}^-\ \text{(ReductioninCB)} \qquad (4)$$

$$O^\bullet{}_2{}^- + H_2O \rightarrow 2OH^\bullet\ \text{(RadicalgenerationinCB)} \qquad (5)$$

$$OH^\bullet + \text{Organicpollutants} \rightarrow CO_2 + H_2O\ \text{(Decomposition)} \qquad (6)$$

If the generated charge carriers ($e^-{}_{CB}$ and $h^+{}_{VB}$) are not involved in any further reactions, the electron in the conduction band can recombine with the hole in the valence band, because the latter is strongly oxidizing and so favors retrieval of the electron [20]. This is normally the case with undoped photocatalysts, and so interfacial transfer and consequent decomposition by photocatalysis is less likely to have the opportunity to occur.

Many studies have described the process to enhance charge separation and increase the photocatalytic activity of CeO_2 by many routes, such as metal doping or coupling with other metal oxide materials [21,22]. However, the major improvement to be achieved in this project is to increase the degradation efficiency. One of the factors to determine the efficiency is adsorption of the organic pollutant to the CeO_2 surface. The introduction of an adsorbent enhances not only the pollutant's removal efficiency, due to the bi-mechanism of adsorption by adsorbents and photo-oxidation by $CeO_{2,}$ but also the separation possibility of the particles, due to the increase of particle size [23]. In addition to common adsorbents used in waste water treatment, typically activated carbon, alumina, silica, and zeolite have been shown to increase the adsorption [24,25]. All studies demonstrated that most of the metal oxide-covered adsorbents are more efficient than the metal oxide alone.

In recent years, SiO_2 has been widely used in the material synthesis field. It is believed to be a very good medium, which not only facilitates adsorbing organics and transfers those adsorbed compounds to active sites on a metal oxide catalyst, but also benefits the dispersal of the metal oxide particles [26,27]. Besides, SiO_2 modification is effective in separating the photogenerated electrons and holes, which is of great importance for the photocatalytic activity [28]. For example, TiO_2/SiO_2 composite materials have been widely investigated, and in most cases of these catalysts show a higher photocatalytic activity than the neat $TiO_{2,}$ prepared in parallel for the oxidation of organic pollutants in water [29]. The studies cited above are also recommend combining SiO_2 adsorbent with $CeO_{2,}$ so that the high adsorption capacity of the CeO_2 photocatalyst is facilitated.

Therefore, the aim of this study is to synthesize a binary composite material that combines the photocatalytic activity of CeO_2 with the adsorption ability of the adsorbent produced from SiO_2. The synthesized binary composite CeO_2/SiO_2 was then applied in Rhodamine B removal from an aqueous solution under visible light exposure.

2. Experimental

2.1. SiO_2 preparation

Firstly, SiO_2 was prepared following the method by Xiaolan, et al., with a slight modification [30]. The hydrolysis and polycondensation was started by dissolving ammonia solution and absolute ethanol in deionized water. The solution was then sonicated in ultrasonication for 1 h under 50 °C. After that, tetraethoxy silicate (TEOS) was added into the solution drop by drop, with proper agitation to disperse the droplets. The mixed solution was continually stirred for 2 h and aged for 24 h. The resulting dispersions were separated by centrifugation, and washed several times with deionized water/ethanol before drying at 60 °C for 12 h. Finally, a SiO_2 particle was obtained by calcining at 500 °C for 1 h, for further use.

2.2. CeO_2 preparation

The synthesis of CeO_2 composite was achieved by homogeneous precipitation and subsequent calcination process, as given in our previous work [31]. In a typical preparation, cerium (III) nitrate hexahydrate was dispersed in 80% ethylene glycol/water-mixed solvents, with continuous stirring at 50 °C. The resulting solution was added with 3 M ammonia solution drop-by-drop. During this time, the color of the solution changed from yellow to purple; however, after 12 h of aging, a turbid yellow suspension became visible again. The precipitant was centrifuged, washed with distilled water/ethanol, and dried at 80 °C for 24 h. Finally, the prepared CeO_2 particles were calcined at 500 °C for 1 h.

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