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Research paper

Metal oxide nanoparticles deposited onto carbon-coated halloysite nanotubes

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ABSTRACT

Halloysite nanotubes (HNTs) can serve as high aspect ratio templates for the deposition of functional nanoparticles to form novel nanocomposites. We reported here on the synthesis of carbon-coated HNTs (CCH) via the carbonization of sucrose-coated HNTs in the presence of sulfuric acid. Metal oxide (MO) nanoparticles (ZnO, TiO_2) were subsequently deposited on the surface of the CCH to produce MO/CCH nanocomposites. The samples were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, and N_2 adsorption–desorption analysis. The results indicated that graphitic carbon could improve the conductivity of HNTs, and electron transfer across the interfaces between MO and graphitic carbon led to a significant change in photocatalytic properties. MO/CCH showed good photocatalytic performance for photodegradation of methylene blue dye. The nanocomposites had two excellent advantages as a result of the unique properties of carbon, and increased adsorption of pollutants and easy charge transportation. The as-synthesized nanocomposites could have potential application in the field of wastewater treatment.

1. Introduction

In recent years, there has been progress in the development and characterization of new materials based on clay mineral nanotubes (Abdullayev et al., 2012; Dvoyashkin et al., 2012; Yang and Zhang, 2012; Yucelen et al., 2011; Yucelen et al., 2012). Imogolite (Demichelis et al., 2010; Guimarães et al., 2007; Liu et al., 2012; Ma et al., 2012; Thill et al., 2012a, 2012b), halloysite (Burridge et al., 2011; Guimarães et al., 2010; Joussein et al., 2005; Zhang and Yang, 2012b) and chrysotile (Falini et al., 2002; Luca et al., 2009; Piperno et al., 2007) were examples of naturally occurring nanostructured clay minerals. Among these, nanostructured aluminosilicates have been the most investigated for new advanced materials due to their availability, ease of functionalization, and well-defined structures. Their structures have been modified to give specific chemical and physical properties (Kang et al., 2011). In particular, aluminosilicate nanostructures were modified for use as adsorbents (Gascon et al., 2012; Kang et al., 2010), catalysts (Dong et al., 2009; Zatta et al., 2011; Zhang and Yang, 2012a) or catalyst supports (Nakagaki and Wypych, 2007; Papoulis et al., 2010). In the field of environmental catalysis, modified aluminosilicate nanostructures have various advantages such as the use of catalytic amounts, simple recovery and high turnover rates, ease of set-up and work-up, mild experimental conditions, and high yields and selectivities, making them useful tools in establishing environmentally friendly technologies.

Halloysite 7 Å [$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$] is a hydrated layered aluminosilicate of the kaolinite group, containing octahedral gibbsite $Al(OH)_3$ and tetrahedral SiO_4 sheets. Halloysite nanotubes (HNTs) consist of hollow cylinders formed from multiple rolled halloysite layers, and have attracted much attention due to their highly specific surface areas, porosities, and cation-exchange capacities compared with other minerals of the kaolinite group. HNTs have interesting features and potential applications as enzymatic nanoscale reactors (Shchukin and Sukhorukov, 2005). However, natural untreated HNTs have a very low ability to catalyze chemical reactions. In addition, they are insulators and rigid, like other inorganic nanotubes, and do not have enhanced electron transfer ability. The structure and properties of HNTs can be modified via various activation methods to produce catalysts with high sorption abilities, electronic conductivities, and thermal stabilities. In our previous study, HNTs were loaded with semiconductors for photocatalysis, such as ZnS and Co_3O_4 (Zhang and Yang, 2012a), but it was mainly focused on the adsorption and dispersion.

The poor conductivity of HNTs should be addressed. The outer surface of HNTs is net negatively charged and the adsorbed positive ion cannot move freely, while carbon coating could effectively improve conductivity on the surface. Carbon coating has been usually realized by vapor-phase growth (Deck and Vecchio, 2005; Sinnott et al., 1999), template-assisted (Klepel et al., 2007; Zhong et al., 2003) or solvothermal methods (Kuang et al., 2004; Wang et al., 2009), which

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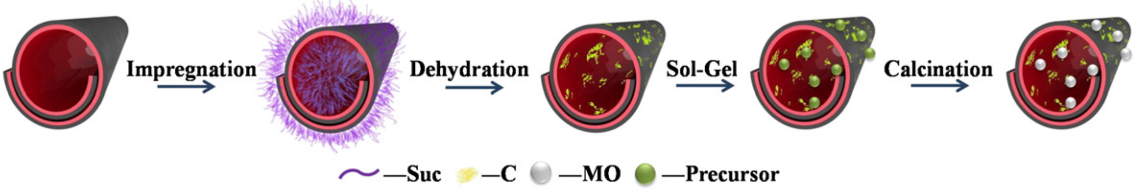

Fig. 1. Schematic of the fabrication process for MO/CCH nanocomposites. Halloysite nanotube (HNT) has been often employed as supporter for loading compounds, especially the metal oxides (MO). For this purpose, HNTs should be coated with an oxide precursor or a gel. In the first step, HNTs were impregnated with sucrose solution, which will soak the inner and outer surfaces of nanotubes in order to ensure the complete filling of the HNTs and the protection of the inner tubes from metal deposition. Secondly, carbon-coated HNTs (CCH) were synthesized through sucrose-coated HNTs via the carbonization of sucrose as carbon precursor in the presence of sulfuric acid. It is very common reaction which demonstrates the dehydrating and oxidizing properties of concentrated sulfuric acid. Carbon was adopted as coating material since it had superior physicochemical properties as an electrocatalyst support compared with the commonly used carbon black or active carbon. After the dehydration by sulfuric acid, the surface of substrate has more hydroxyl and carboxyl groups. Metal oxides were deposited on CCH by sol–gel method. The aqueous solution containing the metal precursor was added, it couldn't completely penetrate CCH due to HNTs coated with carbon. Thus, the inner remained protected and the metal oxide nanoparticle deposition was realized on the outer surface.

could effectively improve the electric conductivity. However, these synthetic methods are restricted to ambient temperature or deoxygenated atmospheres.

In this work, HNTs were used as support materials. We reported the synthesis of carbon-coated halloysite (CCH) from sucrose-coated halloysite (SCH), and the sucrose was dehydrated by concentrated sulfuric acid (Liang et al., 2010). The process is relatively simple, and expected to be cheaper than high-temperature carbonization process in the preparation of CCH. Metal oxide (MO) nanoparticles (ZnO, TiO_2) were then assembled on the CCH surface to produce MO/CCH nanocomposites. We investigated the interfacial characteristics of MO, carbon, and halloysite, and the possibility of enhanced photocatalytic activity in detail.

2. Experimental

HNTs were obtained from Hunan, China. All chemicals were analytical grade and used without further purification. Raw HNTs were washed with deionized water (pH = 7.2) and dried at 60 ºC for 12 h.

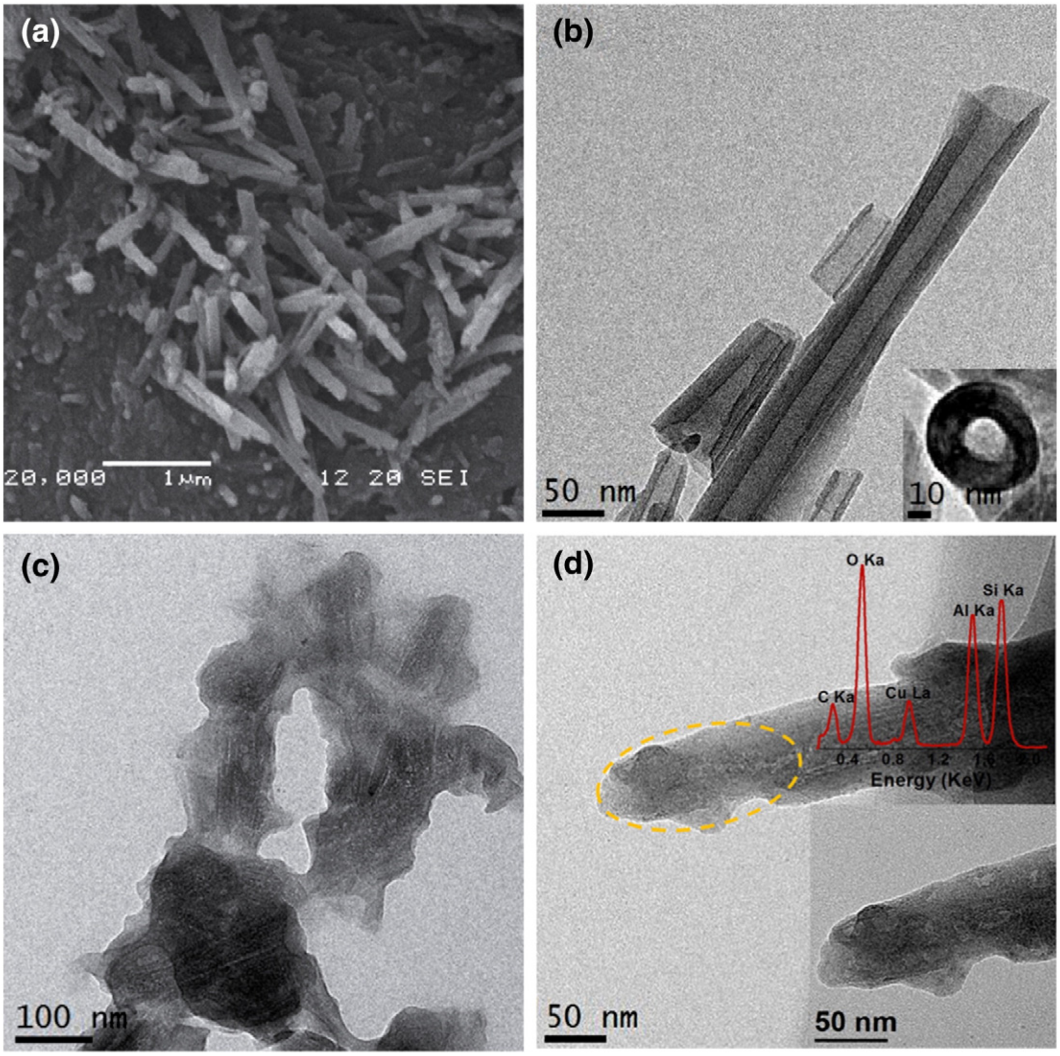

Fig. 2. (a) SEM image of HNTs and TEM images of (b) HNTs (inset is the tubular morphology), (c) SCH and (d) CCH samples (inset is the corresponding EDX spectrum).