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Facile synthesis of high-thermostably ordered mesoporous TiO_2/SiO_2 nanocomposites: An effective bifunctional candidate for removing arsenic contaminations

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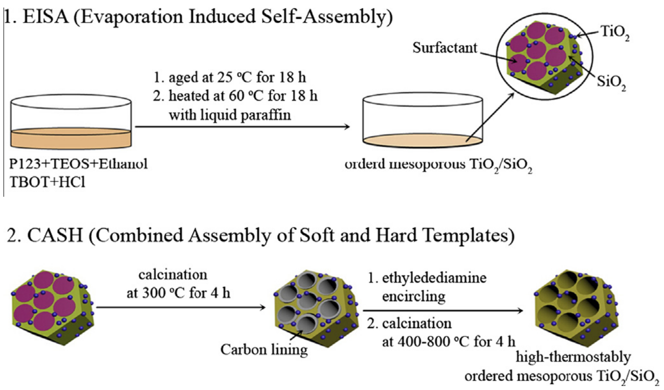
GRAPHICAL ABSTRACT

High-thermostably ordered mesoporous TiO_2/SiO_2 nanocomposites are fabricated via evaporation-induced self-assembly method combined with ethylenediamine bounding strategy, which could be maintained up to 700 °C and exhibit excellent adsorption and photocatalytic oxidation performance for high-toxic As (III) to low-toxic As (V) under various pH values simultaneously.



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ABSTRACT

High-thermostably ordered mesoporous TiO_2/SiO_2 nanocomposites are successfully prepared through evaporation-induced self-assembly method combined with ethylenediamine bounding strategy and subsequent high-temperature calcinations (700 °C). The prepared samples are characterized in detail by thermogravimetric-differential scanning calorimetry, X-ray diffraction, Raman, transmission electron microscopy and N_2 adsorption. The results indicate that the samples are ordered mesostructure and the presence of SiO_2 inhibits the anatase-to-rutile phase transformation at high temperature. Significantly, the experimental results show that the high-thermostably ordered mesoporous TiO_2/SiO_2 nanocomposites play bifunctional roles on effectively adsorbing As (III) and completely oxidizing higher toxic As (III) to lower toxic As (V) under various pH values by one time. Moreover, after recycling for ten times the

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composites still keep wonderful photocatalytic and adsorption performance. The subtly nanostructured bifunctional composites will have broad application prospects in contaminated water treatment.

1. Introduction

Arsenic is a significant and long-term exposure contaminant in drinking water, which has been recognized as a carcinogenic element by public organisms, threatening the health of human beings [1–3]. With the development of technology and production, the concentration of arsenic in the environment will be increased in the future which may be caused by mine tailing, industrial waste discharges from electroplating, gold mining, burning of fossil fuels, fertilizers and pesticides/insecticides [4–6]. Notably, among different arsenic oxidation states As (III) is more toxic than As (V) owing to its high mobility and low affinity for adsorbents, which tends to have long persistence during water treatment [7,8]. Then the oxidation of As (III) should be required in common arsenite removal technologies to reduce its toxicity and mobility. However, typical chemical strategies in the pre-oxidation step including ozone, chlorine and chlorine dioxide may lead to the formation of dangerous oxidation/disinfection products [9,10] and some separation methods including coagulation/precipitation and lime softening have different drawbacks related to sludge treatment and disposal [11]. Therefore, there is urgent to develop efficient method for the oxidation of As (III) to As (V) and enhance the subsequent removal.

Up to now, TiO_2, as one of promising semiconductor photocatalysts, has attracted considerable interest to eliminate contamination both in water and air [12–16]. The photocatalytic conversion of As (III) to As (V) in the presence of TiO_2 has already been reported [17–19]. However, TiO_2 adsorbs As (V) produced from the photoreaction leading to a progressive deactivation of the catalytic system [20] and the adsorption property of TiO_2 is not very good [21], which may lead to the inefficient removal of As (V). Then the low photonic efficiency and poor adsorption have always been the significant problem. Fortunately, these defects can be overcome when a special material is introduced in the system [22–24]. Mesoporous silica materials with highly ordered pore structures and high specific surface areas are considered to be the promising host material and adsorbent [25]. The derived composite have shown attractive potential applications in optics [26], catalysis [27] and electronics [28]. The ordered mesoporous TiO_2/SiO_2 composites have been well-studied owing to the interesting chemical and physical properties [29,30]. The bifunctional composites possess the photocatalytic ability of TiO_2 for oxidation and the adsorption performance at the same time, which provides a wonderful strategy to remove arsenite completely from contaminated water using single step. However, the preparation of TiO_2/SiO_2 is usually synthetized by loading strategy which has some drawbacks, including complicated processes, multiply operations and insecure composites [31]. In addition, the photocatalytic performance of TiO_2/SiO_2 composites cannot satisfy the practical applications because of the low crystallization of TiO_2 with more surface defects [32]. Therefore, this kind of system should be further developed.

In this paper, a novel nanostructure catalyst, i.e. a high-thermostably ordered mesoporous TiO_2/SiO_2 nanocomposite is designed and synthesized. The composite shows an effective bifunctional candidate for photocatalytic oxidizing and adsorption of arsenic contamination. The ordered mesoporous SiO_2 plays a significant role in the adsorption of arsenite. Significantly, the introduction of SiO_2 contributes to formation of high-thermostably TiO_2 which is high crystallinity of anatase TiO_2 and possesses less surface defects, leading to improving photocatalysis. Under UV irradiation, the As (III) is effectively adsorbed and oxidized to As (V) completely by the prepared bifunctional composites under various pH values. Moreover, after recycling for ten times, the composites still keep wonderful photocatalytic and adsorption performance. The subtly nanostructured bifunctional composites will have broad application prospects in contaminated water treatment.

2. Materials and methods

2.1. Materials

Tetrabutyl titanate (TBOT), tetraethyl orthosilicate (TEOS), absolute ethanol, sodium hydroxide (NaOH), concentrated hydrochloric acid (HCl), ethylenediamine and sodium arsenite ($NaAsO_2$) using as the source of arsenite [As (III)] were purchased from Tianjin Kermel Chemical Reagent Co. LTD, China. Triblock copolymer, $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H$ ($EO_{20}PO_{70}EO_{20}$, Pluronic P123, MW = 5800, Product No. 435465-1L) was purchased from Sigma-Aldrich. All the chemicals used in this study were analytical grade and employed without further purification.

2.2. Preparation of high-thermostably ordered mesoporous TiO_2/SiO_2

1.0 g of P123 and 2 mL of TEOS were successively dissolved into 10 mL of absolute ethanol under magnetic stirring for 0.5 h. While under stirring, 4 mL of TBOT and 1 mL of concentrated hydrochloric acid were added to the above solution, respectively. After magnetic stirring for 0.5 h, the homogenous solution was transferred into a ceramic vessel and aged for 18 h at room temperature (25 °C) in air to produce a rigid gel. The gel was covered with a layer of liquid paraffin 2–3 mm thick and heated at 60 °C for 18 h to completely remove the absolute ethanol. After the heat treatment, the liquid paraffin on the surface of the products was collected and cleared by filter paper, and the as-prepared samples were calcined at 300 °C for 4 h. Subsequently, the products were refluxed with ethylenediamine aqueous solution for 48 h at 90–100 °C and the pH value was kept at 11–12 [33]. Then, the obtained powders were washed by deionized water and dried at 60 °C overnight. Finally, the resulting samples were calcined at 400, 500, 600, 700 and 800 °C for 4 h, respectively, at a heating rate of 3 °C min^{-1} from room temperature to the objective temperature. Notably, the various samples calcined at 400, 500, 600, 700 and 800 °C were denoted as TS-400, TS-500, TS-600, TS-700, and TS-800, respectively. For comparison, the pure mesoporous SiO_2 was also synthesized under the same condition without adding TBOT.

2.3. Characterization

The thermogravimetric-differential scanning calorimetry analysis (TG-DSC) was performed using thermoanalytical apparatus (STA 449C, NETZSCH) under an air atmosphere at a heating rate of 5 °C min^{-1}. X-ray diffraction (XRD) was performed on a Bruker D8 Advance diffractometer by using Cu Kα radiation source ($\alpha = 0.15418$ nm). The Raman measurements were performed by