Journal of Colloid and Interface Science 528 (2018) 109–115

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

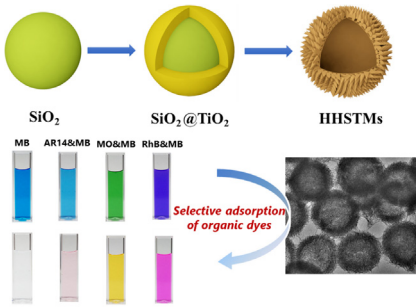
Synthesis of hierarchical hollow sodium titanate microspheres and their application for selective removal of organic dyes

Ye Zhang [a], Gongyi Li [a], Junming Liu [b], Tao Wang [b], Xue Wang [b], Bin Liu [b], Yunling Liu [b], Qisheng Huo [b,*], Zengyong Chu [a,*]

[a] College of Liberal Arts and Sciences, National University of Defense Technology, Changsha 410073, PR China
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

GRAPHICAL ABSTRACT

This work demonstrated the synthesis of hierarchical hollow sodium titanate microspheres through a template-assisted alkaline hydrothermal process and investigated their adsorption properties toward organic dyes in water.



ARTICLE INFO

Article history:
Received 15 March 2018
Revised 21 May 2018
Accepted 21 May 2018
Available online 22 May 2018

Keywords:
Sodium titanate
Hierarchical hollow microspheres
Selective adsorption
Organic dyes

ABSTRACT

Titanate-based materials are attractive inorganic adsorbents for wastewater treatment. In this study, hierarchical hollow sodium titanate microspheres (HHSTMs) were successfully synthesized *via* a template-assisted method. Silica microspheres were selected as hard templates, with a uniformly smooth TiO_2 shell first grown onto the surface of the SiO_2 cores. Then, through an alkaline hydrothermal process, the silica core was removed and the TiO_2 shell gradually converted into a sodium titanate shell with a preserved morphology. The as-synthesized HHSTMs are constructed from twined nanobelts, with a high surface area of 308 $m^2 g^{-1}$. A typical organic dye, methylene blue, was employed to investigate the adsorption properties of the HHSTMs. The adsorption process matched well with the Langmuir isothermal model, with the maximum adsorption capacity of methylene blue reaching 443 mg g^{-1}. Moreover, the resulting HHSTMs can be used to selectively capture of methylene blue from a cationic-anionic dye binary system due to their negatively charged surface. All adsorption processes were very fast and could complete in ten minutes.

1. Introduction

Today, water pollution threatens human health and has become a matter of public concern [1,2]. Organic dyes are one of the main

* Corresponding authors.
E-mail address: chuzy@nudt.edu.cn (Z. Chu).

https://doi.org/10.1016/j.jcis.2018.05.069
0021-9797/

hazards in water, and various methods such as adsorption, ozonation, ion exchange and photocatalytic degradation have been used to remove dyes from polluted water [3–6]. Among such methods, adsorption technology has been widely used because it is simple, efficient and low cost. During the past few decades, many adsorbents have been developed, and it is found that the adsorption activities of these materials are closely related to their structures [7–9]. Many studies have indicated that hierarchical hollow structured materials constructed from nanosized building blocks exhibit enhanced adsorption properties due to their large void space, porous structure and high surface area [10–12]. For example, Lou and coworkers found that the adsorption capacity of Congo red by hierarchical urchin-like α-FeOOH hollow spheres can reach 275 mg g^{-1}, mostly higher than that reported for similar materials [13]. Thus, it is of great significance to design and synthesize novel adsorbents with hierarchical hollow structures.

Titanate materials are inorganic materials that are widely used in the energy and environmental fields with the advantages of low cost, wide-ranging sources for the raw materials and environmentally friendly [14–16]. Recently, titanate-based absorbents have attracted much attention and have been widely investigated [17,18]. Lin and coworkers synthesized calcined titanate nanotubes with a maximum adsorption capacity of 133.33 mg g^{-1} toward methylene blue [19]. Lu and coworkers found the methylene blue adsorption capacity of layered protonated titanate nanosheets can reach 184 mg g^{-1} [20]. Hierarchical hollow structures can improve the adsorption performance of materials, but reports for the synthesis of this type of titanate material are very limited [21]. It is still a great challenge to design and synthesize hierarchical hollow titanate materials with enhanced performance for organic dye adsorption.

It is known that different physical and chemical properties of starting materials will significantly affect the morphology and property of the final product. In this paper, we developed a simple template-assisted synthesis method to obtain hierarchical hollow sodium titanate microspheres (HHSTMs) *via* an alkaline hydrothermal process. Silica microspheres were used as hard templates and core-shell structured SiO_2@TiO_2 microspheres (the term "@" is usually used to denote the core-shell structures, with A @ B indicating that A is coated with B) were utilized as a precursor. Moreover, the adsorption performance of these HHSTMs toward organic dyes was discussed, and the max adsorption capacity and the adsorption property for encapsulation of the target dye molecules in a mixture of solutions were also investigated.

2. Experimental

2.1. Chemicals

Tetraethyl orthosilicate (99.0%), sodium hydroxide (96.0%), ethanol (99.7%), 2-propanol (99.7%) and ammonia (28.0 wt% aqueous solution) were purchased from Beijing chemical works, China. Tetrabutyl titanate (98.0%) was purchased from Aladdin. Acid-red 14 (98%) was obtained from Energy Chemical. Methylene blue (99.0%) and methyl orange (99.0%) were purchased from Sinopharm Chemical Reagent Co.. Ltd. Rhodamine B (98%) was obtained from Tianjin Guangfu Fine Chemical Industry Research Institute, China. All chemicals were used as-received.

2.2. Synthesis of SiO_2 microspheres

SiO_2 microspheres were synthesized by a modified Stöber method based on a previous report [22]. In a typical process, 23.5 mL of water, 63.3 mL of 2-propanol and 13 mL of ammonia (28% aqueous solution) were mixed together and heated in a water bath at 35 °C. Then, 0.6 mL of tetraethyl orthosilicate was added dropwise to this mixed solution and reacted for 0.5 h under stirring. Then, 5 mL of tetraethyl orthosilicate was added dropwise to the above-mixed solution again and further reacted for 2 h at 35 °C. The SiO_2 microspheres were collected by centrifugation and then washed with ethanol and water three times.

2.3. Synthesis of SiO_2@TiO_2 core shell structure microspheres

SiO_2@TiO_2 core shell structure microspheres were fabricated according to an extended classic Stöber method [23]. Then, 0.1 g of SiO_2 microspheres were dispersed in 80 mL of ethanol by ultrasonication, followed by the addition of 0.4 mL of ammonia and stirring at 45 °C for 30 min to form a homogeneous dispersion. Then, 0.8 mL of tetrabutyl titanate was added dropwise to this mixed solution and reacted for 8 h under stirring conditions. The resultant product was collected by centrifugation, followed by washing with deionized water and ethanol three times.

2.4. Synthesis of hierarchical hollow sodium titanate microspheres (HHSTMs)

In a typical synthesis, 0.03 g of SiO_2@TiO_2 core shell structure microspheres were dispersed in 5 mL of sodium hydroxide solution (10 M). Then, the mixture was transferred into a 23 mL Teflon-lined autoclave and heated at 170 °C for 2 h under static conditions. The white product was collected by centrifugation and washed several times with deionized water.

2.5. Material characterization

Transmission electron microscope (TEM) images were obtained using an FEI Tecnai G2 F20 S-twin D573 field-emission transmission electron microscope operating at 200 kV. Scanning electron microscope (SEM) images were obtained using a JEOL JSM-6700F field-emission scanning electron microscope operating at 5 kV. The zeta potential was detected using a Nano ZS90 laser particle analyzer (Malvern Instruments, UK) at 25 °C. Powder X-ray diffraction (XRD) data were collected by a Rigaku D/Max 2550 X-ray diffractometer using CuKa radiation (λ = 1.5418 Å) operating at 200 mA and 50 kV. N_2 adsorption-desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2010 sorptometer. UV–Vis spectral data were recorded with a Shimadzu UV-2450 spectrometer. X-ray photoelectron spectroscopy (XPS) was recorded using a Thermo ESCALAB 250.

2.6. Dye adsorption experiments

Dye adsorption experiments were conducted at room temperature in a neutral aqueous solution using a thermostating shaker in a dark environment to avoid the decolorization of organic dyes in light. Adsorption tests for methylene blue (MB) were carried out using HHSTMs as adsorbents first, with the MB concentration set at 20 mg L^{-1} and the adsorbent concentration fixed at 167 mg L^{-1}. Furthermore, to investigate the adsorption capacity of the HHSTMs toward MB, the adsorption isotherm for MB with the HHSTMs was obtained via a stepwise variation of the initial MB concentration from 10 mg L^{-1} to 160 mg L^{-1}. At appropriate time intervals, the adsorbent was separated from the stock solution by filtration and the concentration of the clear solution was analyzed by a UV–Visible spectrophotometer at the maximum absorption wavelength of the dye solution. The adsorption capacity Q_e (mg g^{-1}) of the dye was calculated using the mass balance equation:

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$