

Research Article

Facile Fabrication of Sodium Titanate Nanostructures Using Metatitanic Acid ($\text{TiO}_2 \cdot \text{H}_2\text{O}$) and Its Adsorption Property

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Fluffy sodium titanate nanostructures have been fabricated by a simple hydrothermal method with metatitanic acid as precursor. The obtained nanostructures exhibit as the aggregation of nanosheets, and the surface area of the nanostructure is about $110.59 \text{ m}^2/\text{g}$. Such nanoarchitecture indicates high adsorption capacity to some metal ions, such as Cd^{2+} , and the maximum adsorption capacity has been estimated to be 255.18 mg/g . The possible reasons that are responsible after its high adsorption ability, have been ascribed to the tiny structure, the ion-exchange ability and the large surface area of the sodium titanate nanostructures. And this may greatly enlarge its application potential as an adsorbent.

1. Introduction

Environmental problems have been a global tickler that badgers the human's survival and development [1–5], and various physicochemical methods have been used to remove pollutants from waste water. Nanomaterials have been found to be potential adsorbents that may found great applications in environmental treatment [6–9]. And now there are many kinds of nanostructures that have been fabricated towards high-efficient adsorbents. Materials with enhanced adsorption performance are still challenges.

Sodium titanate is one of the ion exchangers that have been found to have potential application in the treatment of environmental pollutants. In the past decades, many kinds of sodium titanate nanostructures have been fabricated with using various physicochemical methods, including nanotubes, nanowires, nanobelts, and so forth [10–15]. However, as far as we know, many of the fabricated nanostructures have the problem of the cost of the method used. So, it is now a great challenge to fabricate nanostructures with low-cost method. Therefore in this paper, we report fluffy sodium titanate nanostructures which are obtained by a simple hydrothermal method using the low-cost industrial raw materials metatitanic acid ($\text{TiO}_2 \cdot \text{H}_2\text{O}$) as precursor.

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2. Experimental Details

2.1. Materials. The reagents were of purchased from Shanghai Runjie Chemical Reagent Co., Ltd. All chemicals were analytical grade and used without any further purification.

2.2. Synthesis. In a typical synthesis, 3 g metatitanic acid and 1.6 g NaOH were mixed with 40 mL deionized water under agitation for about 2 h. After that, the mixture was transferred into a teflon-lined stainless steel autoclave and heated in an electric oven at 80°C for 30 h. Then the autoclave was cooled down in the air. Then the white product was harvested by filtration and washed with deionized water for several times until the pH was 12 before drying in air.

2.3. Characterization. The characterization experiments were carried out at room temperature. The phase of the powder was identified by X-ray diffraction (XRD) using a Philips X'Pert Pro MPD with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. The morphology, crystalline size, and crystal structure of the sample were determined by Field Emission Scanning

Electron Microscopy (FESEM; FEI Sirion-200), transmission electron microscopy (TEM), and high-resolution Transmission Electron Microscopy (HRTEM; JEOL JEM-2010, 200 kV). Thermogravimetric analysis (TGA) measurements were performed on a TGA (Pyris Diamond DSC, PERKIN-ELMER, USA) at a constant heating rate of 10 deg min^{-1} . The porous structure characteristics, including the BET surface area, the pore volume, and the pore size distribution, were obtained from the conventional analysis of nitrogen isotherms measured with specific surface and void ratio analyzer (Omnisorp 100 CX, Coulter, USA). Metal concentrations were measured by Inductively Coupled Plasma Spectrometer (Thermo Scientific iCAP 6000).

2.4. Adsorption Experiments. Adsorption isotherm experiment was performed with various Cd^{2+} concentrations (500, 400, 300, 200, and 100 mg/L, resp.), and the sodium titanate was 1.25 mg/mL at room temperature and 24 h contact. Time-dependent adsorption experiment was performed at the quantity of sodium titanate was 1.25 mg/mL at room temperature, and the Cd^{2+} concentration is 100 mg/L. The concentration of pollutant adsorbed on sodium titanate hierarchical nanostructures, C_s (mol g^{-1}), was calculated from the difference of initial concentration (C_0) and final concentration remained in solution after equilibrium (C_{eq}), the volume of the solution (V) and the mass of sodium titanate hierarchical nanostructures (m) with the equation $C_s = (C_0 - C_{\text{eq}}) \times V/m$.

3. Results and Discussions

The typical XRD pattern of the as-prepared sample is shown in Figure 1(a). The characteristic peak of titanate has been found at around $2\theta = 10.4^\circ$ accounting for the lamellar ordering of the compound with a high interlamellar distance [16–21]. No other phase, such as TiO_2 , is found. Figure 1(b) is the FESEM image of the as-prepared sample. It can be found that there are lots of loose fluffy nanostructures. From further investigation of the TEM image of Figure 2(a), it can be seen that the fluffy nanostructures are constructed by some nanosheets, which is thinner than 10 nm by comparison to the supported carbon film. And the corresponding SAED image indicates its polycrystalline property, which should be mainly ascribed to the too thin layer. EDS spectrum of the fluffy nanostructures is shown in Figure 2(c). Only C, O, Ti, and Na elements are observed. It should be noted that the C element comes from the carbon film of the specimen holder and partially from the carbon spheres. The proximate integer ratio of Na:Ti is around 2:3, so the chemical formula of the compound should be $\text{Na}_2\text{Ti}_3\text{O}_7$.

The nitrogen ad-desorption isotherms of the sodium titanate nanostructure are investigated in Figure 3(a). The nitrogen ad-desorption isotherms show characteristic type IV isotherm with hysteresis loop, indicating that the sodium titanate nanostructures are composed of connected mesopores. The S_{BET} is evaluated to be $110.59 \text{ m}^2/\text{g}$. Such porous structure and large BET surface area endow the

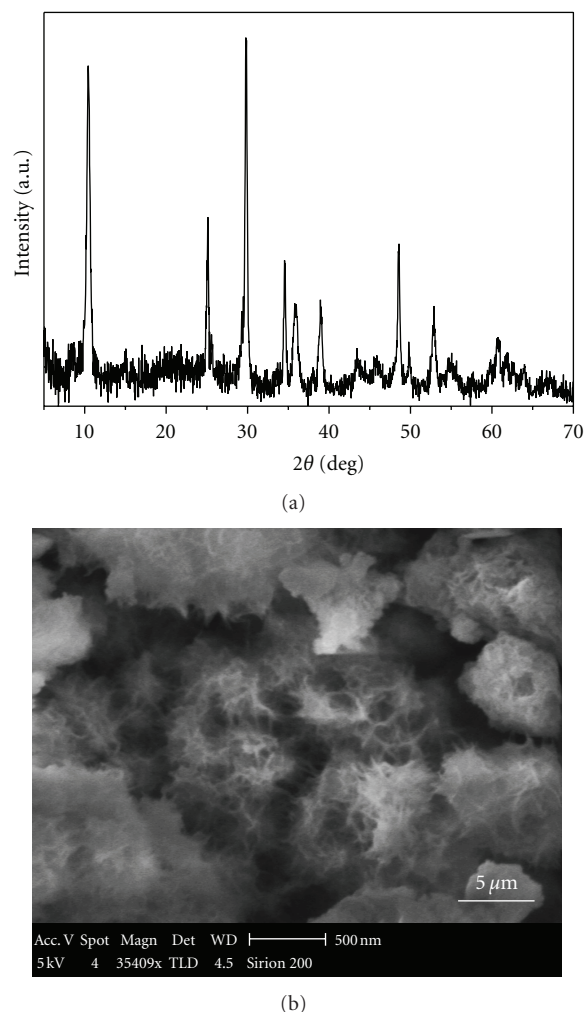


FIGURE 1: (a) XRD pattern of the as-prepared sample; (b) the FESEM image.

sodium titanate hierarchical nanostructures with potential application as adsorbent. Figure 3(b) is the TG curve of the sodium titanate nanostructure. The TG measurement was done in the region of $50\text{--}700^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$. For the fluffy sodium titanate, the weight loss stopped at around 700°C and the total loss was about 15.5%. The weight loss below 200°C (about 12%) can be ascribed to the removal of surface adsorbed/bound water molecules. As increases the annealing temperature to 700°C (mainly in the range of $200\text{--}300^\circ\text{C}$), the residual weight is 3.5%, which should be ascribed to the loss of water molecules from the interlayer.

We chose Cd(II) (heavy metal) to investigate the adsorption performance of the sodium titanate nanostructure. The Cd(II) ion-exchange equilibrium data are graphed in Figure 4(a). Excellent fits of the data were performed with the Langmuir isotherm model expressed as

$$C_s = K_a \cdot q_{\text{max}} \cdot \frac{C_{\text{eq}}}{(1 + b \cdot C_{\text{eq}})}, \quad (1)$$

where C_{eq} is the concentration of adsorbed ions in solution at equilibration, C_s is the amount of ions adsorbed to

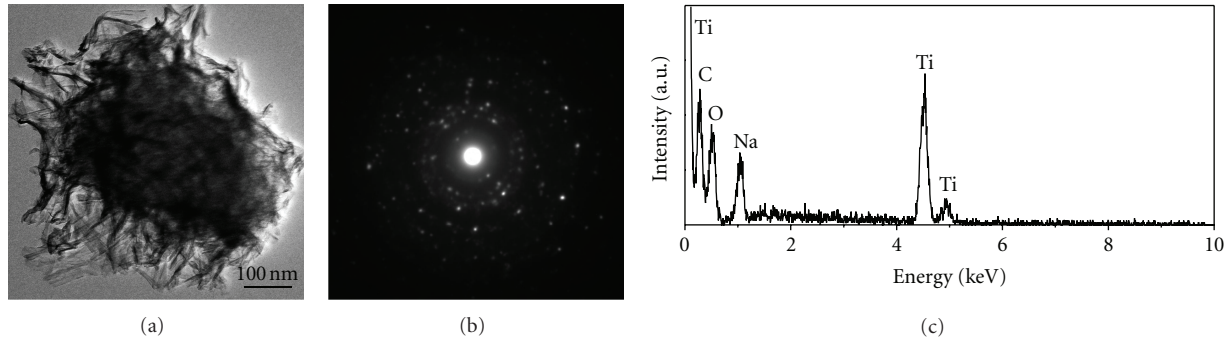


FIGURE 2: (a) TEM image of the as-prepared sample; (b) the SAED pattern.

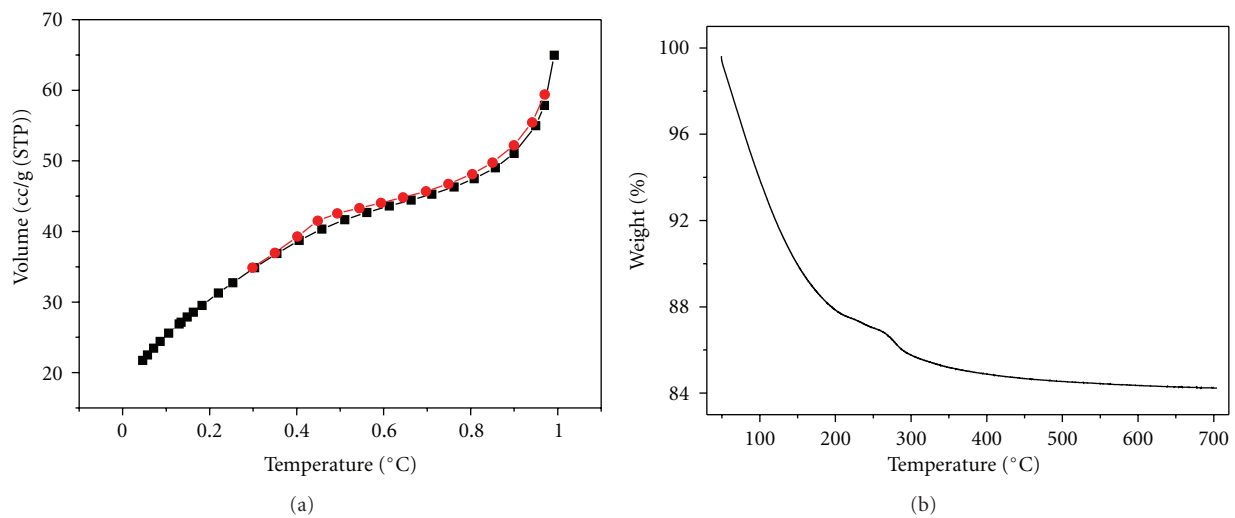


FIGURE 3: (a) Nitrogen adsorption-desorption isotherms of the sodium titanate nanostructures; (b) TG curve of the sodium titanate nanostructure.

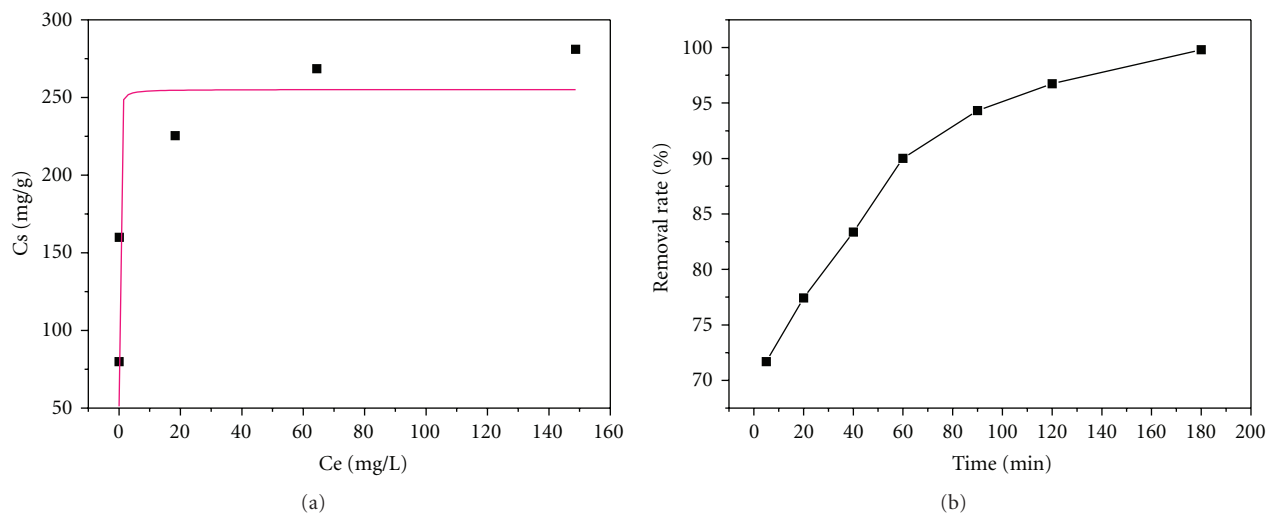


FIGURE 4: (a) Adsorption isotherm of Cd(II) on the sodium titanate nanostructure. $T = 20 \pm 2^\circ\text{C}$, solid line: Langmuir model; (b) time-dependent adsorption curve at pH = 6 and the starting concentration of Cd(II) is 100 mg/L.

form a monolayer coverage on the adsorbent particle, and K_a is the Langmuir adsorption equilibrium constant. The maximum, Cd(II) adsorption capacities calculated by the adsorption isotherms are 255.18 mg/g (calculated from Langmuir simulation). Figure 4(b) is the time-dependent adsorption behavior investigation of Cd(II) on the sodium titanate nanostructures. The adsorption of the Cd(II) ions on the sodium titanate nanostructure depicts a relative fast adsorption process. About 1 h later, almost 90% Cd(II) ions were removed by the adsorbents, and after 3 h, almost all the Cd(II) were removed. The results of the adsorption of Cd(II) are higher than some previously reported [13]. This should not only be ascribed to the ion-exchange ability of the material. It has been well known that the ability of sodium titanate to eliminate the other metal ions is mainly due to the ion-change ability of the interlayered Na^+ ions. However, this should also be affected by the diffusion length of the adsorbents. As we all know, the bigger the scale of the adsorbents, the harder the heavy metal ions to exchange with the Na^+ due to the larger diffusion length from the surface to the inner. So, it can be expected that nanomaterials with very small scale may greatly enhance its adsorption ability via the way to shorten the metal ions diffusion length. Also, it should be noted that as the scale of the adsorbents decreases, the surface area increases greatly. This is also favorable for its adsorption ability.

4. Conclusion

In conclusion, a fluffy sodium titanate nanostructure was successfully fabricated with utilization of hydrothermal reaction. The fluffy sodium titanate nanostructure exhibits a large surface area of about $110.59 \text{ m}^2/\text{g}$, and thus it could be expected to have high adsorption capacity to some heavy metal ions (such as Cd(II)). And the maximum adsorption capacity of Cd(II) has been estimated to be 255.18 mg/g . So, this kind of material could be expected to have great potential in the environmental treatment, especially for the elimination of heavy metal ions, such as Cd(II).

Acknowledgments

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