Short-cut synthesis of tri-titanate nanotubes using nano-anatase: Mechanism and application as an excellent adsorbent

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ABSTRACT

Conventional hydrothermal synthesis of titanate nanotubes (TNTs) by P25 TiO_2 and NaOH has been blamed for its long reaction time (continuous heating for three days). This paper presented a short-cut hydrothermal synthesis of TNTs by nano-anatase and NaOH, which significantly reduced the reaction time from 72 to 6 h while the other experimental conditions were same. Essential interpretation of such a surprising reduction of reaction time was given in terms of TEM, XRD and FTIR analysis. It indicates that the transformation from anatase to sodium tri-titanate nanotubes includes the following three steps: (1) aggregation of spherical anatase particles (0–1 h), (2) morphologic transformation to titanate nanosheets with fewer visible anatase crystal arrays (1–3 h), and (3) crimping of tri-titanate nanosheets and a final generation of TNTs (3–6 h). Further comparison with TNTs synthesis process from P25 TiO_2 (ca. 80% of anatase and 20% of rutile) indicates that the rate-limiting step for breakage of Ti–O–Ti bond is largely controlled by crystal array of the concerned nanomaterials. The as-prepared TNTs are proved to exhibit similar Cd adsorption capacity compared with conventional TNTs based on batch adsorption experiments. The widely distributed anatase in nature as well as its over 90% reaction time saving in TNTs preparation process under facile conditions makes the proposed short-cut synthesis of great potential in engineering applications.

1. Introduction

Titanate nanotubes (TNTs) firstly reported by Kasuga et al. [1,2] are regarded as one of the most promising materials, due to their special physicochemical properties such as uniform microstructure, small tube diameter, large specific surface area and so on [3]. Up to now, three major methods (i.e. template-assisted method [4], electrochemical anodic oxidation method [5] and hydrothermal method [6–10]) have been established in fabricating TNTs. Compared with the previous two, hydrothermal method has

prominent advantages like easier route to obtain nanotube morphology and more feasible for extensive applications, but the need of long reaction time and high NaOH concentration limit its further use [11].

Hydrothermal method was a one-step procedure for TNTs preparation. In this method, titania precursors were mixed with high concentrated NaOH solution and heated in a tightly closed vessel until TNTs formed. P25 TiO_2, a mixture of nano-anatase and nano-rutile, was conventionally used as the titania precursors [12–15], and the heating process usually lased for 72 h at temperature of 130 °C.

TNTs prepared via hydrothermal method possessed abundant hydroxyl groups (–OH) on the surface, which could effectively capture cations via ion-exchange [15–17]. Consequently, TNTs showed great potential application in adsorption of toxic heavy metal cations (e.g. Cd^{2+} Pb^{2+} Cr^{3+} Cu^{2+} and Ni^{2+}) [18–24] and basic organic dyes (e.g. methylene blue) in aqueous solution [25]. What's

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more, TNTs could be efficiently regenerated [19], which significantly extended their practical applications.

Applied temperature, treatment time, concentration of alkali solution, and the Ti precursor were considered as the predominant factors for TNTs synthesis in the hydrothermal reaction [11]. Literature are available on the synthesis of TNTs under these different conditions [7—9,26—30]. Among these studies, many researchers focused on the effects of reaction time and temperature, and tried to find ways to reduce both time and energy cost. In special, the reaction temperature was usually controlled from 130 to 180 °C, and the reaction time varied from 24 to 72 h, while less reaction time often companioned with higher heating temperature (e.g. above 160 °C) [7—9,28]. Some methods that attempted to form tubular structures in an extremely short time (within 6 h) has been provided [31], however, since TiO_2 precursors did not transform to sodium titanate (or not totally transformed) in such methods, the as prepared materials did not show so good adsorption performance due to inadequate −OH/Na sites.

This paper presented a short-cut hydrothermal process for TNTs synthesis using pure nano-anatase powders instead of P25 TiO_2. Interpretation was given for the greatly simplified synthesis process. In addition, adsorption performance of Cd^{2+} onto the newly prepared TNTs was also investigated. Simple synthesis of nano-anatase [32,33] from easy-get raw materials, significant saving of reaction time for TNTs preparation and eminent adsorption performance as cycled adsorbents made the proposed method promising in engineering applications.

2. Materials and methods

2.1. Materials

All chemicals and reagents were of analytical grade and used without further purification. $Cd(NO_3)_2$ (purity > 99.0%, Tianjin Guangfu, Tianjin, China) was used to prepare Cd^{2+} stock solution (1000 mg/L). Nano-scale TiO_2 powder (anatase, 99.7%, mean diameter of 25 nm) was purchased form Sigma−Aldrich. TiO_2, NaOH (purity > 98.0%, Xilong Chemical, Guangdong, China) and absolute ethanol were used to fabricate TNTs through alkaline hydrothermal method. All waters used herein were treated by Milli-Q deionized water equipment.

2.2. Preparation of TNTs and IMs under different reaction times

For the synthesis of TNTs via hydrothermal method, 0.8 g of anatase powder was firstly added into 80 mL NaOH solution with a concentration of 8 M. After fully stirring, the mixture was transferred into a 100 mL Teflon autoclave and heated at 130 °C for 6 h. Afterwards, the suspension was washed with deionized water for several times until the supernatant pH dropped to ca. 7. Finally, the products were dispersed with ethanol and dried at 80 °C for 4 h. To examine the morphology and crystal change during the preparation process, the intermediate materials (IMs) with reaction time from 1 to 12 h at the same condition were also been synthesized. These products are marked as IM-1h, IM-3h, IM-6h (TNTs), and IM-12h, respectively.

2.3. Characterization

Morphology, crystal phase and functional groups of TNTs and all the IMs were characterized. For morphology measurement, transmission electron microscopy (TEM) images were obtained on a microscopy (Tecnai F30, FEI, USA), which was operated at 200 kV after the samples were dispersed on a copper microgrid with carbon membrane. Energy Dispersive X-ray (EDX) spectra were also captured using TEM. X-ray diffraction (XRD, Rigaku DMAX 2500, Japan) was used to analyse the crystal phase of materials, with a scanning range (2θ) of 5−70° and scanning speed of 4°/min. Fourier transform infrared spectroscopy (FTIR, Bruker, Germany) was chosen to test diversifications of functional groups with a scanning range of 4000−400 cm^{-1} and resolution of 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was conducted on a AXIS-Ultra XPS instrument (Kratos Analytical, England) with an Al $K\alpha$ X-ray source (225 W, 15 mA, 15 kV), and all binding energies were calibrated using C 1s peak at 284.8 eV to compensate for surface charging effects. Specific surface area of TNTs was got through nitrogen adsorption−desorption isotherms at −196 °C by means of the Brunauer−Emmett−Teller (BET) theory on an ASAP 2010 adsorption apparatus (Micromeritics, USA). Nitrogen adsorption volume at a relative pressure (P/P_0) of 0.99 was used for the measurement. Zeta potentials of IMs under various pH were detected using a Nano-ZS90 Zetasizer (Malvern Instruments, UK).

2.4. Batch adsorption experiments

All batch experiments were performed in erlenmeyer flasks. Adsorption capacities, desorption rates and regeneration efficiencies of various IMs were compared under the same conditions. In addition, as to fully understand the adsorption behaviors of Cd^{2+} onto TNTs, the pH effect, adsorption isotherms and kinetics were performed only for TNTs.

2.4.1. Adsorption of Cd^{2+} on different IMs

Batch Cd^{2+} adsorption experiments were carried out by adding 0.01 g of IMs into 50 mL $Cd(NO_3)_2$ solution with an initial concentration of 50 mg/L. After shaken for 3 h (225 rpm, 25 °C), the suspensions were centrifuged (10,000 rpm, 25 °C) for 5 min to separate the adsorbents. The Cd^{2+} concentration in the supernates were then determined on an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy, Leeman, USA).

2.4.2. Adsorption of Cd^{2+} on TNTs

For the pH effect experiments, 0.01 g of TNTs was added into 50 mL of $Cd(NO_3)_2$ solution (50 mg/L) with pH varying from 2 to 6. Experiment on adsorption kinetics was conducted with the initial Cd^{2+} concentration of 50 and 100 mg/L, and TNTs dosage of 0.2 g/L. Samples are taken at set times and immediately centrifuged to separate adsorbents. Experiment on adsorption isotherms was conducted with Cd^{2+} initial concentration ranging from 10 to 100 mg/L, and the TNTs dosage was 0.2 g/L. For the kinetics experiments, the adsorption time was lasted for 4 h, while for the other adsorption reactions was 3 h. After shaken at 225 rpm and 25 °C, the suspensions were centrifuged (10,000 rpm, 25 °C) for 5 min to separate the adsorbents, and Cd^{2+} concentrations were measured by ICP-AES.

2.4.3. Reuse of TNTs

The reuse of TNTs were performed based on desorption and regeneration processes. After adsorption, the TNTs and Cd^{2+} suspension was centrifuged (10,000 rpm, 5 min) and the supernatant was removed. Afterwards, 50 mL of 0.1 M HNO_3 solution was added and the mixture was shaken for another 3 h. The desorbed TNTs were then separated and immerged into 0.2 M NaOH aqueous solution and stirred for 3 h to carry out the regeneration process. The regenerated TNTs were weighed and reused as adsorbents to adsorb Cd^{2+} with a dosage of 0.2 g/L. The Cd^{2+} concentration after desorption and re-adsorption was measured by ICP-AES. The reuse procedure cycled for three times.