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# Lignosulfonate-assistant hydrothermal method for synthesis of titanate nanotubes with improved adsorption capacity for metal ions

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## ABSTRACT

Lignosulfonate modified titanate tubes (L-TNTs) were synthesized by a hydrothermal method. The influences of lignosulfonate on the structure and adsorption capacity of the product were investigated. The characterization results indicate that L-TNTs are layered titanates ( $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$ ) with mesoporous structure, and the doped lignosulfonate increases the axial ratio and layer spacing of TNTs. The maximal adsorption capacities of L-TNTs are 740, 148 and 223  $\text{mg g}^{-1}$  for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ , respectively, which are higher than those of TNTs. The results demonstrate that the lignosulfonate-assistant hydrothermal method is promising for improving the adsorption capacity of nanomaterial toward heavy metal ions.

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## 1. Introduction

Titanate tubes (TNTs) have received considerable attention since firstly reported by Kasuga et al. [1]. The synthetic methods, formation mechanisms, structures, properties and applications of TNTs have been extensively studied [2–4]. Recently, TNTs attracted much more attention in the field of water treatment and were considered as a promising adsorbent for pollutants removal due to their good ion-exchange ability and large surface area. Lee et al. have studied the adsorption of organic dyes and  $\text{Cu}^{2+}$  on TNTs and indicated that the amount of  $\text{Na}^+$  within the TNT structure might dominate the adsorption potential of TNTs [5,6]. In addition, the adsorption behaviors of various inorganic contaminant ions on TNTs were also investigated. The results indicated that TNTs showed high adsorption capacity for  $\text{Cu}(\text{II})$ ,  $\text{Pb}(\text{II})$ ,  $\text{Cd}(\text{II})$ ,  $\text{Ni}(\text{II})$  and  $\text{Cr}(\text{IV})$ , and the strengthening O–H bond and the intercalation of  $\text{H}^+$  in the TNT structure might decrease their adsorption capacities [7–10]. Our literature survey shows that the in situ modification of TNTs by organic additives for pollutants removal has been hardly reported. In this work, we have synthesized L-TNTs by a lignosulfonate (LSN)-assistant hydrothermal method. The influences of LSN on the morphology, structure and adsorption capacity of TNTs were investigated.

## 2. Experimental

All chemicals were of analytical grade. Deionized water was used in this study. TNTs were prepared by a hydrothermal process similar to that described by Kasuga et al. [1]. In a typical procedure, 1 g of anatase phase  $\text{TiO}_2$  powders were added into 50 mL of  $10 \text{ mol L}^{-1}$  NaOH aqueous solution. Then 0.15 g of sodium lignosulfonate was added into the above mixture and stirred for 1 h. The resultant suspension was transferred into a Teflon-lined stainless steel autoclave and heated in an oven at  $150 \text{ }^\circ\text{C}$  for 24 h. After being cooled down to room temperature, the as-prepared products were washed with distilled water and  $0.01 \text{ mol L}^{-1}$  HCl until the pH value of the rinsing solution reached 6.5. Finally, L-TNTs were obtained after drying at  $80 \text{ }^\circ\text{C}$  over night. TNTs were prepared by the same method in the absence of LSN.

Samples were characterized by X-ray diffraction (XRD) patterns using a Bruker D8-Advance with  $\text{Cu K}\alpha$  radiation. Raman spectra were measured with a Fourier transform infrared/Raman spectrometer equipped with a diode-pumped YAG laser operating at 1064 nm at a power level of 400 mW. The morphologies were studied by a Hitachi S-4800 field emission scanning electron microscopy (FESEM) and a Hitachi H-7500 transmission electron microscopy (TEM). FTIR spectra were recorded using a Perkin-Elmer Model 1600 FTIR spectrophotometer in the range of  $4000\text{--}400 \text{ cm}^{-1}$  with a scan rate of  $0.2 \text{ cm s}^{-1}$ .

All batch adsorption experiments were carried out in 50 mL polypropylene tubes containing 30 mL metal ions solution with desired initial concentrations. The concentration of adsorbent was

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0.1 g L<sup>-1</sup>. The pH value of the solution was controlled at pH 5.5 by HCl and NaOH solutions. The tubes were put into a gas bath constant temperature oscillator (HZQ-F160, China) maintained at 240 r min<sup>-1</sup> and 25 °C for 4 h. The concentrations of heavy metal ions were detected by an atomic absorption spectrometer (180-70, Hitachi, Japan).

### 3. Results and discussion

The FESEM and TEM images of TNTs and L-TNTs are shown in Fig. 1. It can be seen that TNTs have small axial ratios and contain some nanosheets. While slim nanotubes with smaller inner diameters (about 10 nm) were obtained with the addition of LSN. The XRD patterns of the samples are shown in Fig. 2. The diffraction peaks of TNTs and L-TNTs were assigned to layered titanate, and the peak at  $2\theta \approx 10^\circ$  was attributed to the interlayer distance of  $\text{Na}_x\text{H}_{2-x}\text{Ti}_3\text{O}_7 \cdot n\text{H}_2\text{O}$  (JCPDS no. 31-1329) [5]. The position of this peak shifted to low angle and all the peaks became sharper after the modification by LSN, which can be attributed to the increased layer spacing and crystallinity [11]. The layer spacing of TNTs and L-TNTs calculated from the Bragg formula were about 0.69 and 0.96 nm, respectively. TNTs and L-TNTs were further characterized by Raman spectra. As shown in Fig. S1. The peak at 280 cm<sup>-1</sup> was assigned to the Na–O–Ti, while the peaks at 450 and 660 cm<sup>-1</sup> were caused by Ti–O–Ti vibrations [11]. The intensity and position of the peaks changed slightly after LSN modification, demonstrating that both the samples are layered titanate. Lignin is a heterogeneous and amorphous polymer of a phenolic nature, and it is the second-most-abundant biopolymer on Earth, second only to cellulose. LSN is a derivative of lignin and contains rich organic functional groups such as alkylation hydroxyl, phenolic hydroxyl, sulfonyl, carboxyl, carbonyl, ester, etc. [12].

According to previous studies [2], the formation process of L-TNTs is proposed as follows: TiO<sub>2</sub> reacted with NaOH in solution and formed disordered intermediate phase and sheets of trititanate, which adsorbed the hydrophilic groups (sulfonyl and hydroxyl) of LSN. This might result in hydrophobicity of the adsorption surface and facilitate the scrolling of the titanate sheets and the growth of long nanotubes. Meanwhile, the incorporation of LSN increased the layer spacing. This assumption can be preliminarily confirmed by FTIR analysis. As shown in Fig. 3, a broad and intense band

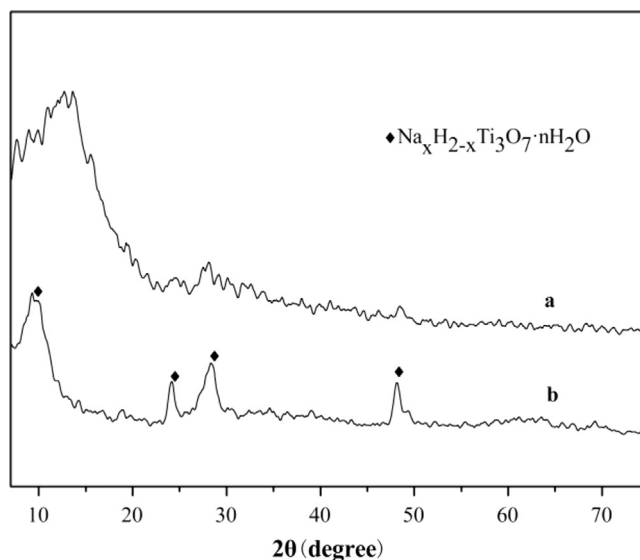


Fig. 2. XRD patterns of (a) TNTs and (b) L-TNTs.

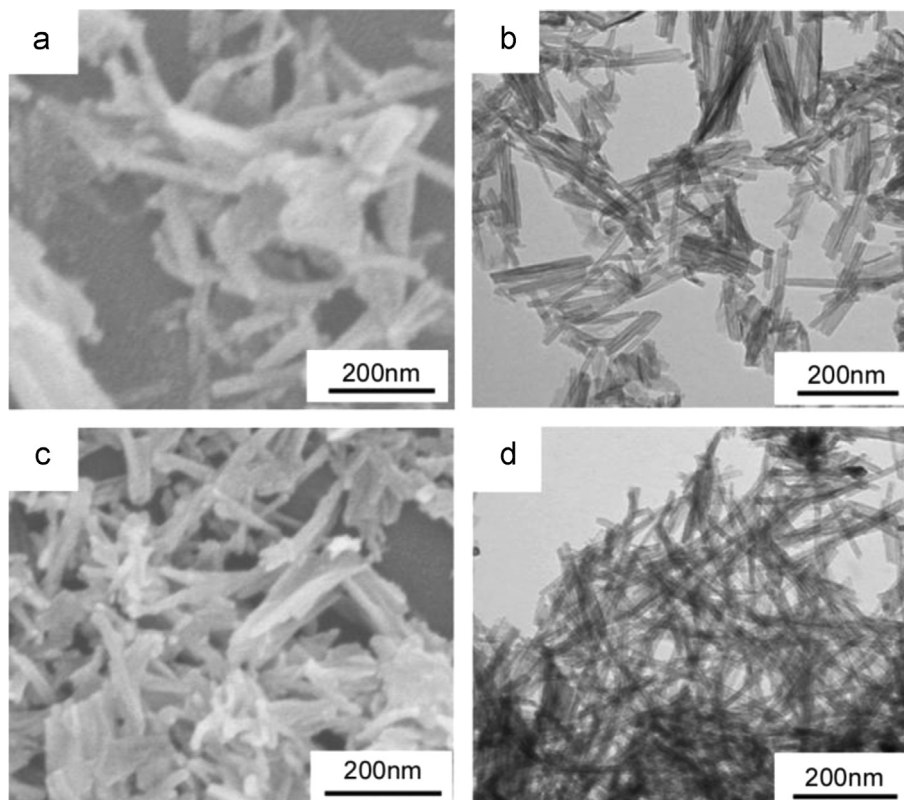


Fig. 1. FESEM and TEM images of TNTs (a and b) and L-TNTs (c and d).

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