

Synthesis of Titanium Oxide Nanotube via Hydrothermal Method and Recovery of Palladium by means of it

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Nanotubes composed of various materials such as carbon, boron nitride, and wolfram disulfide have been studied recently. In this study, the discovery of a hydrothermal route for the synthesis of a nanotube made of titanium oxide by microwave annealing is presented. TiO₂ nanotubes obtained in the present work are anticipated to have great potential for use in the preparation of catalysts, adsorbants, and deodorants with high activities, because their specific surface area is greatly increased. Anastase phase TiO₂ crystals with a diameter of ~10 nm and a length of ~85 nm were obtained when sol-gel-derived fine TiO₂-based powders were treated chemically (e.g., for 30 h at 120 °C) with a 8 M NaOH aqueous solution. The TiO₂ nanotubes have a large specific surface area of 420 m²·g⁻¹. The nanotubes were investigated as adsorbents for the removal of Pd (II) from aqueous solutions. It was shown that the initial uptake of each metal ion was very fast in the first 35 min, and adsorption equilibrium was reached after 120 min. The maximum adsorption capacity of Pd (II) was determined to be 50.54 mg g⁻¹, respectively. Thus, TiO₂ nanotubes were considered to be effective and promising materials for the recovery of Pd (II).

Key words: Titania nanotubes; Hydrothermal; Microwave annealing; Palladium; Adsorption

1. Introduction

A revolution of nanotechnology and its research fields and applications was initiated in the past few years. Nanostructures which is nanoparticles, nanowires, nanotubes, and other nano structures containing Ti such as titania (TiO₂) and titanate (Na_xH_{1-x}Ti₃O and H₂Ti₃O₇) have attracted much attention due to its multiple applications in electronics, optics, catalysis, sensors, and energy conversion [1]. Large specific surface area is one of the most important characteristics of nanotubes compared to bulk materials and titanium nanotubes (TNs) also provide channels for enhanced electron transfer. Thereby, they help to increase the efficiencies for solar cells, electrolysis, and photocatalysis [2]. Besides the larger specific surface area of TNs, they have elongated morphology that helps to exhibit improved photogenerated charged carrier separation than bulk TiO₂ nanoparticles. Because it is low temperature technology, hydrothermal synthesis was used in the fabrication of titania nanotubes and it has been comprehensively investigated in previous reports [3]. Moreover, it is preferred because of the simple control of the aqueous solution. Also, it is environmentally friendly since water is used as a solvent in a closed system.

Nevertheless, this method needs modification for improvement of thermal stabilities, crystalline structures, compositions. Hydrothermal method was introduced by Kasuga *et al* [3] who used it for the production of small diameter TN and they concluded that the as-prepared nanotubes were

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mainly titania and were formed during the process of washing after the hydrothermal treatment. To the best of our knowledge, there is no adsorption study of Pd (II) onto TNs which microwave heating treatment of hydrothermally prepared TN derived from anatase precursor. The purpose of this study is to investigate the feasibility of TNs as high efficient adsorbents for the removal of Pd (II) from aqueous solutions.

2. Materials and Methods

2.1. Preparation of titanate nanotubes

The titanate nanotubes were synthesized by the hydrothermal treatment of TiO₂ powder in concentrated NaOH solution as described in literature [4]. Typically, 1 g of TiO₂ nanoparticle powder was added to 9 mL of 8 M NaOH solution under vigorous magnetic stirring for about 40 min. to form a white suspension. The suspension was transferred into 50 mL Teflon-lined stainless steel autoclave, which was allowed to react at 120 °C for 30 h. The precipitate in the autoclaved mixture was then separated by filtration and washed with deionized water until the pH value of the rinsing solution reached 7.0. Finally, the products were dried in an oven at 70 °C for 2 h.

Nitrogen adsorption–desorption isotherms were determined at –196 °C for Brunauer–Emmett–Teller (BET) measurements on an Quantachrome NOVA 2300. Before adsorption, the samples were degassed at 50 °C. The BET specific surface areas were calculated in the relative pressure (P/P_0) range of 0.06–0.20. Desorption isotherms were used to determine the pore size distributions using the Barret–Joyner–Halender method. Nitrogen adsorption volumes at the relative pressure of 0.99 were used to determine the pore volumes and the average pore diameters.

FTIR measurements were carried out by Perkin Elmer Spectrum Two spectrophotometer at 4 cm⁻¹ resolution in ATR mode using ceramic light source, KBr/Ge beam splitter and a LiTaO₃ detector. FTIR spectra measurements of before and after adsorption on TNs were recorded between 4000 and 400 cm⁻¹ (accumulating 4 scans). The background spectra were recorded with the clean crystal in place to eliminate moisture and CO₂ interference. Perkin Elmer Spectrum two software's (v. 10) ATR-correction was used for correction.

2.2. Methods

The Pd (II) solution was prepared by diluting stock solutions containing 200 mg/dm³ metal ion in distilled water to 50 mg/L concentrations. 50 mL of metal ion solutions prepared for adsorption experiments and stirred after adding 100 mg TN powder for 180 min. (the time required for equilibrium to be reached between metal ions adsorbed and metal ions in solution). The initial pH of the solutions controlled by adding a small amount of HCl, HNO₃, NaOH and HClO₄. At the end of the adsorption period, 15 mL samples were centrifuged and the solutions were filtered through a 0.45 μm Milipore filter paper to avoid any solid particle in the aqueous phase. Samples were measured using AAS. All the adsorption tests were performed at least twice so as to avoid wrong interpretation owing to any experimental errors.

3. Results and Discussions

3.1 Characterization of TNs

According to the adsorption data, Table 1 presents the surface properties of TNs. The BET specific surface areas and the single point total pore volumes were 312.4 m² g⁻¹ and 1.93 cm³ g⁻¹, which were much higher than that of TiO₂ factor of 6 and 7.2, respectively [5]. The obvious increase in surface areas and porosity of TNs could be ascribed to their unique morphology. Both the external and internal sides of the nanotubes contributed to the surfaces. The pores along the lengths and the interlay cavities in the walls were also accessible, in favor of the increase of the pore volumes.

Table 1. Basic structure parameters of TNs.

Parameters	Values
Specific surface area ($\text{m}^2 \text{g}^{-1}$)	312.4
Single point total pore volume ($\text{cm}^3 \text{g}^{-1}$)	1.93
Average pore diameter (nm)	11.2

The FT-IR spectra of TNs and metal ions loaded TNs are shown in Figure 1. Inspection of the presented spectra shows absorption bands at 3268, 1653, 904, 687 and 486 cm^{-1} . Obviously, the broad absorption band at $\sim 3400 \text{ cm}^{-1}$ may be assigned to stretching vibrations of OH groups and strongly bound H_2O molecules on TiO_2 surface [5]. The intensity of this band gradually decreases as the annealing temperature increases indicating the loss of the surface OH groups. Then the band at 1653 cm^{-1} could be attributed to the H–O–H binding vibration. All of these findings are indicating the presence of hydroxyl groups and water molecules in the TNs. The band at 904 cm^{-1} might be related to a four-coordinate Ti–O stretching vibration [5]. The band at 484 cm^{-1} was assigned to the vibration of $[\text{TiO}_6]$ octahedron [6]. After adsorption of Pd (II) by TNs, Figure 1(b), all bands were just slightly shifted within the resolution range, and it can be revealing that both Ti–O bond and $[\text{TiO}_6]$ octahedron had no positive effect on the adsorption of Pd (II). However, it can be apparently seen that the bands of hydroxyl groups in pure TNs were significantly shifted from 3268 to 3318 cm^{-1} in Pd (II) loaded TNs. This indicated that the adsorption could have mainly occurred through the interaction between metal ions and hydroxyl groups of the TNs. It is clear that, the FTIR spectra point to many similar surface chemical characteristics of the titania and titanate nanotubes except that the later has more surface –OH groups. The bands at 486 and 687 cm^{-1} may be attributed to $[\text{TiO}_6]$ octahedron vibration.

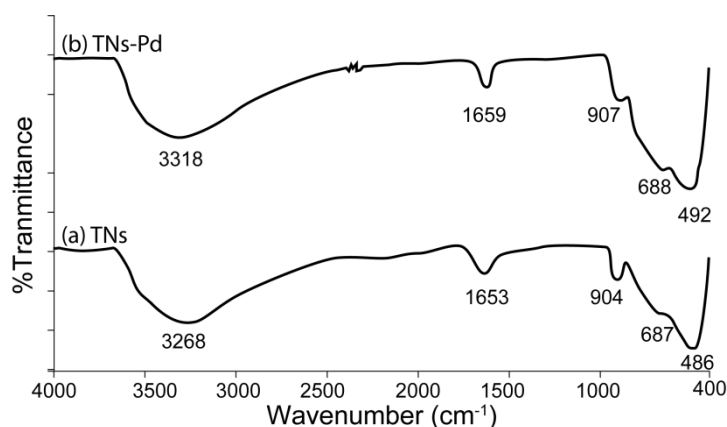


Figure 1. The FT-IR spectra of (a) pure TNs, (b) Pd (II) loaded TNs.

3.2. Adsorption Studies

Figure 2 shows adsorption capacities of Pd (II) ions at various initial metal concentrations. In all cases the plots form a plateau at higher metal concentrations; suggestive of the fact that adsorption has reached out to equilibrium. The Pd (II) adsorption capacity was determined as 50.54 mg/g. Langmuir single layer adsorption capacity of PGNR was found as 55.72 mg Pd (II) /g (calculations not shown here). This result shows TNs can be use efficiently for recover of Pd (II) ions when it compared to literature [7; 8; 9; 10]. The maximum adsorption capacity of the murexide functionalized halloysite nanotubes adsorbent at optimum conditions was found to be 42.86 mg/g for Pd (II) [9].

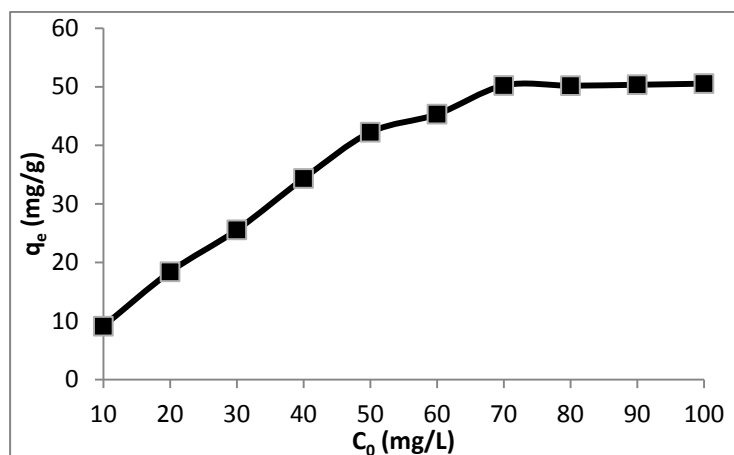


Figure 2. Plots of adsorption capacity vs initial metal concentration (100mg TN, 20°C, pH=2, [Cl⁻]= 10⁻³ M)

Adsorption studies with condensed tannin and nitrogen functional group containing resins, optimum pH which highest adsorption efficiency is around 2 [8]. While, 10⁻² M chloride concentration was especially chosen since the favorable species may occur in this condition [9].

4. Conclusions

Titanate nanotubes were prepared for using an adsorbent by microwave assisted hydrothermal method. Their possible application for the removal of Pd (II) was investigated. The analyses of nitrogen adsorption–desorption isotherms showed that the mesoporous TNs exhibited larger specific surface areas of 312.4 m² g⁻¹ and higher pore volumes of 1.93 cm³ g⁻¹. Furthermore, FT-IR spectra revealed that the hydroxyl groups in the TNs were responsible for Pd (II) adsorption. The adsorption rate of Pd (II) ion was very fast in the first 35 min, and the adsorption equilibrium was achieved after 120 min. The maximum amount of Pd (II) adsorbed was detected in the pH 2. Therefore, the TNs exhibited great potential for the recovery of Pd (II) from chloride containing solutions.

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