

Synthesis and Adsorption Properties of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ Nanobelts

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Abstract. $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts were successfully synthesized by a simple, template and surfactant-free hydrothermal method, in which titanium sulfate ($\text{Ti}(\text{SO}_4)_2$) and concentrated phosphoric acid (H_3PO_4) were used as titanium and phosphorus source, respectively. The synthesized materials were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR). The nanobelts are ca. 60 nm in width as well as 20 nm in thickness, and its length can reach several micrometers. The adsorption performance of the synthesized nanobelts was investigated. The results indicate that the $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts have good adsorption ability to methylene blue (MB). The removal rate of MB could reach to 50 % within 10 min, the equilibrium adsorption time is about 70 min as well as the equilibrium capacity is about 150 mg/g at room temperature. It indicates that the $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ could be a promising candidate for waste water treatment. The possible adsorption mechanism was also suggested.

Introduction

The tetravalent titanium phosphates (TiP) have been synthesized and investigated for many years due to its excellent thermal and chemical stability. There are two kinds of titanium phosphate based on their P/Ti ratio, one is the layered titanium phosphate with a P/Ti ratio of 2:1, such as $\text{Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ [1-3] and so on. Recent years, a kind of new titanium phosphates with a P/Ti ratio of 1:1, including $\text{TiO}(\text{OH})(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$ and $\text{Ti}_2\text{O}_3(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ have been synthesized [4-7]. The TiP compounds have various crystal structures based on their composition [8-11], and can play an important role in the application of ion exchange [12], ion adsorption [5, 13], superhydrophilic or superhydrophobic surface [14], catalyst [15, 16] and lithium ion battery [17]. However, to the best of our knowledge, the investigation on the adsorption properties of TiP has not been reported yet. On the other hand, in order to reduce the environmental pollution which is getting worse, it's urgent to develop new adsorbent materials with excellent adsorption performance and stability. In the present article, we have synthesized a novel $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts, to our knowledge, the belt-like $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanostructures have not been reported yet. We also measured the adsorption properties of synthesized $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts, and it demonstrates good adsorption ability to methylene blue.

Experimental Section

The reagents of concentrated phosphoric acid (H_3PO_4 , $\geq 85.0\%$), hydrogen peroxide (H_2O_2 , $\geq 30.0\%$), ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.7\%$), and distilled water were purchased from Chengdu Kelong Chemical Reagent Co. Ltd; titanium sulfate ($\text{Ti}(\text{SO}_4)_2$, $\geq 96.0\%$) was purchased from Sinopharm Chemical Reagent Co. Ltd, all the chemicals are of analytical grade and were used without further purification.

$\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts were synthesized as follows: At first, 20 ml of distilled water was added to 100 ml of $\text{C}_2\text{H}_5\text{OH}$ to obtain a mixed solution, then 0.01 mol $\text{Ti}(\text{SO}_4)_2$ was added to the mixed solution under vigorous stirring. When $\text{Ti}(\text{SO}_4)_2$ was dissolved completely, 15 ml of above

solution was transferred to a 25 ml Teflon-lined stainless autoclave and 0.5 ml of concentrated phosphoric acid and hydrogen peroxide was added into the solution under vigorous stirring for a few minutes, then the autoclave was sealed and maintained at 180°C for 24h in a electric oven. After cooling at room temperature, the precipitates were collected by centrifugation and washed with distilled water and ethanol until the pH value of supernatant was 7. Finally, the product was dried in an vacuum drying oven at 80°C for 24h, the white powder is collected for further characterization and measurement.

The crystal structure of the samples were identified by X'Pert Pro MPD X-ray diffractometer (XRD, PANalytical B.V. Holland) using Cu K α radiation ($\lambda=0.15406\text{nm}$, 40kV, 30mA) in the 2θ range 5-80°. The morphology of products were observed by using S-4800 Field emission scanning electron microscope (FESEM, Hitachi Co, Japan), Fourier transform infrared spectrum was investigated by using Nicolet 6700 Fourier Transform IR/Visible spectrometer (FT-IR, Thermo Nicolet Co. American) in a wavenumber range from 4000 to 400 cm^{-1} .

Absorbance spectra of the samples were measured by using UV-1101 spectrophotometer (Techcomp, China). The adsorption performance of sample was estimated by measuring the adsorption of MB at ambient temperature and pressure. In a typical process, 20 mg as-prepared product was added into 200 mL methylene blue (MB) solution with the concentration of 20 mg/L under vigorous stirring. After continuous stirring at 150 rpm at a defined time interval, 5 mL of solution was taken out and centrifuged for 5 min at 8000 rpm. The supernatant was collected and measured using UV-Vis spectrophotometer. The adsorption performance was evaluated by calculating the removal rate of MB according to the absorbance.

Results and Discussion

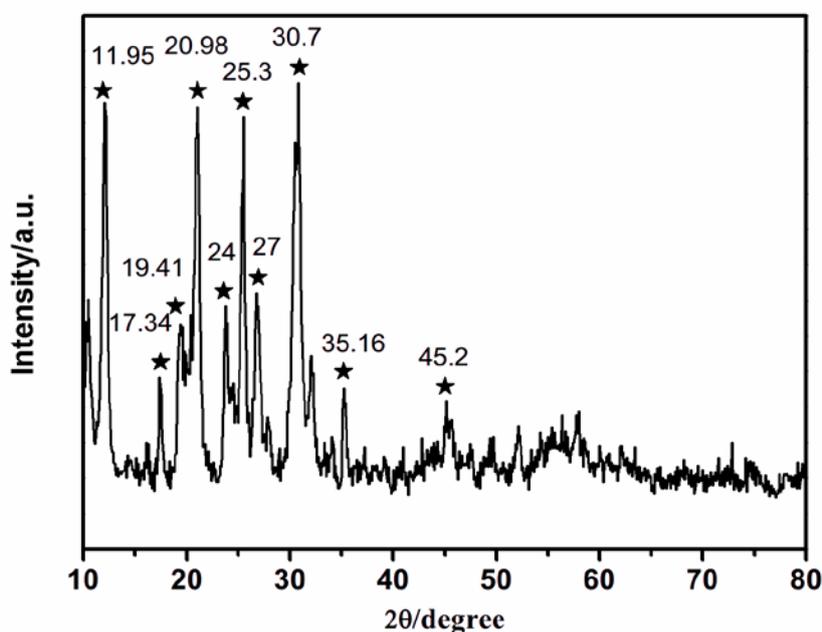


Fig. 1 The XRD pattern of as synthesized sample.

The XRD pattern of as-synthesized sample is shown in Figure 1. All the diffraction peaks could be indexed to $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ (JCPDS No. 52-1530). This compound has a skeleton-like structure. The strong reflection peak located at $2\theta=11.95^\circ$ corresponds to the (110) crystal plane of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ which with an interplanar spacing of 7.39\AA [6,7,11]. The product is pure and there is no other crystal phase is observed in the XRD pattern.

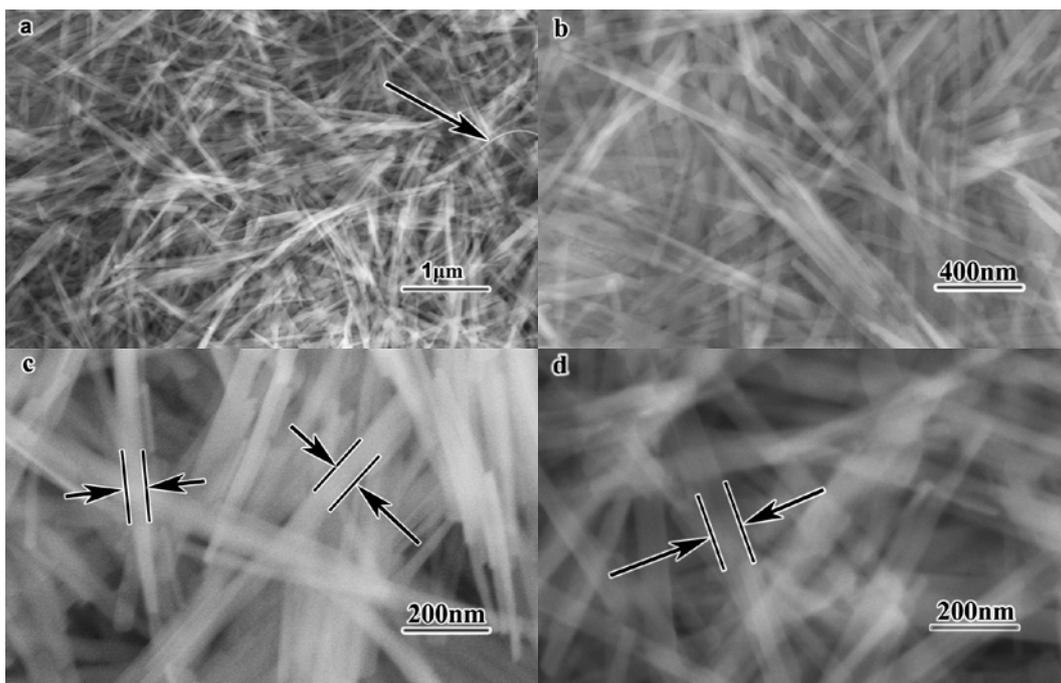


Fig. 2 SEM images of sample.

Figure 2 shows the SEM images of prepared $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ sample with different magnifications. The product are all $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts. The belt-like morphology can be appreciated from the thinning in the smooth bent and wing section indicated by the black arrow in Figure 2a. There is no other nanostructures were observed. Figure 2b to 2d show the SEM images with higher magnification, it indicate that the nanobelts are 60nm in width and 20 nm in thickness, and its length can reach several micrometers. The nanobelts have a uniform width and thickness along the whole length, and the surface of nanobelts is very smooth.

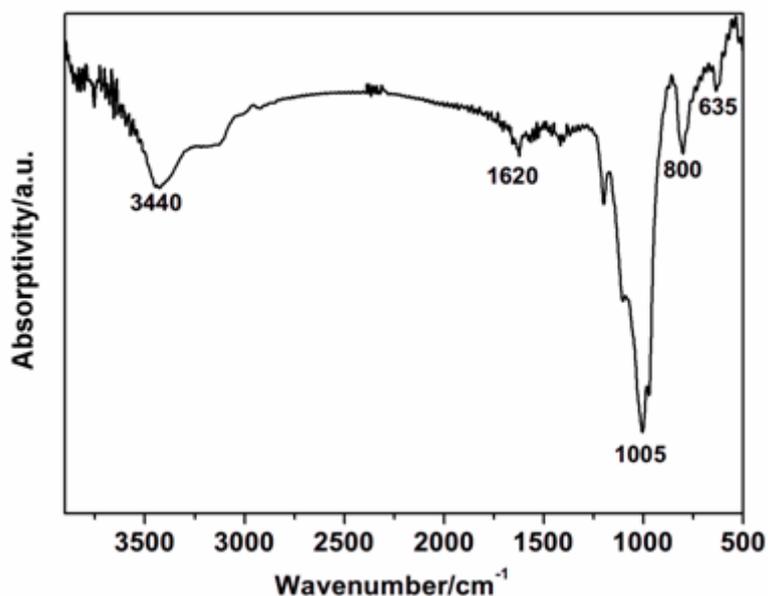


Fig. 3 FT-IR spectrum of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts.

The infrared spectrum of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts is shown in Figure 3. The two peaks at 3440 and 1620 cm^{-1} can be assigned to the hydroxyl symmetrical stretching vibration mode of water molecule in the structure. Compare with literature, the intense absorbance band around 1005 cm^{-1} should be attributed to the characteristic bending Vibration of P-O bond in PO_4 groups. The peaks at 800 cm^{-1} can be assigned to the vibration mode of Ti-O bond of Ti-OH and Ti-O-Ti matrix in the

$\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ structure[6,7,11]. In addition, the weak peak located at 635 cm^{-1} should be attributed to mixed vibration mode of Ti-O bond and PO_4 groups[6].

The absorption curves of MB after different adsorption time are shown in Figure 4 (a). It is obvious that the absorption peak intensity at 665 nm reduce rapidly in 10 min, it indicate that the adsorption of nanobelts to MB is very fast at this stage, and then the adsorption rate decrease continuously accompanying increased adsorption time. About 75.69% MB was removed after 70 min. Figure 4(b) shows the corresponding adsorption rate curve. It shows the reduction of adsorption rate accompanying the increase adsorption time. The adsorption rate decreased significantly after 10 min. The $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts saturate with MB basically after 70 min, the saturated adsorption capacity is ca. 150 mg/g.

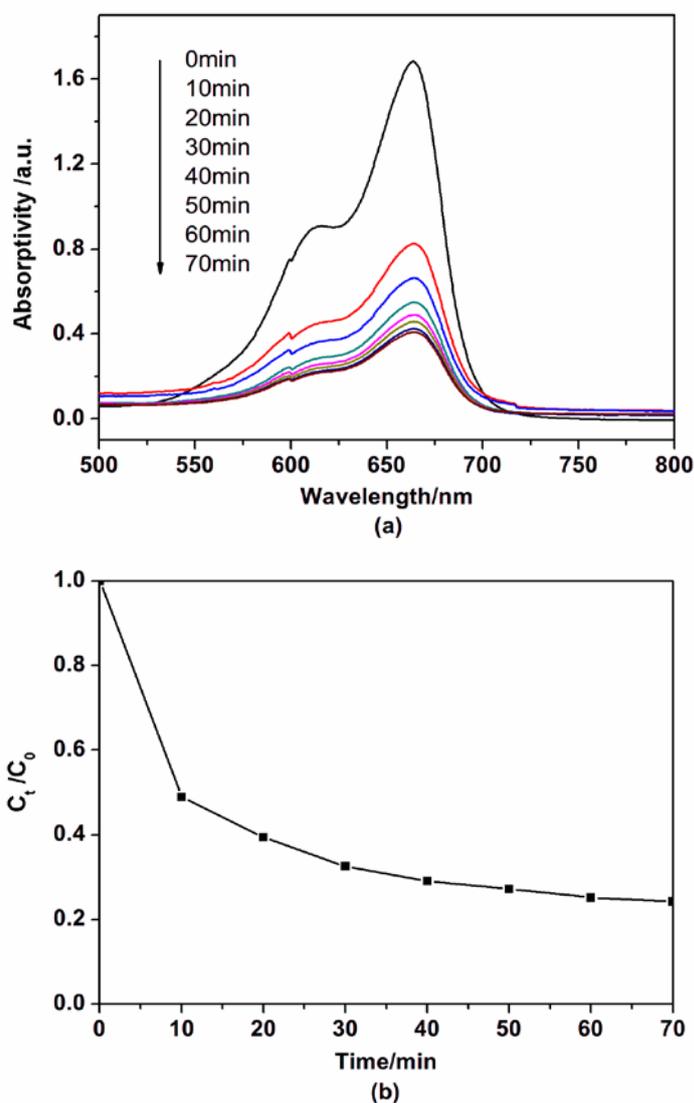


Fig. 4(a) Absorption spectra of MB after treatment with $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts for different time intervals; (b) Corresponding adsorption rates of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts.

The good adsorption performance of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ can be attributed to its inherent crystal structure and the high surface area of nanobelts. According to the previous study of Pooiary et al.[11], $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ has a skeleton structure, it contains an oxygen bridged dimeric TiO_6 octahedra and two independent phosphate groups (PO_4 tetrahedra) which is the basic structural unit of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. There are two kinds of one-dimensional channels with different sizes parallel to the c-axis direction of the crystal structure due to the connected alternately of the PO_4 tetrahedra and TiO_6 octahedra^[6,11], and these channels with the space around it are likely to be area where the dye molecules can be adsorbed and stocked. In addition, according to the investigation of Bortun et

al.^[6], the exchange between $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Ti}_2(\text{OH})_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is suggested in a neutral and alkaline solution based on the possible existence of Ti-OH functional groups, due to existence of this exchange process, one of the Ti-O bond in the Ti-O-Ti bridge will break, the channels in the $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ are opened and expanded which will facilitate the enter of more dye molecules or charged groups as well as the adsorption process can be promoted. On the other hand, more hydroxyl groups may generate from the equilibrium process mentioned above, when the protons in Ti-OH was released in solution, the molecules of products can be given a negative charge, meanwhile, the MB molecules can bring a positive charge when it was dissolved in water thus it can be adsorbed by the adsorbent through electrostatic attraction. The adsorption ability of adsorbent is related to its surface area, amount of active spot for adsorption and the space to hold the dye molecular, so the $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts with high area exhibit good adsorption performance to MB. Further research is needed in the future to understand the detailed adsorption mechanism of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.

Conclusions

The pure and uniform $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ nanobelts were synthesized via a hydrothermal method at 180°C , the titanium sulfate ($\text{Ti}(\text{SO}_4)_2$) and concentrated phosphoric acid (H_3PO_4) were used as precursors. The crystalline nanobelts demonstrate good adsorption ability to methylene blue at ambient temperature and pressure, the equilibrium adsorption time to MB is about 70 min and the saturated adsorption capacity and removal rate is about 150 mg/g, 76%, respectively. The adsorption of nanobelts to MB was very fast, 50% MB can be removed in 10 min. The inherent and unique crystal structure and high special surface area of $\text{Ti}_2\text{O}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ induce its good adsorption performance, and the adsorption process is controlled by the electrostatic attraction between adsorbent and dye molecules. Via surface modification it is possible to further improve the performance of this new TiP nanomaterials in the future.

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