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Cellulose nanocrystals-assisted hydrothermal synthesis of mesoporous α-Fe_2O_3 for photocatalysis

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A hydrothermal process was adopted to synthesize mesoporous α-Fe_2O_3 materials using cellulose nanocrystals as template, and its photocatalytic performance on degradation of dye was investigated. The characteristic results through XRD and N_2 adsorption showed that the mesoporous α-Fe_2O_3 was successfully prepared, which possessed an average pore size of 39.5 nm and surface area of 46.5 m^2 g^{-1}. The photocatalytic capacity of the synthesized mesoporous α-Fe_2O_3 was determined by following the degradation of methylene blue (MB) under visible-light irradiation conditions, and the results showed that the sample prepared with CNC exhibited better photocatalytic activity under the condition studied than that prepared without CNC. These results demonstrated that thus prepared mesoporous α-Fe_2O_3 would have a great potential to be used as a catalyst in degrading organic dyes during a typical industrial wastewater treatment.

Key words: Hydrothermal synthesis, Cellulose nanocrystals (CNC), Template, Mesoporous α-Fe_2O_3, Photocatalysis.

Introduction

Cellulose nanocrystals (CNC) are the abundant and renewable materials in the nature, which can be prepared from lignocellulosic materials [1]. Due to the polymer chains and the nanoscale dimension, CNC have received an increasing interest in different applications for various processes, such as thermal/ pH sensitive hydrogel [2], yarns [3] and nanomaterials [4-8].

Organic dyes are serous pollutants in wastewater, which are very stable in water bodies and very difficult to be degraded during the traditional wastewater treatment processes [9]. The photocatalytic methods are effective for degrading dyes in wastewater [10-13]. In the recent years, α-Fe_2O_3 has received much attention for various applications due to its low-cost, environmental friendliness and non-toxicity. The band gap of α-Fe_2O_3 is 2.2 eV, which implies that α-Fe_2O_3 is suitable as a photocatalyst [14-16].

The performance of α-Fe_2O_3 is strongly influenced by the particles size, morphology and the structure [17]. The mesoporous structures are promising due to its high surface area, high pore volume and defined pore characteristics.

Herein, mesporous iron oxide was synthesized by the hydrothermal process using CNC as templates, and its photocatalytic activity for degrading methylene blue (MB) was investigated. The objective of the study was to further extend the application of CNC in mesoporous materials.

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Experimental Procedures

Chemicals

Ferric chloride hexahydrate was purchased from Sigma-Aldrich reagent Co. Ltd and ammonium hydroxide was from EMD, respectively. Ferric chloride hexahydrate was reagent grade and Ammonium hydroxide was ACS, respectively. Cellulose nanocrystals (CNC) was provided by Tianjin Haojia Cellulose Co., Ltd (China).

Synthesis of mesporous α-Fe_2O_3

All reagents were used without further purification. In a typical synthesis process: a CNC suspension was prepared via 5.714 g of NCC (3.5%, w/ w) dispersed in deionized water by ultrasonic treatment for 10min.The ferric chloride solution (0.33 g of $FeCl_3 \cdot 6H_2O$ dissolved in 10 mL of deionized water) was dropped into CNC suspension and vigorously stirred for 10min. Then, 3 mL of ammonia solution (25%, w/w) was added. After 30 min, the mixture was transferred into a 20 mL Teflon-lined stainless steel autoclave, which was sealed and then heated to 160 °C for 6 hrs. After the reaction was completed, the autoclave was cooled to room temperature naturally. The red products were centrifuged and washed several times with deionized water and absolute ethanol, and then dried in an oven at 100 °C for 12 hrs. Finally, the dried sample was calcined at 450 °C for 2 h to remove CNC. As a control, the α-Fe_2O_3 sample without NCC was prepared under the same condition.

Characterization

X-ray powder patterns for all samples were measured by X-ray diffraction (XRD, a Bruker D8 Advance spectrometer) using Cu Kα radiation. N_2 adsorption was performed with specific surface area measurement (Quanta chrome Instruments). The scanning electron microscopy (SEM, JEOL JSM-6400) and transmission electron microscopy (TEM, JEOL2010) were used to investigate the morphology of samples.

Photocatalysis

50 mL of 5 mg L^{-1} MB solution was put into 250 mL conical flask containing 0.05 g of catalyst. A 250 W filament lamp was used as light source. Prior to irradiation, the solution was shaken for 1h in the dark to sure an adsorption-desorption equilibrium between catalyst and MB. 5 mL MB solution was taken out after certain time intervals for analysis by an ultraviolet (UV)-visible spectrometer (Thermo Electron Corporation, USA) to measure the degradation rate of MB.

Results and Discussion

The XRD patterns in Fig. 1 showed the crystal phase of the samples prepared without and with CNC. It can be found that all the strong diffraction peaks of samples can be assigned to the rhombohedral phase of α-Fe_2O_3, which matched those reported in the literature (JCPD 33-0664) [18, 19]. These results supported the conclusion that both of these samples prepared without and with CNC were α-Fe_2O_3 with good quality.

The N_2 adsorption measurement was carried out to determine the surface area, pore volume and pore size. The results were presented in Fig. 2. It was found that the samples exhibited a type IV isotherm with a hysteresis loop, which was mainly ascribed to the capillary condensation taking place in the mesopores [20], supporting the conclusion that the mesoporous α-Fe_2O_3 was successfully synthesized.

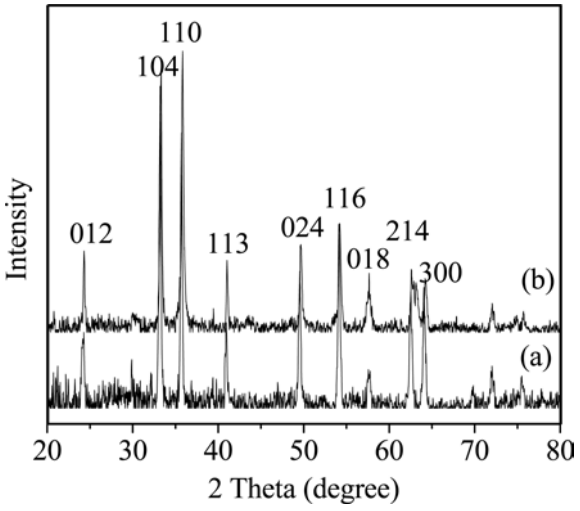

Fig. 1. XRD patterns of the prepared α-Fe_2O_3. (a) the sample prepared without CNC, (b) the sample prepared with CNC.

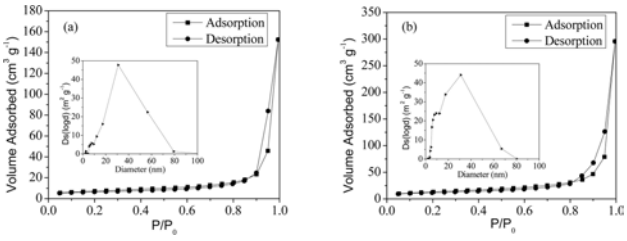

Fig. 2. Nitrogen adsorption-desorption isothems and pore size distribution curve of the prepared α-Fe_2O_3. (a) the sample prepared without CNC, (b) the sample prepared with CNC.

Table 1. BET parameters of the prepared mesoporous α-Fe2O3 samples.

Sample	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
Sample 1 (Without CNC)	24.5	0.24	38.5
Sample 2 (With CNC)	46.5	0.46	39.5

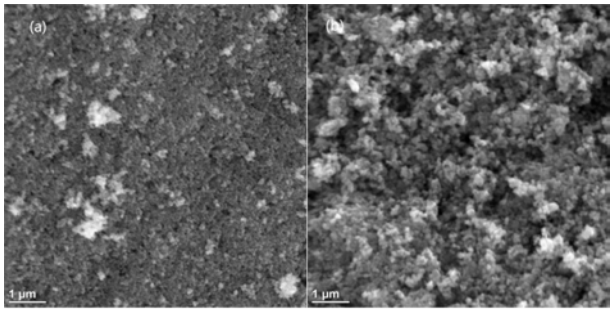

Fig. 3. SEM images of the prepared α-Fe_2O_3. (a) sample prepared without CNC, (b) sample prepared with CNC.

In addition, the average pore sizes of samples were 38.5 nm of sample prepared without CNC and 39.5 nm with CNC, respectively (Table 1). As shown in Table 1, on the other hand, the surface area and pore volume of sample prepared with CNC were higher than those prepared without CNC. In one study [21], the mesoporous α-Fe_2O_3/TiO_2 prepared through the hydrothermal method using carbon spheres as templates, possesses surface area of 31.8 m^2 g^{-1}, which was also smaller to the mesoporous α-Fe_2O_3 prepared with CNC as template reported above.

The surface morphologies of the α-Fe_2O_3 samples were shown in Fig. 3. In Fig. 3(a), it was found that the sample prepared without NCC had uniform size distribution of particles, with less pores present. On the other hand, the sample prepared using CNC has many pores (Fig. 3(b)). These results were consistent with previous discussion that the sample prepared with CNC had a higher surface area and pore volume than prepared without CNC.

In Fig. 4, significant differences in shape and size between the two samples were observed. The sample prepared without CNC was cube-shape, while the

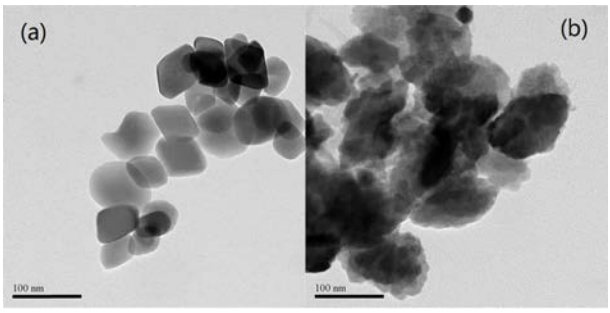

Fig. 4. TEM images of the prepared α-Fe_2O_3. (a) the sample prepared without CNC, (b) the sample prepared with CNC.

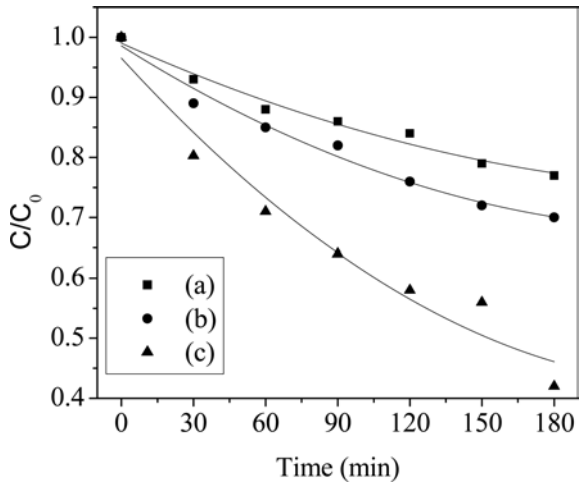

Fig. 5. Photocatalytic degradation of MB by using the prepared α-Fe_2O_3 samples under visible-light irradiation. (a) blank, i.e., without α-Fe_2O_3, (b) the α-Fe_2O_3 sample prepared without CNC, (c) the α-Fe_2O_3 sample prepared with CNC. C and C_0 are the concentration of MB after irradiation in a selected time interval and initial concentration of MB, respectively.

sample prepared with CNC showed ellipse-shape, and irregular. In addition, the size of sample prepared using CNC was larger than that prepared without CNC.

Cellulose is a linear polymer possessing abundant surface hydroxyl groups, which can provide a suitable site for metal oxide to deposit onto the cellulose surface [22]. The surface hydroxyl groups of cellulose can conduct as the nucleation and growth of inorganic particles and induce to form the certain shape [23]. In Fig. 4(b), it can be observed that the samples prepared with CNC inherited the shape of the CNC, which is spindle-shaped.

The photocatalytic properties of the samples were evaluated by measuring the degradation of Methylene Blue (MB) in aqueous solution under condition of visible light irradiation. The MB concentration was determined using an ultraviolet- visible spectrometer at wavelength of 660 nm. From the results shown in Fig. 5, it was found that all of the concentration of MB solutions decreased during the experiments, which was due to the chemical degradation, rather than adsorption [21]. More interestingly, the α-Fe_2O_3 prepared with CNC gave a faster MB degradation rate than that prepared without CNC under the same conditions: about 58% of MB was degraded within 180 min by using sample prepared with CNC under the conditions studied, while only 23% of the initial concentration of MB was consumed by using the sample prepared without CNC. The better photocatalytic activity of sample prepared with CNC was mainly attributed to the improved morphological properties, as noted in the previous sections.

Conclusions

Mesoporous α-Fe_2O_3 materials were synthesized by the hydrothermal method using CNC as template. The surface area and pore volume of the α-Fe_2O_3 sample were 46.5 m^2 g^{-1} and 0.46 $cm^3 \cdot g^{-1}$, respectively, which were compared to 24.5 m^2 g^{-1} and 0.24 $cm^3 \cdot g^{-1}$ of the samples prepared without CNC. Subsequently, the prepared mesoporous α-Fe_2O_3 samples were used as a catalyst during the photo-degradation of methylene blue (MB). The sample prepared with CNC exhibited better photocatalytic activity under the conditions studied than that prepared without CNC. These results indicated that mesoporous α-Fe_2O_3 prepared with CNC would have a great potential to be used as a catalyst in degrading organic dyes during a typical industrial wastewater treatment.

Acknowledgements

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