Mesoporous zirconium phosphate from yeast biotemplate

Xiuying Tian [a], Wen He [a,b,*], Jingjie Cui [c,d], Xudong Zhang [a], Weijia Zhou [a], Shunpu Yan [a], Xianan Sun [a], Xiuxiu Han [a], Shanshan Han [a], Yuanzheng Yue [a,e,*]

[a] Shandong Key Laboratory of Glass and Ceramic, School of Materials Science and Engineering, Shandong Institute of Light Industry, Jinan 250353, People's Republic of China
[b] Biomaterials Research Center, South China University of Technology, Guangzhou 510640, People's Republic of China
[c] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China
[d] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, People's Republic of China
[e] Department of Biotechnology, Chemistry and Environmental Engineering, Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark

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ABSTRACT

Mesoporous zirconium phosphate has attracted increasing interest due to its extraordinary functionalities. In particular, great progress has been made in the synthesis of mesoporous zirconium phosphate using traditional approaches. However, synthesis of mesoporous zirconium phosphate using yeast as biotemplate has not been well studied so far. Here, we show that zirconium phosphate with a mesoporous structure has been synthesized under ambient conditions using yeast as biotemplate. The derived samples were examined by X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDX), transmission electron microscopy (TEM), thermogravimetry/differential thermal analysis (TG/DTA), fourier transform infrared spectroscopy (FTIR), and N_2 adsorption–desorption isotherms. A biotemplated mesoporous zirconium phosphate, possessing a specific surface area (Brunauer–Emmett–Teller, BET) of 217.64 $m^2\,g^{-1}$, a narrow pore distribution centered at 2.7 nm, and pore volume of 0.24 $cm^3\,g^{-1}$, was obtained. We discover that amide carboxyl groups of yeast play an important role in the chemical interaction between protein molecules and zirconium phosphate nanoparticles. Interestingly, an air electrode fabricated using mesoporous zirconium phosphate exhibits remarkable electrocatalytic activity for oxygen reduction reaction (ORR), compared to that of the electrolytic manganese dioxide (EMD) air electrode employed commercially, which has important applications in fuel cell technologies.

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1. Introduction

Mesoporous zirconium phosphate has outstanding chemical and physical properties, and widespread applications in ion exchange [1–3], intercalation [4], proton conduction [5,6], catalysis [7,8], and so on. Recently, mesoporous zirconium phosphate has been intensely studied also as promising materials for application in fuel cell technologies [9–11]. Much effort has been devoted to the template-assisted synthesis of mesoporous zirconium phosphate [12–14]. However, to our best knowledge, the synthesis of mesoporous zirconium phosphate using yeast as biotemplate has not been reported. As known, yeast cells, which have abundant biomacromolecules, are very easy to cultivate and resistant to low pH values and high sugar and ethanol concentrations [15]. The biomacromolecules could induce nanoparticles to form mesoporous structures [16]. Compared to other templates, yeast cells are nontoxic, easy to degrade, and pollution free, which is consistent with environmentally friendly chemistry [17].

Here, we show that mesoporous zirconium phosphate has been synthesized using yeast as a template under ambient conditions. This study explores the influence of amount of yeast and heat treatment temperature to structure morphology and performance of obtained materials. Interestingly, an air electrode fabricated using mesoporous zirconium phosphate exhibits remarkable electrocatalytic activity for oxygen reduction reaction (ORR), compared to that of the electrolytic manganese dioxide (EMD) air electrode employed commercially, which has important applications in fuel cell technologies.

2. Materials and methods

2.1. Materials

The reagents used in this work included $ZrOCl_2\cdot8H_2O$ (99%, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China), $Na_2HPO_4\cdot12H_2O$ (99%, Tianjin Bodi Chemical Co., Ltd.), HCl (36–38%, Yantai Shuangshuang Chemical Co., Ltd), and yeasts (Instant dry

yeast, Angel Yeast Co., Ltd.). Distilled water was used throughout all the experiments.

2.2. Sample preparation

In a typical synthesis procedure, the quantitative dry yeasts were incubated in an aqueous solution of glucose (2 wt.%, 100 mL) at ambient temperature for 30 min. Then 3.22 g of $ZrOCl_2 \cdot 8H_2O$ powders was put into the mixture under the condition of stirring. After stirring vigorously for 12 h, an aqueous solution of 0.2 M (100 mL) disodium hydrogen phosphate was gradually added to the mixture drop by drop. An aqueous solution of hydrochloric acid (0.05 M) was employed to adjust the pH value of the reaction solution to 1–3, which is the range of the presence of zirconium phosphate precipitation. After continued stirring of the mixture for another 2 h, a white gel was formed, which was aged for 48 h. The resulting deposition was recovered by centrifugation at a rotation speed of 4500 rpm, washed five times with distilled water until the conductivity of the filtrate was less than 2 ms/m, and washed one time with ethanol. The resultant product was dried at 353 K for 24 h. The dried sample was calcined at 573, 773, 973, and 1173 K for 2 h. The control sample without yeast cells was prepared by using a similar process.

2.3. Characterization techniques

The as-synthesized samples and samples calcined at different temperatures were examined by XRD technique, on a PANalytical X'Pert PRO X-ray diffractometer (Netherlands) with Cu Kα radiation (λ = 0.15418 nm). The diffraction patterns were collected over the diffraction angle 2θ range of 0–10° and 10–90°, with an acquisition time of 12.0 s at 0.02° step size. Qualitative elemental composition of the sample was carried out by EDX with a S-UTW (super-ultrathin window) detector (EDAX, USA). The BET specific surface areas were measured by a Micromeritics apparatus (ST-08A, Beijing Huapu Analytic Instrument Co., Ltd, China) after the samples were dried at 423 K for 5 h. DTA and TG were carried out on a CRY-2 differential thermal analyzer and TGA/SDTA851^e gravitational thermal analysis in air at a heating rate of 5 K min^{-1}.

The nitrogen (N_2) adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distributions were carried out at 77 K using a computer-controlled sorption analyzer (Micromeritics, Gemini V2380, USA) operating in the continuous mode. Before measurement, the samples were degassed in vacuum at 423 K. TEM (JEM-100X, Japan) operating at 100 kV was employed to characterize the morphologies of the samples. FTIR was performed using a Nicolet Nexus spectrometer (Nicolet, NEXUS 470, USA) by using a KBr wafer technique in order to study the composition of the samples. Infrared spectra were recorded in the region 4000–400 cm^{-1}, with a resolution of 4.00 cm^{-1}.

2.4. Electrochemical setup

The catalyst, acetylene black (AB), activated charcoal, and polytetrafluoroethylene (PTFE) suspension (60 wt.% in H_2O) with weight ratio of 4:1:2:2 were uniformly mixed and dispersed in excess of ethanol. The mixing was finished when a dough-like paste had been produced. The paste was rolled into a sheet of 0.3 mm thickness. Another sheet containing only AB and PTFE with weight ratio of 1:1 was prepared by the same process. The two sheets were then rolled together and pressed into a piece of nickel foam. The foam loaded with active materials was heat-treated at 473 K for 2 h, and thus a 0.5-mm-thick air electrode was obtained.

The electrochemical measurements were performed in a three-electrode configuration. A large-area Pt disk and an Hg/HgO/OH$^-$ (35 wt.%) setup were used as the counterelectrode and the refer-

ence electrode, respectively. A 1 cm^2 active air electrode was served as the working electrode. Aqueous potassium hydroxide solution (35 wt.%) was used as the electrolyte in all experiments. The electrochemical measurements were conducted with an Auto-Lab PG2. STAT 30 electrochemical work station (Autolab, Netherlands). The polarization curves were acquired under sweeping rate of 10 mV/s. The electrochemical impedance spectra were recorded in the frequency range of 100 mHz–100 kHz.

3. Results and discussion

3.1. Thermal analysis

The thermal behavior of the as-prepared sample has been investigated. TGA of the as-prepared sample (Fig. 1a) shows gradual mass loss. The first mass loss, ca. 9.2% from ambient temperature to 400 K, is attributed to loss of adsorption water. The second mass loss, ca. 5.9% in the range 400–536 K, is assigned to loss of crystal water. Another mass loss in the range of 536–645 K is attributed to combustion of the organic template (ca. 9.0%). The last mass loss in the range of 645–923 K is ascribed to the combustion of carbonaceous organic residuals, and the mass loss reaches equilibrium after 923 K. The DTA curve of the as-prepared sample is shown in Fig. 1b. The area up to 400 K in the curve may be attributed to loss of adsorption water. The endothermic valley (400–536 K) could be assigned to loss of crystal water. An exothermic peak in the range of 536–645 K could be ascribed to combustion of the organic template. Another exothermic peak from 645 to 923 K may be attributed to the decomposition of carbonaceous organic residuals. The exothermic peak is broader and lower, which may be attributed to the masking effect of the exothermic peak in the range of 536–645 K. A crystallization peak is observed after 1100 K, which may be derived from the formation of zirconium pyrophosphate (ZrP_2O_7). It is confirmed that the samples calcinated before 1100 K are amorphous.

3.2. Influence of dry yeast amount and heat treatment temperature

In order to investigate the effect of amount of dry yeast and heat treatment temperature on structure morphology, a series of samples has been synthesized. Fig. 2 shows the effect of dry yeast amount and heat treatment temperature on the BET surface areas of samples measured by an ST-08A system. In the range of 353–973 K, for different amounts of yeast, BET values increase first and then decrease with increase of temperature. For the 0.4 g of yeast, the sample calcined at 573 K has a max value of 198.5 m^2 g^{-1}. The high BET surface area may be attributed to the open mesoporous structure of the sample. At 573 K, the organic
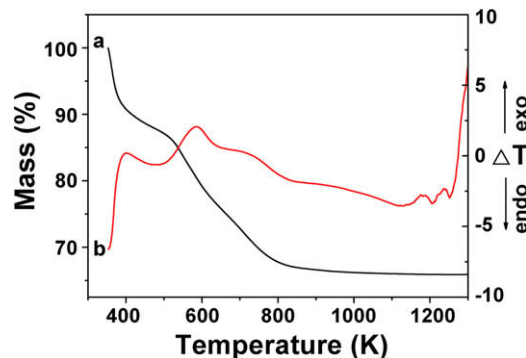

Fig. 1. TGA and DTA profiles of the as-prepared zirconium phosphate sample heated in air.