In situ Formed Fan-Shaped Nanowires in Biomimetic SiO₂: A Multidimensional Composite of Hierarchical Porous Material and Organic Pollutant Adsorption Behavior

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Abstract Fan-shaped SiO₂ nanowires modified SiO₂@C composites with a bio-inspired hierarchical porous structure and a high accessible surface area were prepared by in situ molten salt template method. The combination of biogenic hierarchical porous structure and one-dimensional nanostructure with similar features was successfully obtained by one-pot heat treatment in the presence of rice husk SiO₂ with SiO₂ acting as precursor and ZnCl₂ acting as molten salt and growth template. A large amount of fan-shaped SiO₂ nanowires with numerous tiny branches sprouting from the central nanowires were grown in the inter-porous epidermis and on the surface of rice husk SiO₂ for temperatures up to 1200 °C. The in situ ZnCl₂ molten salt template base-growth mechanism is responsible for the initial formation of SiO₂/ZnCl₂ co-melting nanowires and the subsequent growth of fan-shaped SiO₂ nanowires. The as-prepared samples have been successfully employed as organic absorbers with high efficiency in the field of wastewater treatment.

KEY WORDS: Agricultural waste; Fan-shaped SiO₂ nanowires; Rice husk; Biomimetic porous SiO₂; Waste water

1 Introduction

Considerable attention has been paid to prepare these novel structures via crystallites self-assembly to form three-dimensional (3D) morphologies resembling natural organisms or template methods to produce a hierarchical interconnected framework [1–3]. Many natural materials such as plants possess unique microstructures in the scale

from micrometer to nanometer, thus owning promising adsorption, optical, electronic and magnetic properties. In the past few years, numerous investigations have been carried out for preparing bio-inspired systems with diverse topologies and coordination structures [4–6]. Biomimetic TiO₂ with an extremely high light-harvesting efficiency was prepared by replicating green leaves [7]. Wang et al. [8] prepared sea cucumber-like LiMn₂O₄/C with unique structure of inner nanocrystals and outer microcrystals using spirulina as sacrificial templates. The bio-inspired LiMn₂O₄/C possessed an excellent capacity retention, satisfactory rate property, and a reversible discharge capacity, which could retain 94% of its initial capacity after 200 cycles at a rate of 10 °C [8].

Quantum size effects by nanostructures may provide efficient means to improve the electrical, thermodynamic and photophysical properties of expected functional materials [9–11]. Thus, for an artificially modified biomimetic structure system, it may be essential to have both hierarchically porous structures for providing an

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interconnected structure and one/two-dimensional (1D/2D) nanostructures networks in connection with functional modules. Padmanathan *et al.* [12] designed a hetero-structured supercapacitor electrode from a combination of NiO and In_2O_3 nano-rods with a hierarchical hybrid microstructure on nickel foam. They found that hybrid nanostructures on hierarchically porous structures show a great potential for high-performance energy storage [12]. Biomimetic LDHs/ Al_2O_3 composites with hierarchical pore structures were prepared by combining the biological template method and the hydrothermal method, which employs cotton fibers as bio-templates [13]. The 2D LDHs nano-platelets were fabricated into complex 3D architectures by in situ growth on the surface of Al_2O_3 fibers in a closed hydrothermal system, which presented high specific surface areas up to $292.51 \text{ m}^2/\text{g}$ and relatively high adsorption properties for their hierarchical macro-mesoporous structure. Therefore, in order to improve the performance, biomimetic structures should be modified with nanomaterials, which can be ordered and strongly interconnected, eliminating randomization of the grain network and increasing contact points for good electrical connection, electron transfer and energy transduction. This may be realized through a hierarchical combination of independently controlled, well-connected smaller and larger meso- and macro-pores [12–14].

Generally, most biomasses contain substantial concentrations of amorphous silica which can form in situ SiO_2 nanowires in their hierarchical pores with intrinsic structural properties [15, 16]. Extensive investigations on the synthesis routes of SiO_2 nanowires have been carried out, including chemical vapor deposition and thermal evaporation [17, 18]. However, it may be unsuited to use these methods for biomass SiO_2 to form SiO_2 nanowires and in the meanwhile guarantee to avoid to the internal hierarchical structure.

Therefore, an artificial modified bio-inspired synthesis has been carried out in the present work to construct biogenic hierarchically porous structures with a 1D nanostructure network connection. Uniform fan-shaped SiO_2 nanowires modified biomimetic porous SiO_2/C composites with bio-inspired hierarchical porous structure were prepared using rice husk as main raw material. The biological SiO_2 originated from the decomposition of rice husk played the role of porous skeleton. It was also the silica source for forming fan-shaped SiO_2 nanowires. The formation mechanism of fan-shaped SiO_2 nanowires was discussed in the paper to demonstrate that the artificial hierarchical porous materials with 1D/3D-chain morphology could be elaborated from well-known plants. The as-prepared samples were further employed as an adsorbent for the wastewater treatment.

Fig. 1 XRD patterns **a**, FT-IR spectra **b** and nitrogen adsorption–desorption isotherms **c** pore size distribution **d** of specimens containing 1 wt% R-Ni synthesized at various temperatures

2 Materials and Methods

2.1 Preparation of Samples

All of the reagents used were purchased from the Sino-pharm Group Co. Ltd., without further purification. A lab-made deionized water was applied for all the treatment and synthesis processes. The RH was from Jingmen city, in Hubei Province in China. The original RH was treated with 1 wt% HCl solution under vacuum at 100 °C for 1 h to open the surface structure of epidermis. After being washed for 3 times, the RH was immersed in a zinc chloride (ZnCl_2) solution under vacuum at room temperature for 24 h and then was dried at 80 °C for 24 h and 120 °C for 58 h (ZRH). $\{[\text{Ni}(\text{phth})(\text{phen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ and the dark powder (wt% proportions of Ni element: ZRH = 1:100) were dispersed in a mixed solution of glacial acetic acid and anhydrous alcohol, followed by stirring for 60 min. After the mixtures were dried in an oven at 100 °C for 24 h, the precursor of porous silica @ micropore silicon oxide nanowire materials can be obtained (Ni-RH). $\{[\text{Ni}(\text{phth})(\text{phen})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ was prepared by the reported procedure [19] (R-Ni). The Ni-RH were heat-treated at various temperatures (800–1200 °C) for 3 h with a heating speed of 3 °C/min in a flow of nitrogen to obtain the products (FS-RH). In addition, ZRH were also treated in the same condition to better understand the effect of the R-Ni on the formation of SiO_2 nanowires.

2.2 Characterization

The as-prepared products were characterized by field emission scanning electron microscopy (FESEM, Quanta 400, FEI Company, USA) and transmission electron microscopy (TEM, JEM-2100UHRJEOL, Japan) equipped with energy dispersive X-ray spectroscopy (EDS, Noran 623 M-3SUT, Thermo Electron Corporation, Japan). X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered CuK_α radiation. Fourier transform infrared spectroscopy (FT-IR) data were collected with a PerkinElmer Lambda 35 spectrophotometer over the wavenumber range of 400–4000 cm^{-1} . The specific surface areas and pore sizes of the samples were determined by means of N_2 adsorption–desorption isotherms at 77.35 K by using volumetric adsorption system (ASAP2010 Micromeritics Instrument).

2.3 Adsorption Properties

The as-prepared materials were further employed as an adsorbent for the wastewater treatment. Batch experiments were performed to investigate the adsorption process of

Rhodamine B (RhB) by the as-prepared materials. 100.00 mL of 250 mg/L mg L^{-1} RhB solution was introduced into a 250-mL stoppered conical flask to which 0.1000 g of the prepared adsorbent was added later. The suspension was stirred in a temperature-controlled shaking water bath at a constant speed of 200 r/min. The effect of temperature on the sorption characteristics was investigated by determining the adsorption isotherms at 303, 313 and 323 K. At a given time interval of irradiation, the concentration of RhB in the solution was analyzed using a Lambda 35 spectrophotometer. The effect of temperature on the sorption characteristics was investigated by determining the adsorption isotherms at 293, 303, 313 and 323 K.

3 Results and Discussion

3.1 Structural Properties

Figure 1a shows the XRD pattern of as-synthesized samples. At 1100 °C, two small peaks appear, corresponding to NiO (JCPDS No. 73-1519) and quartz (JCPDS No. 83-2472), respectively. After increasing the temperature to 1200 °C, the NiO peak intensity decreases whereas Ni_2Si (JCPDS No. 48-1339) peaks appear. When the temperature is further increased to 1300 °C, the NiO peaks disappear and $\text{Si}_2\text{N}_2\text{O}$ (JCPDS No. 83-1853) and Ni_2Si peaks are observed.

Figure 1b shows the FT-IR spectra of specimens over the range of 400–4000 cm^{-1} . The band at 3728 cm^{-1} can be attributed to germinal Si–OH groups [15]. The predominant absorbance peak at 1095 cm^{-1} is due to the Si–O–Si asymmetric stretching vibration of the structural siloxane bond [16]. The intensity of this peak decreases at 1200 °C and then disappears after warming up to 1300 °C, suggesting the formation of stretching vibration of the Si–N bond, which can be observed at 800–1100 cm^{-1} from the original Si–O–Si silica structure.

The nitrogen adsorption–desorption isotherms and the pore size distribution of samples are shown in Fig. 1c, d, respectively. The isotherms displaying a sharp knee at the

Table 1 BET parameters obtained from nitrogen adsorption studies

Temperature (°C)	S_{BET} (m^2/g)	V_t (cm^3/g)	D_p (nm)
1100	10.5.031	0.166	1.9124
1200	971.518	0.159	1.9051
1300	786.347	0.282	1.9105

S_{BET} BET surface area, V_t total pore volume, D_p average pore diameter

Fig. 2 a, c, e low- and b, d, f high-magnification SEM images of specimens heated at 1100 °C a, b and 1200 °C c–f; g TEM image (the *inset* is its EDX) f magnified TEM image (The *inset* is its SAED) of SiO₂ nanowire

relative pressure (P/P_0) < 0.5 are type-IV isotherms according to the IUPAC classification [20, 21], indicating the presence of textural meso-pores as well as macro-pores in morphology analysis. The pore sizes of samples are distributed between 1.7 and 100 nm (Fig. 1d).

The pore structure parameters of the samples prepared at different temperatures are listed in Table 1. As seen in Table 1, the BET surface area decreases with the increase in temperature, while total pore volume increases. The BET specific surface areas of samples are 1035.031, 971.518 and 786.347 m²/g, while the total pore volumes are 0.166, 0.159 and 0.282 cm³/g, respectively. The decreased specific surface areas of samples are mainly for epidermal thermal decomposition of active carbon. At the same time, the pores in cross section through central region of lemma appear, which makes the total pore volume be increased.

To better understand the effect of temperature on the morphology evolution, SEM analyses of the specimens

synthesized at different temperatures are shown in Fig. 2. The organic materials (e.g., cellulose, hemicellulose and lignin) and silicon species around the RH can be pyrogenically decomposed to form SiO₂/C epidermal in a suitable temperature range. At 1000 °C, SEM images show that the surface of the sample is not smooth, while the inside epidermal loosens (Fig. 2a). The in situ formed SiO₂ nanowires are formed under the SiO₂/C epidermal (Fig. 2b). After increasing the temperature to 1200 °C, two different morphologies of fan-shaped SiO₂ nanowires form on the rice husk matrix. As shown in Fig. 2c, a large amount of fan-like structures with numerous tiny branches sprouting from the central nanowire appear in the inter-epidermis pores of rice husk SiO₂ (Fig. 2c). The fan-like structure, ca. 20–200 nm in diameter and 7 μm in length, is clearly straight in general (Fig. 2d). The remaining structure is composed of assembled spindle-like branches, which are closely packed (Fig. 2e) and tend to grow in groups on the outer surface of lemma

Scheme 1 Schematic interpretation of multistep formation mechanism of fan-shaped SiO₂ nanowires modified biomorphic porous SiO₂ with RH

with a size of 5–15 μm in length and 2–5 μm in diameter (Fig. 2f).

Figure 2g, h presents TEM images of as-received SiO_2 nanowire, along with its SAED pattern. The diameter of the nanowire is about 250 nm and a few microns in length. The EDX analyses (the right upper inset) indicate that the nanowire is composed of Si and O with an atomic ratio of Si to O of about 60.64:39.36. The result from SAED (the inset) further clarifies that the nanowire is amorphous. Treatment at 1300 $^{\circ}\text{C}$ produces $\text{Si}_2\text{N}_2\text{O}$ nanowires, while the SiO_2 nanowires disappear.

3.2 Formation Mechanism

To explain the formation process of the fan-shaped SiO_2 assemblies, SEM studies of the samples obtained at 700 and 900 $^{\circ}\text{C}$ were carried out. In addition, ZRH were also treated in the same conditions to better understand the effect of the R-Ni on the formation of the SiO_2 nanowires. The main steps are schematically illustrated in Scheme 1. As it is known, most biomasses (including RH) have a hierarchical pore structure, where the outer surface is high ridge with a linear profile, while two layers of thick-walled

Fig. 3 a, c low- and b, d high-magnification SEM images (the inset is its EDX) of specimens containing 1 wt% R-Ni treated at 700 $^{\circ}\text{C}$ a, b and at 900 $^{\circ}\text{C}$ c, d; The low- e high- f magnification SEM images of specimens without R-Ni addition treated at 1200 $^{\circ}\text{C}$

fibers underlay the outer epidermis (Scheme 1) [22]. RH has a unique sandwich structure and a perfect absorption capability. Apart from lignocellulose, there is a high concentration of silica in rice husk. Silica and lignocellulose are connected networks in RH undergoing biomineralization via their root in a soluble form.

After treating by acid solution and immersing in ZnCl_2 solution, Zn ions can diffuse into the RH to form ZRH because ZnCl_2 has excellent hygroscopic and swelling properties. Since molten ZnCl_2 is expected to ionize in the melt as ZnCl^{4+} , which exists in a polymeric network [23–25], the amorphous silica nanoparticles can be obtained from the RH. When the treatment temperature is above the melting point of ZnCl_2 (275 °C), it begins to melt [Scheme 1(3a)] and dissolves some amorphous silica nanoparticles [Scheme 1(3b)]. With an increase in the treatment temperature, $\text{SiO}_2/\text{ZnCl}_2$ co-melting nanowires form continually [Scheme 1 (3c)]. The $\text{SiO}_2/\text{ZnCl}_2$ co-melting nanowires are formed at 700 °C as proved by SEM and EDS (Fig. 3a, b). As temperature is further increased up to the boiling point of ZnCl_2 (733 °C), ZnCl_2 gasifies, making the remaining SiO_2 nanowires. It deserves to note that substantial number of nanopores is left in SiO_2 nanowires as ZnCl_2 gasifies at 900 °C (Fig. 3c, d). When the temperature reaches 1100–1200 °C, ZnCl_2 gasifies

completely. At the same time, it produces hot SiO and Si vapor continuously because of the reaction of SiO_2 with C [Eqs. (1) and (2)]. These vapor phases could diffuse to the SiO_2 nanowires forming the more complete SiO_2 nanowires [Scheme 1(3d, e)].

To better understand the effect of the R-Ni on the formation of SiO_2 nanowires, SEM analyses of specimens without R-Ni synthesized at 1200 °C are shown in Fig. 3e, f. The SiO_2 nanowires appear under the SiO_2/C epidermal. This illustrates that the R-Ni compounds play an important role in promoting the decomposition of the organic matter of rice husk into intermediate species of smaller molar mass and volatile [26–28]. When the temperature reaches 1100–1200 °C, the R-Ni compounds are decomposed forming a dense and hot Ni vapor. Then, this hot vapor is rapidly condensed into small Ni clusters since Ni atoms are cooling down via collisions with the cold buffer gas. RH SiO_2 on the surface can react with Ni clusters to form Ni_2Si as initial nucleation sites [Eq. (3)], which can act as catalyst for the volatilization of carbon.

Fig. 4 **a** Equilibrium adsorption isotherms of RhB on specimens containing 1 wt% R-Ni treated at 1200 °C at different temperatures, **b** pseudo-second-order kinetics for adsorption of RhB at different temperatures, **c** Weber and Morris intra-particle diffusion plot kinetics for adsorption of RhB at different temperatures (concentration of RhB = 240 mg/L, mass of adsorbent = 0.1000 g, volume of RhB = 100.0 mL)

$$q_t = k_{id}t^{0.5} + C. \quad (6)$$

where k_{id} is the intra-particle diffusion rate constant [$\text{mg}/(\text{g min}^{1/2})$] and C (mg/g) is a constant, which is helpful in determining the boundary thickness and may determine the rate-limiting step in FS-RH adsorption.

As shown in Fig. 4c, the intra-particle diffusion model describes well the experimental data in view of the high correlation coefficient, which indicates that the intra-particle diffusion plays a significant role but is not the only rate-controlling step. The possible physisorption, which occurred between the FS-RH and RhB, can be divided into two stages. A fast adsorption step is attributed to the boundary layer and macro-pore diffusion of RhB molecules. A slow adsorption corresponds to the meso-pore gradual adsorption stage. The parameters fitting the Weber and Morris intra-particle diffusion model at different temperatures are also shown in Table 2. It can be seen that intra-particle diffusion controls the adsorption rate because the values of k_{i1} are higher than those of k_{i2} .

4 Conclusion

A facile process is developed to synthesize fan-shaped SiO_2 nanowires modified biomorphic porous $\text{SiO}_2@\text{C}$ composites with bio-inspired hierarchical porous structure and a high accessible surface area with in situ molten salt template method. The in situ ZnCl_2 molten salt template base-growth mechanism is responsible for the initial formation of $\text{SiO}_2/\text{ZnCl}_2$ co-melting nanowires and the subsequent growth of fan-shaped SiO_2 nanowires. The as-prepared products show a good adsorption ability in the removal of RhB from wastewater. The adsorption capacity of FS-RH is about 243–252 mg/g . These distinctive structural materials are expected to be useful in many other applications including catalysis, ceramics and fillers.

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