Foaming-assisted electrospinning of large-pore mesoporous ZnO nanofibers with tailored structures and enhanced photocatalytic activity

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1D large-pore mesoporous ZnO materials have attracted tremendous attention because of their outstanding properties and promising applications in a wide range of fields. In the present work, we report the fabrication of large-pore mesoporous ZnO nanofibers via an improved electrospinning strategy, namely, the foaming-assisted electrospinning technique, combined with subsequent calcination treatment. The as-fabricated large-pore mesoporous nanofibers were systematically characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) specific surface area ($S_{\text{BET}}$). The obtained products possess well-designed 1D mesoporous nanostructure with high purity and homogeneous large pore sizes. It is found that the content of the foaming agent within the solutions plays a crucial role in the formation of large-pore mesoporous ZnO nanofibers, enabling the growth of the fibers in a controlled manner. The resultant large-pore mesoporous nanofibers exhibit excellent photocatalytic activity and significant stability for hydrogen production compared to conventional solid nanofibers. The present work suggests a facile preparation of the large-pore mesoporous ZnO nanofibers, which may open new doors for their potential applications in photocatalysts.

1. Introduction

Hydrogen production by photocatalytic water splitting is a promising technology for the alleviation of the limited fossil fuels supply and environmental contamination. Following the seminal publication of Fujishima and Honda on illuminated TiO$_2$ splitting electrodes for water splitting four decades ago, considerable efforts have been devoted worldwide to design and pursue high-performance photocatalysts with improved photoactivity and stability. Recently, major attention has been devoted to the preparation of mesostructured photocatalysts owing to their intrinsic structural features. Compared with the bulk counterparts, mesoporous materials have the ability to interact with atoms, ions, molecules or even nanoparticles not only at the external surfaces, but also throughout the internal surface of the materials. Particularly, the large-pore mesostructured materials possess more fascinating features such as enlarged pore sizes that could favor the efficient ability of infiltrating the heterogeneous components into the mesoporous channels for achieving considerably higher loadings, which result in large surface areas, abundant surface states, and enhanced photocatalytic performances. Of the various mesoporous architectures, the one-dimensional (1D) nanostructures hold a robust geometry that could remarkably inhibit the agglomeration of nanoparticles, which contributes to a stable photocatalytic performance. Therefore, semiconductor photocatalysts designed for 1D large-pore mesostructures are of paramount interest as potential candidates.

Zinc oxide (ZnO) is one of the most important semiconductors because of its outstanding features such as non-toxicity, direct wide band gap (3.37 eV), large exciton binding energy (60 meV), shortened pathways for electron transport, and chemical stability, which make it a promising gas sensor, photocatalyst and drug carrier. Mesoporous structures of ZnO have inspired prominent research interest owing to its photocatalytic applications, as they can supply more surface active sites and make charge carrier transport easier, leading to performance enhancement. Nevertheless, the photocatalytic capability and efficiency are still relatively low because of the inherently low porosity and instability of the traditional mesoporous ZnO materials. It is important to note that the 1D large-pore mesostructures completely embody the substantial
advantages, and also exhibit a promising morphology that has potential applications in the photocatalytic fields. Therefore, it is of a great significance to explore a simple and economical approach to conveniently synthesize 1D large-pore mesoporous ZnO materials with high porosity and satisfactory pore sizes.

Here, we report a simple strategy for the synthesis of large-pore mesoporous ZnO nanofibers through a foaming-assisted electrospinning process inspired by our previous work, using diisopropyl azodicarboxylate (DIPA) as the foaming agent, wherein the initially released abundant vapor is used for the creation of pores with uniform spatial distribution in the spun precursor fibers during the subsequent calcination process. The as-fabricated nanofibers exhibit a well-defined 1D nanostructure with homogeneous pores, high purity and large pore sizes of \( \sim 35 \) nm. We also find that the content of DIPA in the precursor solutions play a crucial role in the growth of large-pore mesoporous ZnO nanofibers. The as-fabricated ZnO products were examined for their photocatalytic activity during hydrogen photocatalysis and their properties were evaluated. It is believed that the present work will inspire the study of large-pore mesoporous ZnO materials, which could show excellent performance as photocatalysts.

2. Experiments

2.1. Sample preparation

The formation process of the large-pore mesoporous ZnO nanofibers is based on a foaming-assisted electrospinning method. All the reagents were purchased from Aladdin Chemical Reagent Co. Ltd and were directly used without any purification. In a typical procedure, 1.0 g of polyvinylpyrrolidone (PVP, \( M_n = 130000 \)) was dissolved in a mixture of ethanol (6 g) and deionized water (6 g) under continuous stirring at room temperature to form a homogeneous viscous solution. Then, 2.8 g of zinc acetate (ZnAc, \( \text{Zn(CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O} \), 99.99%) were added to the abovementioned solution and the mixture was stirred at 60 \( ^\circ \text{C} \) for 20 min. Subsequently, a varying amount of diisopropyl azodicarboxylate (DIPA, \( \text{C}_8\text{H}_{14}\text{N}_2\text{O}_4 \), 95%) was added to the pellucid solution. The DIPA compositions were obtained samples were referred to as A, B, C, D and E. A molecular sieve column). Once the photocatalytic reaction was complete, the products were naturally cooled down to the ambient temperature.

2.2. Characterization

Scanning electron microscopy (SEM) analysis and energy-dispersive X-ray (EDX) spectrum were carried out by an S-4800 microscope (Hitachi, Japan) operated at an acceleration voltage of 5 kV. X-ray powder diffraction (XRD) pattern was recorded using an X-ray diffractometer (D8 Advance, Bruker, Germany) with Cu K\( \alpha \) radiation (\( \lambda = 1.5406 \)). The Brunauer–Emmett–Teller (BET) specific surface area (\( S_{\text{BET}} \)) of the as-obtained sample was analyzed by nitrogen adsorption using a Micromeritics ASAP 2020 HD88 nitrogen adsorption apparatus (USA). The sample was degassed at 200 \( ^\circ \text{C} \) for 2 h before nitrogen adsorption measurements. The adsorption isotherm was used to determine the pore size distribution using the Barret–Joyner–Halender (BJH) method, assuming a cylindrical pore model. Transmission electron microscopy (TEM) images were collected with a JEM-2010F electron microscope (JEOL, Japan), using a 200 kV accelerating voltage.

2.3. Photocatalytic hydrogen production

The photocatalytic hydrogen production experiments were performed in an online photocatalytic hydrogen generation system (CEL-SPH2N, Beijing China Education Au-Light Co. Ltd) at 10 \( ^\circ \text{C} \) and 0.1 Mpa. A 300 W xenon arc lamp (CEL-HXF300, Au-Light, Beijing) was used as the light source (14 V, 16 A, 16 cm far away from the photocatalytic reactor). In a typical photocatalytic experiment, 100 mg of the catalyst was dispersed with constant stirring in 50 mL of a mixed aqueous solution containing 0.35 M Na\( _2 \)S\( \geq 98.0\% \) and 0.25 M Na\( _2 \)SO\( _4 \) (ACS). Before irradiation, the suspension of the catalyst was dispersed in an ultrasonic bath for 20 min, and then was vacuumized for 30 min to remove the air inside and to ensure that the reaction system was under anaerobic conditions. An 8 mL sample of the generated gas was collected intermittently through the septum, and the hydrogen content was analyzed by gas chromatography (GC7900, TECHCOMP, China, nitrogen as the carrier gas and 5 Å molecular sieve column). Once the photocatalytic reaction for a testing cycle in was completed in 6 h, the reactor was degassed in vacuum for 30 min before starting the subsequent cycle.

3. Results and discussion

3.1. Phase structures and morphology

The obtained as-spun precursor nanofibers and their corresponding calcined products were firstly observed under SEM. Fig. 1(a) shows a typical SEM image of the as-spun polymer precursor of Sample D under low magnification, revealing that the obtained products exhibit a dense fiber-like morphology with a diameter in the range of \( \sim 500 \) nm and length up to
several micrometers. Under higher magnification (Fig. 1(b)), the precursor nanofibers appear uniformly sized along the axial direction and show a smooth surface texture owing to their amorphous polymeric property. Fig. 1(c–f) displays the typical SEM images under different magnifications of the corresponding calcined nanofibers. Notably, the initial long precursor fibers are completely converted into porous nanofibers with a high purity (Fig. 1(e)). However, as compared to the straight precursor nanofibers, the obtained porous products show a curled morphology and the fiber diameter increases to ~570 nm (Fig. 1(d)). These variations are mainly due to the decomposition of the foaming agent, which produces huge amounts of gas during the annealing process, leading to fiber swelling and distortion. A closer observation of the fiber bodies under higher magnification (Fig. 1(e)) suggests that numerous pores with irregular shapes are randomly distributed within the nanofibers and the average pore size approximately exhibits a mean width of ~35 nm, indicating that large-pore mesostructured 1D products are obtained via the present foaming-assisted electrospinning method. Fig. 1(f) depicts a representative cross-section of the large-pore mesoporous nanofibers, confirming that the 3D interconnected pores exist throughout the fiber body.

The element composition and crystal structure of the result product were studied by EDS and X-ray diffraction (XRD). Fig. 2(a) illustrates the typical EDS spectrum of Sample D, confirming the presence of Zn and O in the mesoporous nanofibers. The atomic ratio of Zn to O is close to 1:1, indicating that the mesoporous nanofibers are ZnO with a high purity. The detected C signal arises from the conducting resin to support the SEM sample. Fig. 2(b) presents the XRD pattern of the as-prepared large-pore mesoporous nanofibers. All of the diffraction peaks can be well indexed to the wurtzite phase of ZnO (JCPDS: 36-1451) and no characteristic peaks of other impurities are observed, which further confirms the high purity of the prepared products. The average crystallite size of ZnO was calculated to be ~33.8 nm from the three different prominent planes of (100), (002), and (101) using the Scherrer formula. It is worthy to note the sharp diffraction peaks that suggest a good crystallinity of the large-pore mesoporous nanofibers under the current experimental conditions.

Further characterization of the large-pore mesoporous nanofibers was carried out using TEM. Fig. 3(a) and (b) show the typical TEM images of the randomly selected fiber under different magnifications. In good agreement with the SEM observations, a homogeneous mesoporous structure is clearly observed. It is worthy to mention that such a long mesoporous nanofiber survived the scratching and ultrasonic treatments during the TEM sample preparation process, indicating their high structural robustness. Fig. 3(c) shows the corresponding selected area electron diffraction (SAED) pattern (Fig. 3(c)) recorded form the marked area of A in Fig. 3(a). The diffraction spot rings indicate its polycrystalline nature and could be sequentially indexed to the crystal planes of a wurtzite phase of ZnO (JCPDS: 36-1451). Furthermore, a representative high magnification TEM (HR-TEM) image (Fig. 3(d)) recorded from the marked portion B, shown in Fig. 3(b), indicates that the large-pore mesoporous nanofibers possess a well-defined crystal structure with few defects such as dislocations and stacking faults. Fig. 3(e) is an enlarged lattice fringe image of the marked area of C in (d) and the measured d-space of 0.282 nm between two sets of fringes corresponds to the (100) plane of the hexagonal wurtzite structure ZnO, as already indicated by the XRD analysis.

To achieve the fabrication of the large-pore mesoporous ZnO nanofibers in a controlled manner, another four experiments were carried out by adjusting the DIPA content in the initial solutions (Table 1). Fig. 4 display the representative SEM images under different magnifications of the result products of Samples A, B, C and E. The results suggest that when DIPA is absent from the solutions (Fig. 4(a1) and (a2)), only ordinary solid fibers without pores can be obtained, suggesting that the introduced foaming agents are critical for the formation the mesoporous structures. However, once the DIPA content is increased to 7 wt% (Fig. 4(e1) and (e2)), the obtained products show mesoporous microspherical structures instead of fiber shapes. This could be attributed to excessive vapor released after introducing the DIPA foaming agents, which creates plethoric pores and segments the fibers with nano/microsized units, thus forming the mesoporous microspheres in the end. Thus, the exorbitant content of DIPA used in the solutions is also not suitable for the growth of the large-pore ZnO mesoporous nanofibers. Moreover, it should be noted that the low content level of DIPA (such as 4 wt%) is insufficient for the growth of well-defined mesoporous fibers and there is merely some sporadic pore distribution in the fiber bodies (Fig. 4(b1) and [b2]). According to the present experimental results, when the DIPA content is 5 wt% and 6 wt%, the well-defined large-pore mesoporous ZnO nanofibers can be obtained via the foaming-assisted electrospinning method.
As a consequence, it may be guaranteed for the growth of large-pore mesoporous ZnO nanofibers when the DIPA content in the solutions was designed in the range of 5–6 wt%.

3.2. Tentative mechanism of sample formation

The formation mechanism of the large-pore mesoporous structure is attributed to the special chemical properties of the foamer, which could produce abundant gas during its decomposition. To account for this, a proposed schematic diagram is illustrated in Fig. 5. First, the DIPA is added into the initial solutions and uniformly assembled into the precursor fibers via electrospinning. During the calcination process, once the heating temperature reaches the value for DIPA decomposition (~120 °C), it continually releases abundant vapors (e.g. CO₂, NO₂ and H₂O), leaving behind the highly uniform mesopores distributed in the precursor fibers. This is confirmed by the observation of the fibers after air calcination at 300 °C (Fig. S1, ESI†). Then, with an increase in the temperature, PVP completely decomposes into the vapor phase and is brought out of the furnace. Moreover, ZnAc gets converted into inorganic ZnO to construct the large-pore mesoporous fiber matrix.

Fig. 2 The EDS spectrum (a) and XRD pattern (b) of Sample D calcined at 500 °C for 2 h.

Fig. 3 TEM images of the large-pore mesoporous ZnO nanofibers of Sample D: (a and b) typical TEM images of a single large-pore mesoporous ZnO nanofiber under different magnifications; (c) the corresponding SAED pattern recorded from the marked area A in (a); (d) HRTEM image recorded from the marked area B in (b); (e) the enlarged image recorded from the marked area of C in (d).

Fig. 4 Respective SEM images of the products calcined at 500 °C for 2 h of Sample A (a1 and a2), Sample B (b1 and b2), Sample C (c1 and c2) and Sample E (e1 and e2).
3.3. BET surface areas and pore size distributions

The effect of DIPA on the BET surface area and pore structure of the prepared samples was investigated by using nitrogen adsorption measurements. Fig. 6 shows the typical nitrogen adsorption–desorption isotherms and the corresponding pore size distribution curves for Samples A, B, C, D and E. All the nitrogen adsorption–desorption isotherms exhibit type IV curves with H3 hysteresis, indicating the presence of mesopores. As shown in Table S1 (ESI†), the BET surface area ($S_{\text{BET}}$) of Samples A, B, C and D increases with increasing DIPA content, from 8.23 to 12.6 m$^2$ g$^{-1}$, indicating that the foaming agents can create the pores throughout the entire body of fibers and significantly enhance the $S_{\text{BET}}$ of the resultant nanofibers. The results are further confirmed by the corresponding pore size distribution. As shown in the inset of Fig. 6, Sample A has macropores with a peak pore diameter of around 100 nm. When DIPA is introduced, mesopores begin to appear in samples and the amount of macropores decreases. It should be noted that the peak pore diameter of the samples gradually decreases with the increasing DIPA content, and Sample D has the minimum peak pore diameter with an average pore size of 35 nm. However, for Sample E, the high quantity of the foaming agent destroys the fiber structure and makes them grow into micro-sized spheres, resulting in the decrease of the $S_{\text{BET}}$.

3.4. Photocatalytic activities

The as-prepared five ZnO products were used as the photocatalysts for the evaluation of their photocatalytic H$_2$-production activities under xenon arc lamp irradiation by using Na$_2$S and Na$_2$SO$_3$ mixture as sacrificial reagents. The plots in Fig. 7(a) correspond to the amount of hydrogen evolving from the aqueous suspensions of the five photocatalysts with the increasing irradiation time, as calculated from the standard curves for hydrogen production. It can be seen that the H$_2$ yield in case of all the five photocatalysts continually increases with the irradiation time, suggesting the sustainability of the prepared products. After a 6 h irradiation, the hydrogen evolutions of Samples A to E are ca. 3863, 4170, 4494, 4748, 3704 μmol g$^{-1}$, and the dependence of the different products on the corresponding average hydrogen production is depicted in Fig. 7(b). The imporous ZnO fiber photocatalyst of Sample A and the microsphere morphology of Sample E show a low photocatalytic activity because of their lower BET surface areas. Interestingly, the introduction of a large-pore mesoporous architecture into the fiber resulted in a beneficial improvement in the photocatalytic H$_2$ production activity of ZnO. More interestingly, the hydrogen evolution rate of present larger pore mesoporous ZnO nanofibers is higher than that reported in most other studies for other nano-sized ZnO nanomaterials (Table S2, ESI†). Furthermore, the large-pore mesoporous ZnO fiber photocatalyst of Sample D exhibits the highest hydrogen production rate as compared to that of the two other samples, confirming the relationship between the BET surface area and the photocatalytic activity. To further investigate their reusability and stability, Sample D was chosen as the example photocatalyst and reused for photocatalytic H$_2$ production under the same conditions. As shown in Fig. 7(c), there is nearly no loss of the H$_2$ evolution rate after three recycles (18 h),...
indicating its steady photocatalytic performance during the photocatalytic reaction. The results suggest that the as-fabricated large-pore mesoporous ZnO fibers could serve as potential photocatalyst candidates for energy conversion in order to achieve a highly efficient and stable H₂ evolution. To account for this, a tentative schematic illustration is illustrated in Fig. 7(d). First, the one-dimensional (1D) nanofibers could remarkably inhibit the agglomeration of the nanoparticles, which contributes to a more stable photocatalytic performance. Moreover, the columnar large-pore mesoporous architecture possesses the interconnected channels, which offer more active sites for adsorbing the reactants (e.g., water, Na₂S, and Na₂SO₃ groups) and allows the effective transportation of products (e.g., H₂). In other words, the 1D large-pore mesoporous nanofibers benefit the participating materials for moving easily into/out of the framework to yield a higher reaction rate. The combined effects as mentioned above might be responsible for the enhanced photocatalytic activities of the large-pore mesoporous nanofibers with a higher activity and stability as compared to their solid counterparts.

4. Conclusions

In conclusion, large-pore mesoporous ZnO nanofibers were synthesized via foaming-assisted electrospinning strategy combined with the subsequent air calcination treatment. The obtained ZnO mesoporous nanofibers are thoroughly meso-structured, with a high purity and a large pore size of ~35 nm. The employment foamer (DIPA) in the initial solutions plays a crucial role in the growth of the large-pore mesoporous ZnO nanofibers by enabling the fabrication of the nanofibers in a controlled manner. The photocatalytic activity for the hydrogen evolution under the splitting water of the as-fabricated products shows that the large-pore mesoporous nanofibers exhibit the highest photocatalytic activity of 791 μmol h⁻¹ g⁻¹, which is higher than that of the conventional solid nanofibers. The methodology and results described in the present work may offer a straightforward guideline for the immobilization of high performance ZnO mesoporous materials, and could possibly be utilized for photocatalytic hydrogen production.

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References
