One-Step Facile Preparation and Photoluminescence Properties of *Tetrakis*(4-carboxyphenyl)porphyrin Functionalized Zinc Oxide Nanostructures

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We developed facile synthetic procedure to prepare zinc oxide nanorods functionalized with a *tetrakis*(4-carboxyphenyl)porphyrin molecules by a better understanding of their coordination chemistry. The obtained samples are hexagonal Wurtzite structures characterized by X-ray diffraction spectra. FTIR data verify the porphyrin functionalized zinc oxide nanorods through coordination interaction between zinc of zinc oxide nanostructures and carboxylic groups of *tetrakis*(4-carboxyphenyl)porphyrin molecules. TEM images reveal that optimal reaction time of the uniform nanorods with sharp tips is about 60 min. A possible formation mechanism of the zinc oxide nanorods with sharp tips has also been proposed. Photoluminescence (PL) characterization of the functionalized nanorods shows that these nanorods exhibit strong emission at 460 nm, a red-shift of about 15 nm at UV wavelength (393 nm) and special optical properties in yellow-green emission, compared with that of the corresponding nanorods and nanowires in previous reports.

Keywords: Porphyrin, Zinc oxide, Nanorods, Photoluminescence, One-step.

INTRODUCTION

Zinc oxide, an environmentally friendly oxide semiconductor, has become one of the most important functional materials with a wide range of envisaged applications¹⁻³. Therefore, considerable efforts have been directed towards the preparation of zinc oxide nanostructures. In particular, zinc oxide nanostructures have emerged as a fascinating metal oxide semiconductor in solar cells, due to their wide band gap as well as excellent thermal, chemical and structural features⁴⁻⁸. Zinc oxide nanomaterials with 1D structures, such as nanowires or nanorods, are especially attractive, owing to their tunable electronic and optoelectronic properties, together with the potential applications in the nanoscale electronic and optoelectronic devices⁹⁻¹¹. Recently, a few studies on zinc oxide nanowires prepared by chemical vapor transport⁹, physical vapor deposition approaches¹⁰, anodic alumina membrane templates¹¹, hydrothermal method were reported¹².

Porphyrin derivatives, which have been extensively and intensively investigated as advanced molecular materials¹³⁻¹⁵, are of special interest as they possess well-defined π -conjugated electronic systems from chlorophyll units that are exploitable for artificial light harvesting, electronic memory or switch devices and optical devices¹⁶⁻¹⁸.

In recent years, porphyrin derivatives can be used as a kind of dye to modify some inorganic semiconductor nano-

materials^{5,19,20}. Metalloporphyrins such as iron-porphyrin, cobalt-porphyrin and manganese-porphyrin exhibited good electrocatalysis toward many small molecules related to life processes²¹⁻²³. However, their photochemical and photoelectrochemical applications are limited, due to the inhibitive transition from $3a_{2u}(\pi)$ to $4e_g(\pi^*)$ in the presence of these central metal ions²⁴. In contrast, free-base porphyrin are good alternatives with good photochemical and photoelectrochemical properties since they have ultrafast electron injection, slow charge recombination kinetics and high absorption coefficients²⁵⁻²⁸. Nevertheless, it is through two steps that inorganic semiconductor materials were modified with this kind of functional molecules in previous studies. That is to say, firstly, zinc oxide nanostructures were prepared by hydrothermal method, template method and other conventional methods. Secondly, dye molecules were employed to modify the surface of zinc oxide nanostructures obtained²¹. However, to the best of our knowledge, it is rarely reported on zinc oxide nanostructures functionalized with *tetrakis*(4-carboxyphenyl)porphyrin by one-step facile prepare without the assistance of surfactants.

In this study, we used carboxylic-group-containing free-base porphyrins to functionalize zinc oxide nanorods by a facile method without the assistance of surfactants. 5,10,15,20-*tetrakis*(4-carboxyl phenyl)-porphyrin possess four carboxylic groups, which can be used to coordinate with zinc initially and then stabilize zinc oxide nanostructures in the process of

reaction. Hence, this simple system would avoid a possible surface occupation by the co-stabilizers, which may block the fixation of the *tetrakis*(4-carboxyphenyl)porphyrin molecule on the surface of zinc oxide nanorods. Thus, the porphyrin functionalized zinc oxide nanostructures have a potential application in photoelectric conversion, biosensor and photocatalysis.

EXPERIMENTAL

5,10,15,20-*Tetrakis*(4-carboxyl phenyl)-porphyrin shown in Fig. 1 was synthesized according to the reported method²⁹.

Powder X-ray diffraction (XRD) patterns were obtained on a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite monochromatized high-intensity $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The accelerating voltage was set at 50 kV, with 100 mA fluxes at a scanning rate of $0.06^\circ \text{ s}^{-1}$ in the 2θ ranges $10\text{--}90^\circ$, respectively. The transmission electron microscopy (TEM) images and electronic diffraction (ED) patterns were recorded on a JEM-2100 (JEOL, Japan) with an accelerating voltage of 200 kV. The room-temperature photoluminescence spectrum was recorded on a Perkin-Elmer LS-55 luminescence spectrometer with a Xe lamp as the excitation source. The excitation wavelength used in the photoluminescence measurement was 310 nm.

Fig. 1. Molecular structures of 5,10,15,20-*tetrakis*(4-carboxyl phenyl)-porphyrin (a) and H_2TCPP^+ (b), respectively

Preparation of zinc oxide nanorods: In a typical preparation, A solution of zinc nitrate (1.45 g) was added to a solution of sodium hydroxide (2 g) in 15 mL deionized water under magnetic stirring at room temperature. The transparent colloid is assigned as solution A. In addition, *tetrakis*(4-carboxyphenyl)porphyrin (0.0124 g) to a solution of sodium hydroxide (0.0025 g) in 5 mL deionized water under magnetic stirring at room temperature, which is assigned solution B. Subsequently, solution B was rapidly added to solution A. After being stirred vigorously for a further 0.5 h, the mixture was sealed in a Teflon-lined stainless-steel autoclave of 25 mL capacity and heated at 120°C for different time. The products was collected by filtration, washed several times with NaOH dilute aqueous solution ($\text{pH} = 8$), distilled water and ethanol in turn and then dried at 60°C for 6 h.

RESULTS AND DISCUSSION

The XRD pattern of the as-prepared zinc oxide nanorods functionalized with *tetrakis*(4-carboxyphenyl)porphyrin molecules in a typical procedure is shown in Fig. 2. All the diffraction peaks are in well agreement with the JCPDS file for zinc oxide (JCPDS 36-1451, $a = 3.249 \text{ \AA}$, $c = 5.206 \text{ \AA}$), which can be indexed as the hexagonal wurtzite structure of zinc oxide. The sharpness of the peaks implies a high crystallinity of the as-produced sample.

Fig. 2. XRD pattern of *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods with sharp tips

Fig. 3 shows the morphologies of the porphyrin functionalized zinc oxide samples at hydrothermal conditions for 60 min. As shown in Fig. 3A and 3B, most functional zinc oxide nanorods with sharp tips are uniform with a diameter ranged from 650 to 850 nm and length ranged from 4 to 5 μm and the uniform nanorods assembled into flower-like structures. To gain further insight into the nanorods, a HRTEM image taken from a typical area of an individual nanorod shown in Fig. 3C was exhibited in Fig. 3B. It can be clearly seen that the lattice fringes of an interplane distance was measured to be 0.256 nm which correspond to the (002) plane of zinc oxide nanorods, indicating that the zinc oxide nanorod is a single crystal in nature. The selected area electron diffraction (SAED) pattern

inserted in Fig. 3D indicates that the nanorod is single crystalline and can be indexed as the hexagonal zinc oxide phase. This result is in accordance with the XRD results in Fig. 2. The SAED patterns and the HRTEM image of the nanorod indicate that (001) is the growth direction of the zinc oxide nanorods.

Fig. 3. TEM images (A), (B) and HRTEM image (C) of *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods with sharp tips obtained for 60 min. The SAED pattern of *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods (D)

To understand the evolution process of porphyrin functional zinc oxide nanorod with sharp tips, several experiments were performed for different experimental times. In the typical procedure, the autoclave was heated at 120 °C for 15, 30, 45 and 60 min, respectively. The morphologies of nanostructures at different hydrothermal time are shown in Fig. 4. From Fig. 4, it can be seen that amorphous fragments formed after hydrothermal reaction for 15 min at 120 °C (Fig. 4A). Then, most of the nanorods of zinc oxide without tips formed when the hydrothermal time lasted for 0.5 h (Fig. 4B). However, the zinc oxide nanorods formed at the experimental conditions are not uniform in length and width, which size varied from 93 nm to 533 nm in width and from 1.03 to 1.82 μm in length. Furthermore, as shown in Fig. 4C, a few porphyrin functionalized zinc oxide nanorods with sharp tips began to form when the hydrothermal time lasted for 45 min, while most morphologies of porphyrin functionalized zinc oxide were kept rod shapes. Finally, uniform zinc oxide nanorods with sharp tips functionalized with *tetrakis*(4-carboxyphenyl)porphyrin molecules formed when the hydrothermal time lasted for 60 min (Fig. 3A). Moreover, the angle of the conical structure varied from 31 to 37°.

Fig. 4. TEM images of *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanostructures formed at different hydrothermal reaction time: (a) 15 min, (b) 30 min, (c) 45 min

Zinc oxide nanorods functionalized with *tetrakis*(4-carboxyphenyl)porphyrin molecules through one-step method were proved by FTIR analysis. Fig. 5 comparatively studied FTIR spectra of *tetrakis*(4-carboxyphenyl)porphyrin and *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods, respectively. The FTIR of *tetrakis*(4-carboxyphenyl)porphyrin showed a peak at 1697 cm⁻¹ due to the carboxylic group of *tetrakis*(4-carboxyphenyl)porphyrin and another peak at about 1401 cm⁻¹ attributed to the B_{3u} vibration of porphyrin

(Fig. 3a)³⁰. By comparing the FTIR spectra of *tetrakis*(4-carboxyphenyl)porphyrin with that of *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods, a transformation of the carboxylic group of TCPP at 1697 cm⁻¹ to typical carboxylate species with a broad band at 1640 cm⁻¹ was observed in the *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods (Fig. 5b). Moreover, an additional peak at 1390 cm⁻¹ could be observed due to the B_{3u} vibration of *tetrakis*(4-carboxyphenyl)porphyrin on the FTIR of *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods. These results suggested that *tetrakis*(4-carboxyphenyl)porphyrin molecules were successfully combined with zinc oxide nanorods through the coordination bond between zinc oxide nanoparticles and the carboxylic groups of *tetrakis*(4-carboxyphenyl)porphyrin.

Fig. 5. FTIR spectra of *tetrakis*(4-carboxyphenyl)porphyrin (A) and *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods (B), respectively

Growth mechanism: Various surfactants can be used in synthesis of various inorganic nano-materials^{31,32}. During the experimental process, *tetrakis*(4-carboxyphenyl)porphyrin molecules serve not only as a good template to confine the growth of zinc oxide to form the one dimensional zinc oxide nanorods, but also as a substitute of some surfactants through coordination interactions between zinc oxide and carboxyl groups of porphyrin molecules. This interaction was verified by FT-IR data. On the basis of information obtained, a growth process of zinc oxide nanorods with sharp tips can be proposed via the following mechanism.

At the beginning of our experiment, the element zinc exists as $\text{Zn}(\text{OH})_4^{2-}$ as colloids formed according to reaction (1), whereas *tetrakis*(4-carboxyphenyl)porphyrin molecules are changed to anions with four negative charges (Fig. 1b) by the

addition of NaOH aqueous solution (reaction 2), which benefits coordination occurred between carboxyl groups of ionizing porphyrin molecules and Zn^{2+} . Then, OH^- from $\text{Zn}(\text{OH})_4^{2-}$ would be partially substituted by carboxyl groups of porphyrin anions (reaction 3). In other words, a competitive coordination reaction occurred between OH^- of $\text{Zn}(\text{OH})_4^{2-}$ and carboxyl groups of porphyrin anions in the mixing process. Finally, $\text{Zn}(\text{OH})_2$ and $\text{Zn}(\text{OH})\text{X}(\text{H}_2\text{TCPP})\text{Y}$ can be decomposed into zinc oxide nanostructures with the aid of porphyrin molecules by hydrothermal treatment (reactions 4-6). According to the previous reports, it is known that CTAB not only accelerates the reaction speed of the growth units, but also leads to their oriented-growth³³. However, in this study, it can be found that porphyrin molecules served as the similar function to CTAB to induce the growth of zinc oxide nanorods. Hence, when the precursor was heated at 120 °C under hydrothermal process, the $\text{Zn}(\text{OH})_2$ rapidly decomposed and transformed to zinc oxide in a relatively short time via reaction (5). Simultaneously, according to the previous studies^{34,35}, the (001) plane with the most rapid growth rate, disappears in hydrothermal processes, leading to zinc oxide nanorods with a sharp tips.

Photoluminescence spectra: The *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods obtained by one-step facile method, since this suggests possible interesting optical properties of the *tetrakis*(4-carboxyphenyl)porphyrin functionalized 1D structures. The room temperature photoluminescence spectrum of the as-obtained *tetrakis*(4-carboxyphenyl)porphyrin functional zinc oxide nanorods with sharp tips was examined, shown in Fig. 6. Emission at 395 nm in *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods was observed, which comes from recombination of excitonic centers in the 1D nanoparticles^{36,37}. Interestingly, it is worth noting that the UV emission exhibits a red-shift of about 15 nm, compared with that of zinc oxide nanorods and nanowires without porphyrins in the previous report³⁸. In addition, it can be found several emission bands, including a weak emission at 435 nm, a strong blue emission at 460 nm, as well as a weak blue-green emission at 480 and 490 nm, which may originate from the electron transition from the level of the ionized oxygen vacancies to the valence band³⁹. However, the broad yellow-green emission can be observed at 500-

Fig. 6. Photoluminescence spectrum of *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanorods

600 nm, which is ascribed to binding porphyrin molecules to zinc oxide nanorods with sharp tips as well as the relatively strong interaction between zinc oxide and porphyrin molecules⁴⁰. The photoluminescence of porphyrin nanoaggregates were found to be quenched, due to the intensive interactions between porphyrin molecules in the formed nanoaggregates⁴¹. This similar results can also be observed in other fluorescence molecules, according to the previous investigations^{42,43}. Zinc oxide may also interact with O/N atoms of the porphyrin molecules, thus weakening the fluorophore bond and enhancing its fluorescence emission⁴⁴.

Conclusion

In summary, porphyrin functionalized zinc oxide nanorods with sharp tips have been successfully prepared through one-step facile method. The *tetrakis*(4-carboxyphenyl)porphyrin functionalized zinc oxide nanohybrids formed through the coordination bond between zinc of zinc oxide and carboxylic groups of *tetrakis*(4-carboxyphenyl)porphyrin rather than only physical absorption. This route provides a facile approach for one-step synthesis of inorganic-organic composites/hybrids for potential applications.

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