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# Microstructure, growth process and enhanced photocatalytic activity of immobilized hierarchical ZnO nanostructures

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The hierarchical ZnO nanostructures, branched nanorods, were prepared through a multi-step growth method on glass substrates without any capping agents. The process includes magnetron sputtering deposition of ZnO seed particles and hydrothermal growth of ZnO nanorods. The morphology, growth process and microstructure were characterized using scanning electron microscopy (SEM), high

- <sup>10</sup> resolution transmission electron microscope (HRTEM) and X-ray diffraction (XRD). The hierarchical structure consists of large primal nanorods as the trunks and much smaller secondary nanorods as the branches. Both the trunks and branches are single crystal grown along [0001] direction. The ZnO seed particles which experienced Ostwald ripening are essential for the growth of branched nanostructures. Raman scattering, photoluminescence (PL) emission and UV-Vis absorption were applied to measure the
- <sup>15</sup> defects and optical property. The hierarchical ZnO nanostructures exhibited the enhanced photocatalytic performance in degradation of Rhodamine B (RhB) under UV light, which can be attribute to the increased surface area, improved light harvesting, active surfaces, dense branch network and large amount of defects.

#### **1. Introduction**

- <sup>20</sup> Semiconductor based nanostructures have stimulated a great interest in contemporary materials researches due to their unique property and huge potential in chemical, physical, electronic, and optical applications.<sup>1, 2</sup> As a II-VI compound n-type semiconductor, ZnO has a direct wide band gap of 3.37 eV at <sup>25</sup> room temperature and large exciton binding energy of 60 meV.<sup>3</sup>
- ZnO has shown considerable useful feature including high photoreactivity, chemical and thermal stability and low environmental toxicity.<sup>4,5</sup>
- The wide attractions to ZnO nanostructures, especially one <sup>30</sup> dimensional (1D) structures (*e.g.*, nanorods, nanowires, nanobelts and nanotubes), come from the ease of crystallization and simplicity of fabrication process. In comparison with the normal ZnO 1D nanostructures, the hierarchical configurations are particularly desirable for their unique characteristics of increased
- <sup>35</sup> surface area, advanced geometric structures, specific morphology and atomic arrangements, dense network, and favourable electron transportation.<sup>6-8</sup> These advantages are linked to the functional properties of ZnO, making the hierarchical architectures more attractive in the applications of dye-sensitized solar cells,<sup>6-9</sup> gas <sup>40</sup> sensors<sup>10, 11</sup> and photocatalysis.<sup>12-14</sup>

As a response, considerable efforts have been devoted to fabricate hierarchical ZnO nanostructures. In general, two main approaches have been employed: gas phase processes<sup>15, 16</sup> and solution based routes.<sup>6-9, 13, 14, 17, 18</sup> Hierarchical ZnO <sup>45</sup> nanostructures on In<sub>2</sub>O<sub>3</sub> nanowires have been grown by using a

thermal vapour transport and condensation process.<sup>15</sup> Highdensity ZnO heterostructures were grown on various 1D nanomaterials, including carbon nanotubes, GaN nanowires, SiC nanowires, by thermochemical vapour deposition of Zn.<sup>16</sup> The <sup>50</sup> vapour-liquid-solid protocols generally require high temperatures, involve complicated equipment, and have a low yield.

Aqueous solution approaches are more attractive because of their low-energy consumption, low cost and feasibility for industrial-scale manufacturing. Pioneering hierarchical ZnO <sup>55</sup> crystals were fabricated via site-specific nucleation and growth in solutions with sequential branching events by Zhang and Sounart *et al.*<sup>17, 18</sup> Ko *et al.* reported the "nanoforest" composed of high density, long branched "treelike" multigeneration ZnO nanowire photoanodes selectively grown by a hydrothermal method.<sup>6</sup> Seeded growth of ZnO hexabranched nanostructures was achieved by a laterally epitaxial solution growth strategy.<sup>14</sup> Hierarchical tree-like ZnO arrays with increasing branching order and complexities have been prepared by a simple hydrothermal oxidation of Zn foils in an aqueous medium.<sup>19</sup>

<sup>65</sup> During the solution based preparation, capping agents (*e.g.*, diaminopropane, citrate, ethylene diamine, diaminobutane, and polyethylene glycol) have been frequently applied as structure tuning additives.<sup>14, 17-19</sup> The capping agent molecules can slightly etch the surface of ZnO to produce nucleation sites for the <sup>70</sup> secondary growth. Without these structure directing agents, hierarchical ZnO structures could not be produced owing to the absence of the nuclei <sup>19</sup>. However, reports on the physical introduction of nucleation sites are very limited.<sup>6</sup>

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In this paper, we report a multi-step nucleation-growth process

without using capping agents to form ZnO branched nanorods. To the best of our knowledge, although hierarchical ZnO nanostructures have been fabricated as described above, there is still no report on the realization of branched architectures via <sup>5</sup> magnetron sputtering. We used such a technique to obtain the seed particles, from which the branches of hierarchical ZnO nanostructures have developed. A possible mechanism has been suggested to elucidate the formation and growth process of the ZnO branches. The morphology, microstructure, crystallographic <sup>10</sup> phase, optical property and photocatalytic performance of the ZnO samples were investigated.

Furthermore, the prepared ZnO nanostructures were immobilized on glass substrates, offering themselves the advantages of easy recycling over the free-standing powders <sup>15</sup> when they are served as photocatalysts. As expected, the hierarchical ZnO nanostructures displayed the high photocatalytic activity in organic dye degradation. The influencing factors for the photocatalytic enhancement such as the branched structure, active facets and instinct defects have also been discussed.

#### 20 2. Experimental

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#### 2.1 Preparation of hierarchical ZnO nanostructures

#### 2.1.1. Growth of ZnO nanorods (NRs)

All chemicals of analytical grade and de-ionized (DI) water were used throughout this study. Glass substrates were pre-coated with <sup>25</sup> ZnO seed layers by magnetron sputtering. The details are described elsewhere.<sup>20</sup> The ZnO NRs were grown from the ZnO seed layers via a hydrothermal method.<sup>21, 22</sup> An aqueous solution containing 25 mM zinc nitrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 98%) and hexamethylenetetramine (HMT) (C<sub>6</sub>H<sub>12</sub>N<sub>4</sub>, 99%) with an equal <sup>30</sup> molar ratio was prepared. Diluted nitride acid (HNO<sub>3</sub>, 5M) was

- added dropwise to adjust the initial pH value to 5. The aqueous solution was then transferred into a sealable glass jar, in which the glass substrates with the ZnO seed layers were held facedown. The whole set was put into an oven at 95°C for 4 h, after <sup>35</sup> which the glass substrates were withdrawn from the solution,
- rinsed with DI water and dried at 60°C overnight.

#### 2.1.2 Deposition of ZnO seed particles

The glass substrates with the ZnO NRs were then loaded into a magnetron sputtering unit installed with a ZnO target (99.99%).

<sup>40</sup> The background vacuum pressure of the sputter chamber was lower than  $6.7 \times 10^{-4}$  Pa. Argon gas (99.999%) was introduced into the chamber as the working gas with a flow rate of 10 sccm and a pressure of 1.33 Pa. Sputtering was performed with a DC current of 0.25 A for 2 h to deposit ZnO seed particles onto the <sup>45</sup> ZnO NRs.

#### 2.1.3 Growth of ZnO branched nanorods (BNRs)

The ZnO BNRs were acquired via the second hydrothermal method. The procedure was the same as the first hydrothermal method in section 2.1.1, except that no HNO<sub>3</sub> was added to the <sup>50</sup> aqueous solution and the initial pH value was 7. The ZnO

nanorods with seed particles (NRs-SPs) were immersed upside down into an aqueous solution containing 25 mM Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and HMT with an equal molar ratio. After holding the samples at 95°C for 4 h, the hierarchical ZnO <sup>55</sup> nanostructures were obtained on the glass substrates.

#### 2.2 Sample characterization

The crystal structure of the ZnO NRs, ZnO NRs-SPs and ZnO BNRs was identified by X-ray diffraction (XRD, Bruker D2 phaser) using Cu Ka radiation. The morphology and <sup>60</sup> microstructure of the ZnO samples were characterized by a fieldemission gun scanning electron microscope (FEG-SEM, Philips XL-30S) and a high resolution transmission electron microscope (HRTEM, Philips Tecnai G<sup>2</sup> F20, 200 KV). The composition of the ZnO BNRs was conducted with energy dispersive <sup>65</sup> spectroscopy (EDS) equipped on SEM. Raman spectra were observed on Renishaw Raman spectrometer (System 1000) with Ar<sup>+</sup>-ion laser at 488 nm excitation. Room temperature photoluminescence (PL) properties were measured by a Perkin-Elmer LS55 luminescence spectrophotometer with a Xe lamp as

<sup>70</sup> the excitation source at a wavelength of 325 nm. The optical absorption spectra were recorded on an Agilent 8453 UV-vis spectrophotometer.

#### 2.3 Photocatalytic degradation

Degradation of Rhodamine B (RhB) dye aqueous solution was <sup>75</sup> used to evaluate the photocatalytic activity of the ZnO NRs, ZnO NRs-SPs and ZnO BNRs. The photocatalysts grown on glass slides of 25 mm  $\times$  10 mm were immersed into RhB solutions (3 ml, 2.5 mg L<sup>-1</sup>). Prior to the degradation test, they were kept in dark for 30 min to establish an adsorption/desorption equilibrium <sup>80</sup> of RhB with photocatalysts. This guarantees that the measured concentration changes during UV irradiation would be solely caused by photocatalysis. Then the RhB solutions were exposed to two 9 W UV lamps ( $\lambda = 254$  nm, Philip).

The variation of RhB concentration with irradiation time was measured using a UV-vis spectrophotometer (Perkin Elmer Lambda 35). The intensity of the absorption band peak (553 nm) was recorded at a certain time interval. The degradation rate was estimated as  $C/C_0$ , where  $C_0$  is the equilibrium concentration before UV irradiation and C is the concentration at the sampling of time. According to the Beer-Lambert law, the concentration of RhB is linearly proportional to the absorbance value (A) at 553 nm, thus  $C/C_0 = A/A_0$ .

#### 3. Results and discussion

#### 3.1 Morphology and composition

95 Fig. 1 shows the SEM images of the ZnO NRs, ZnO NRs-SPs and ZnO BNRs. The ZnO NRs randomly tilt from the glass substrate, which are 800-1000 nm in diameter and several micron in length. These ZnO rods distribute separately and they are in the hexagonal shape with sharp edges and smooth surfaces, <sup>100</sup> indicating their growth direction is along the c-axis (Fig. 1a). The ZnO NRs-SPs are still in the hexagonal shape, but the surfaces become uneven and the edges are blunt because they were covered by many seed particles (Fig. 1b). The ZnO BNRs are composed of the primal nanorods as trunks and the secondary 105 nanorods as branches. Abundant radial nanorods with much smaller size emanate from the ZnO NRs can be observed on both the top and side surfaces (Fig. 1c-d). The composition of the ZnO BNRs was analysed by EDS. Apart from Si and Ca of the glass substrates and Pt from the pre-SEM coating, Zn and O are the 110 only detected elements, proving no contamination was introduced (Supporting Information Fig. S1).

The formation process from the ZnO NRs to the ZnO BNRs is

schematically illustrated in Fig. 2. The ZnO NRs were firstly grown in an acid aqueous solution by a hydrothermal process, and then the seed particles were placed by magnetron sputtering thereon. After that the intermediates, ZnO NRs-SPs, were <sup>5</sup> undergone another hydrothermal protocol in a neutral solution and finally developed into the hierarchical ZnO nanostructures, ZnO BNRs.

#### 3.2 Growth process of ZnO BNRs

The secondary hydrothermal growth was applied to the ZnO <sup>10</sup> NRs-SPs for different times and the growing process of the ZnO BNRs was monitored as demonstrated in Fig. 3.

Before the ZnO NRs-SPs were immersed in the aqueous solution, a lot of densely distributed crystalline nanoparticles can be observed on the hexagonal bodies to form the rough surfaces. <sup>15</sup> These particles are the ZnO seeds introduced by magnetron sputtering (Fig. 3a). In the early stage, the seed particles enlarge but their quantity reduces. It looks like some seed particles merge with each other and become big embryos with convex shape (Fig. 3b). This can be explained by Ostwald-ripening effect. Ostwald-

- <sup>20</sup> ripening is a spontaneous process triggered by energetic selfdecline, in which the larger crystals grow at the expense of the smaller ones.<sup>23</sup> Smaller crystals are thermodynamically less stable and they rapidly vanish, transferring their mass to the surface and onto larger crystals.<sup>24</sup> In our case, the seed particles are <sup>25</sup> metastable due to the small size, hence they transform into larger
- ZnO crystals through Ostwald-ripening. The embryos keep expanding and gradually contact with each other to form new layers on the primal nanorods (trunks). Meanwhile, the nascent secondary nanorods (branches) with much smaller size emerge
- <sup>30</sup> from the trunk surfaces (Fig. 3c). Some energetically favourable embryos with smaller size became the nuclei for the secondary nanorods during Ostwald-ripening as indicated by the arrows in Fig. 3b. As abundant Zn<sup>2+</sup> and OH<sup>-</sup> existed in the neutral aqueous solution, ZnO branches then grew from these nuclei.
- <sup>35</sup> With the progress of incubation, the branches grow continuously and some parts of the new layers exceed the top surfaces of the trunks (Fig. 3d). The continuing expansion of the new layers also results from the adequate supplement of zinc and oxygen species in the bulk solution. The protuberant parts then
- <sup>40</sup> gradually become the new branches sprouting from the top surface edges, which are perpendicular to the branches on the side surfaces (Fig. 3e). The secondary nanorods enlarge rapidly in length after 3 h, and their hexagonal body shape become more obvious (Fig. 3f-g), implying that the branches are in the same
- <sup>45</sup> growth direction as the primal nanorods. The driving force comes from the intrinsic growth impetus of ZnO crystals, which favours both the trunks and branches growing along the c-axis direction. Some of the ZnO branches are not exactly vertical to their substrates (the side surfaces of ZnO trunks), possibly because
- <sup>50</sup> their root parts were oppressed more or less as the new layers outspreading in the early stage, making their bodies oblique slightly.

As such, the ZnO BNRs have been developed from the ZnO NRs through the growth of the secondary nanorods. The resultant

<sup>55</sup> individual nanostructure shows a hierarchical configuration, which is made up of a big trunk and many smaller branches on its top and side surfaces (Fig. 3h).

#### 3.3 Effect of ZnO seed particles

The necessity of ZnO seed particles was verified by a <sup>60</sup> counterevidence study. The second hydrothermal process was directly applied to the ZnO NRs before the magnetron sputtering in section 2.1.2, which means there were no intentionally-induced seed particles. Fig. 4 gives the morphologies of the products after the ZnO NRs were incubated in the identical aqueous solution for

- <sup>65</sup> 4 h. As expected, very different nanostructures were obtained. Some nanowires appear on the top surfaces of the primal nanorods, but no secondary crystals can be observed on the side surfaces. The nanowire tips are apt to "gluing" together and the nanowires assemble into clustered aggregates (Supporting <sup>70</sup> Information Fig. S2). Since the polar {0001} planes of ZnO are more energetic than the nonpolar {10-10} planes, nuclei for the new crystals would favourably emerge on the top surfaces rather than the side surfaces. As a result, without the seed particles, no
- secondary nanorods have grown from the side surfaces. This result confirms that the ZnO branches are not the derivatives of the ZnO trunks but grown from the seed particles introduced by magnetron sputtering. Thus, the seed particles are essential for preparing the hierarchical ZnO nanostructures.

#### 3.4 Crystal structure

- <sup>80</sup> XRD was performed on the ZnO samples to investigate their crystal structure and orientation. As shown in Fig. 5, all the diffraction peaks are indexed to a typical hexagonal wurtzite ZnO crystal. The highest (100) peak for the ZnO NRs results from the oblique nanorod bodies, which allow a large number of side <sup>85</sup> surfaces with {1010} planes to be exposed to the incident X-ray. It is worth noting that the (002) diffraction enhances and becomes the strongest one for the ZnO NRs-SPs, indicating that the seed particles have a strong c-axis texture. This can be confirmed by the sole (002) peak in the XRD pattern of the ZnO film, which <sup>90</sup> was deposited on glass substrates by the same magnetron sputter
- <sup>50</sup> was deposited on grass substrates by the same magnetion sputter (Supporting Information Fig. S3). The significant increase of the (002) peak for the ZnO BNRs is contributed by the abundant branches grown from the trunk surfaces. The overwhelming (002) diffraction also reveals that the ZnO branches have a preferential <sup>55</sup> growth along c-axis in [0001] orientation. No peaks related to other Zn complexes, such as Zn(OH)<sub>2</sub> and Zn(NO<sub>3</sub>)<sub>2</sub>, are observed, evidence of the pure ZnO phase.

#### 3.5 TEM analysis

The morphology and crystallographic orientation of the ZnO <sup>100</sup> hierarchical nanostructures were further investigated by HRTEM as shown in Fig. 6. It can be seen that a ZnO BNR includes a big nanorod and several smaller nanorods with a straight shape and uniform diameters to form a trunk-branch structure (Fig. 6a & Fig. S4). Fig. 6b-c and 6d-e are typical HRTEM images recorded <sup>105</sup> from a segment of the ZnO trunk and a ZnO branch, from which regular lattice fringes are parallel to their growth axis direction. The distance between the lattice planes was measured to be 0.28 nm, corresponding to the interspacing of the (100) planes of wurtzite ZnO. The results verify that both the trunks and the <sup>110</sup> branches have wurzite single-crystalline structure in a preferential growth along the [0001] c-axis direction, even the two components of the ZnO nanostructures did not form simultaneously.

#### 3.6 Raman studies

Raman scattering is a sensitive characterization method to assess the microstructure and defects of materials. The hexagonal wurtzite ZnO structure belongs to the space group  $C_{60}^{4}$  (P6<sub>3</sub>mc). <sup>5</sup> On the basis of group theory, Raman phonon modes at the  $\Gamma$  point of the Brillouin zone for wurzite ZnO are A<sub>1</sub>+2B<sub>1</sub>+2E<sub>2</sub>+E<sub>1</sub>. Among them, the B<sub>1</sub> mode is normally silent and others are Raman active.<sup>7</sup> The A<sub>1</sub> and E<sub>1</sub> modes are polar and can split into the transverse optical (TO) and longitudinal optical (LO) phonon <sup>10</sup> modes. The nonpolar E<sub>2</sub> mode is composed of two optical phonon modes with a low (E<sub>21</sub>) and a high frequency (E<sub>211</sub>).<sup>25</sup>

Fig. 7 shows the Raman spectra of the ZnO NRs, ZnO NRs-SPs and ZnO BNRs. For all the samples, vibrational peaks can be clearly observed at 334, 380, 439, 581 cm<sup>-1</sup>. The most intensive <sup>15</sup> one at 439 cm<sup>-1</sup> is characteristic of the high frequency  $E_{2H}$  mode of ZnO hexagonal wurtzite structure. The peaks at 334 and 380 cm<sup>-1</sup> can be assigned as the second order Raman scattering arising from zone-boundary phonons  $3E_{2H}$ -  $E_{2L}$  and the transverse optical  $A_1$ (TO) phonon mode, respectively.<sup>7, 26</sup> The peak at 581 cm<sup>-1</sup> <sup>20</sup> corresponds to the longitudinal optical  $E_1$ (LO) phonon mode, which is generally believed to relate to the defects in ZnO, such as oxygen vacancies and zinc interstitials.<sup>10, 26, 27</sup>

The most prominent feature, however, of the results presented in this graph, is the three anomalous Raman vibrational modes at 25 275, 510 and 644 cm<sup>-1</sup> for the ZnO BNRs. Some explanations have been proposed for the origin of these Raman modes observed in ZnO, but no agreement has been reached yet. As these modes have been observed for the doped ZnO with various elements such as Fe, Sb, Al, Ga, and N,<sup>28-30</sup> they were linked to 30 the intrinsic host-lattice defects or doping element related complexes.<sup>28, 29</sup> Manjon et al. showed that the anomalous peaks are attributed to the silent Raman mode B1 of wurtzite ZnO allowed by the breakdown of the translational crystal symmetry induced by defects and impurities.<sup>31</sup> In our experiments, no 35 doping was applied, therefore, we deduce that the three Raman peaks may be originated from the silent B1 mode activated by the intrinsic defects, which is also evidenced by the huge peak of the defect related E<sub>1</sub>(LO) mode of the ZnO BNRs.

It can be noticed that none of the three peaks are seen from the  $_{40}$  ZnO NRs, and as for the ZnO NRs-SPs, the peaks are quite small and only one at 275 cm<sup>-1</sup> is observable. Interestingly, the appearance number of the additional peaks from the ZnO NRs to the ZnO BNRs is in accordance with the relative intensity of their  $E_1(LO)$  mode at 581 cm<sup>-1</sup>. The variation of the anomalous and  $_{45}$   $E_1(LO)$  modes reveals that the intrinsic defects increase from the ZnO NRs to the ZnO BNRs.

#### **3.7** Photoluminescence properties

As an effective technique to investigate the intrinsic defects and the separation efficiency of photo-generated electrons and holes

<sup>50</sup> of ZnO, photoluminescence (PL) analysis was applied. The room temperature PL emission spectra of the ZnO samples are shown in Fig. 8.

The ZnO NRs exhibit a dominant UV emission around 395 nm, which corresponds to the near band edge (NBE) emission of

<sup>55</sup> ZnO. The NBE emission is usually ascribed to the excitonic recombination of the photo-generated holes in the valence band and the electrons in the conduction band.<sup>3</sup> The highest emission

peaks of the ZnO NRs-SPs and the ZnO BNRs, however, are centred at 408 and 423 nm, respectively. It is known that the deep <sup>60</sup> level emission in the visible range is related to the defect states such as oxygen vacancies and zinc interstitials, which would act as luminescence centres.<sup>25, 32</sup> The dominant peaks for the ZnO samples experience red shifts from NBE emission to deep level emission, indicating that the combination of photo-generated

65 electrons and holes reduces from the ZnO NRs to the ZnO BNRs. The highest relative intensity of the blue emission (423 nm) and the blue-green emission (486 nm) of the ZnO BNRs also suggests that the hierarchical ZnO nanostructures possess the largest number of defects, which is consistent with the Raman analysis.

With the reduction of electron-hole combination and most defects, the hierarchical ZnO nanostructures would have a greater potential in photocatalytic applications than the simple ZnO samples (discussed thereinafter).

#### 3.8 UV-Vis absorption

<sup>75</sup> As shown in Fig. 9, the absorption band edges for all the ZnO samples locate in the UV region with an obvious red shift from the ZnO NRs to the ZnO BNRs. Two edges appear for the ZnO NRs-SPs, which may be caused by the light adsorption of the rough surfaces resulting from the deposition of seed particles and <sup>80</sup> the multi-reflection among the seed particles. The absorption

- edge of ZnO BNRs exhibits an obvious red shift to 380 nm, indicating the best light utilization rate. This is because when light passes through the hierarchical ZnO nanostructures, multiple scattering and reflection could happen among the branches and
- 85 the trunks, favouring the light trapping and absorption. The enhanced light harvesting of the ZnO BNRs would also benefit their photocatalytic activity.

#### 3.9 Photocatalysis

The photocatalytic degradation of RhB under UV irradiation was <sup>90</sup> conducted to evaluate the photocatalytic ability of the ZnO NRs, ZnO NRs-SPs and ZnO BNRs. Fig. 10 displays the degradation rate of RhB using different ZnO samples. The blank experiment under identical UV light but without any photocatalyst shows the self-degradation of RhB is very slow. It can be seen that 91.7% of RhB is degraded by the ZnO BNRs after 4 h UV irradiation, in contrast, 73.4% and 52.2% of RhB are removed by the ZnO NRs-SPs and the ZnO NRs, respectively. Obviously, the ZnO BNRs exhibits the best photocatalytic activity, followed by the ZnO

NRs-SPs and the poorest one is the ZnO NRs. The photocatalytic degradation mechanism of semiconductor photocatalysts, such as ZnO, has been well understood and can be formulated as follows:<sup>11, 33, 34</sup>

 $ZnO + hv \rightarrow ZnO (e^{-} + h^{+})$ 

$$e^- + O_2 \rightarrow O_2 \bullet$$

105

110

 $h^{+} + H_{2}O \rightarrow OH \bullet + H^{+}$  $O_{2}\bullet^{-} + H^{+} \rightarrow HO_{2}\bullet$ 

 $HO_{2}\bullet + H_{2}O \rightarrow H_{2}O_{2} + OH\bullet$  $H_{2}O_{2} + hv \rightarrow 2OH\bullet$ 

 $OH \bullet + RhB \rightarrow CO_2 + H_2O$ 

- $h^+ + RhB \rightarrow CO_2 + H_2O$ 
  - $e^{-} + h^{+} \rightarrow$  recombination

Generally, when ZnO nanocrystals are irradiated by UV light with a photon energy hv higher or equal to the band gap, an electron  $(e^{-})$  in the valence band (VB) can be excited to the

conduction band (CB) with the simultaneous generation of a hole (h<sup>+</sup>) in the VB, so the electron-hole pairs will appear.<sup>33, 34</sup> The photo-generated electrons can be accepted by the surfaceabsorbed O<sub>2</sub> molecules or the dissolved oxygen to produce <sup>5</sup> superoxide radical anions (O<sub>2</sub>•<sup>-</sup>). O<sub>2</sub>•<sup>-</sup> will be further transformed into hydroxyl radicals (OH•), which are powerful oxidants to decompose RhB molecules. Similarly, the photo-generated holes can be trapped by the H<sub>2</sub>O molecules and break them apart into OH•. Meanwhile, the holes can directly participate in the <sup>10</sup> decomposition of RhB as OH•.<sup>11, 34</sup> However, the photo-generated electrons and holes can readily recombine to dissipate the energy as light or heat, which will inhibit the photocatalysis process.

Based on the proposed mechanism, several advantages of the <sup>15</sup> hierarchical ZnO nanostructures may contribute to their superior photocatalytic performance. The branched structure of the ZnO BNRs enables the best light harvesting, hence more UV light can be utilized for the photocatalytic process. The branches not only provide the additional surface area for the reaction sites for RhB <sup>20</sup> degradation, but also allow more O<sub>2</sub> molecules to be absorbed, therefore, more OH• can be produced by the ZnO BNRs.

The photo-generated electrons and holes are essential for the phtocatalytic reaction. However, the electron-hole recombination is always unavoidable, leading to a reduction of subsequent redox <sup>25</sup> reactions.<sup>11, 12</sup> If the electrons or holes can be separated or captured by any means, the recombination can be prevented and the photocatalysis will be improved accordingly. The 1D ZnO branches attached to the ZnO trunks create a dense network with direct conduction pathways, which supplies more diffusion paths <sup>30</sup> for electron quick transfer<sup>8</sup> and facilitates the electron-hole separation. Besides, ZnO intrinsic defects, such as oxygen vacancies, can serve as electron acceptors and trap the photoinduced electrons temporarily to restrain the undesirable recombination.<sup>34, 35</sup> Therefore, the largest amount of intrinsic <sup>35</sup> defects also plays a vital role in the predominant photodegradation efficiency of the ZnO BNRs.

Furthermore, it has been reported that the highly polar and energetic {0001} planes (top surfaces) of ZnO crystals are more photoelectrically active than other non-polar planes such as {10-

<sup>40</sup> 10} planes (side surfaces).<sup>5, 36, 37</sup> The ZnO BNRs actually have a large areal proportion of exposed active surfaces, because the ZnO trunks are covered by ample ZnO branches whose {0001} facets are exposed as rod tips, which can be also indicated by the huge (002) peak in the XRD pattern. Consequently, the

<sup>45</sup> photocatalytic activity of the ZnO BNRs is much higher than that of the ZnO NRs whose major exposed surfaces are the inert {10-10} facets. Accordingly, with all the above merits, the ZnO BNRs represent the highest photocatalytic activity.

Among these virtue, we are inclined to believe that the light <sup>50</sup> harvesting is the most significant factor for the improved photocatalytic activity. Because of the unique multi-level morphology, the light scattering and trapping would happen repeatedly among the branches and the trunks, the utilization of the UV light which is the "direct stimulation" of the

<sup>55</sup> photocatalytic reactions will be heightened. This feature is not only beneficial for photocatalysis <sup>38, 39</sup>, but also has vastly contributed to the solar cell efficiency<sup>6-8, 40, 41</sup>.

Finally, the photocatalytic reusability of the ZnO BNRs was

evaluated. Fig. 11 shows the cyclic degradation rate of RhB using on ZnO BNRs sample. After four cycles, the photocatalytic performance is stable and the decrease of the degradation rate is negligible, suggesting that the ZnO BNRs maintain relatively high photocatalytic activity. Thus, the ZnO hierarchical nanostructures are expected to have a long service life as of photocatalysts with high efficiency and durability. Moreover, the ZnO BNRs are supported on removable substrates, which simplify the recycling process such as filtration or centrifugation, making the hierarchical ZnO nanostructures a steady and economical photocatalyst.

Throughout the sample preparation, the ZnO seed particles, the "origin" of ZnO branches, were introduced by magnetron sputtering, which is a key step to realize the hierarchical ZnO nanostructures. Under different deposition time, sputtering energy and/or working pressure, the size and/or the distribution of ZnO 75 seed particles would be varied and the microstructure of the ZnO BNRs can be changed subsequently. It would be interesting to investigate the influence of magnetron sputtering condition on the morphology and photocatalytic property of the hierarchical ZnO

nanostructures, which is under further study.

#### 80 4. Conclusion

In summary, the immobilized hierarchical ZnO nanostructures, branched nanorods, have been synthesized through a combination of magnetron sputtering and hydrothermal growth without capping agents. The ZnO branched nanorods compose of the <sup>85</sup> primal nanorods as trunks and the much smaller secondary nanorods as branches, both of which are single crystal with hexagonal wurtzite phase grown along the c-axis. ZnO seed particles were introduced to the ZnO trunks by magnetron sputtering, which is a crucial step for the formation of the trunk-<sup>90</sup> branch structure. The seed particles went through Ostwaldripening, new layer formation, and rod growth into the ZnO branches in a hydrothermal process.

The ZnO branched nanorods possess a large amount of intrinsic defects which would reduce the recombination of photo-<sup>95</sup> generated electrons and holes. Moreover, the trunk-branched construction enhances the light harvesting, facilitates the electron transport, and provides the additional surface area with exposed active facets. All these jointly result in the superior photocatalytic performance of the hierarchical ZnO nanostructures in RhB <sup>100</sup> degradation.

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#### Notes and references

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- <sup>†</sup> Electronic Supplementary Information (ESI) available: EDS spectrum
  <sup>5</sup> of the ZnO BNRs. SEM image recorded from the top section of a ZnO NR after the second hydrothermal growth. XRD pattern of the ZnO film produced by magnetron sputtering. TEM image of the ZnO BNRs. See DOI: 10.1039/b000000x/
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Fig. 1 SEM images of (a) ZnO nanorods (NRs), (b) ZnO nanorods with seed particles (NRs-SPs), (c-d) ZnO branched nanorods (BNRs); Inset in (a), (b) and (c) is a corresponding cross-sectional SEM image of each sample.



Fig. 2 Schematic illustration of the formation procedure of the immobilized hierarchical ZnO nanostructures.



Fig. 3 SEM images of the ZnO BNRs for different incubation times: (a) 0 h; (b) 0.5 h; (c) 1 h; (d) 2 h; (e-f) 3 h; (g-h) 4 h.



Fig. 4 SEM image of the ZnO NRs after the second hydrothermal growth.



Fig. 5 XRD patterns of the ZnO NRs, ZnO NRs-SPs and ZnO BNRs.



Fig. 6 (a) TEM image of an individual ZnO BNR; HRTEM images of a segment from (b-c) the ZnO trunk and (d-e) a ZnO branch marked with squares in panel (a).



Fig. 7 Raman spectra of the ZnO NRs, ZnO NRs-SPs and ZnO BNRs.

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Fig. 8 Room temperature photoluminescence (PL) spectra of the ZnO NRs, ZnO NRs-SPs and ZnO BNRs.



Fig. 9 UV- Vis absorption spectra of the ZnO NRs, ZnO NRs-SPs and ZnO BNRs.



<sup>10</sup> Fig. 10 Photodegradation rate of RhB by different ZnO photocatalysts.



Fig. 11 Cyclic photodegradation of RhB by the ZnO BNRs.