Cost-effective large-scale synthesis of oxygen-defective ZnO photocatalyst with superior activities under UV and visible light

Jing Wang^{a, b}, Ruosong Chen^a, Yi Xia^{a, c}, Guifang Wang^b, Hongyuan Zhao^b, Lan Xiang^{a*}, Sridhar Komarneni^{b*}

Abstract

A cost-effective solution method was developed to produce ZnO photocatalyst in large quantity, through the conversion of ϵ -Zn(OH)₂ to ZnO in NaOH solutions. Experimental results indicated that the concentrated NaOH solution (4 mol·L⁻¹) promoted the rapid formation of ZnO owing to the enhanced dissolution-precipitation reactions. The large-scale synthesis was also achieved with high-yield and solvent-recyclability. Structural analysis based on X-ray photoelectron spectroscopy, electron spin resonance and photoluminescence revealed that the as-prepared ZnO photocatalyst was rich in oxygen vacancies (V_O). The V_O-rich ZnO photocatalyst exhibited improved visible-light absorption, higher photocurrent responses and superior activities toward the degradation of rhodamine B under both UV ($\lambda \sim 254$ nm) and visible-light illumination ($\lambda > 420$ nm) compared to commercial ZnO and P25 TiO₂ powders, as well as good cycle stability.

Based on the results of photoluminescence and active species detection, the V_O -enhanced photocatalytic activity was attributed to the generation of V_O -isolated level in the band structure. Under UV light, the V_O -level could promote charge separation by trapping the photoinduced electrons, while under visible-light, the V_O -level improved visible-light absorption and facilitated the charge generation. The presently developed synthesis may potentially benefit the large-scale production and low-cost application of ZnO photocatalyst for solar energy utilization.

Keywords: D. ZnO; B. Defects; C. Optical properties; Photocatalysis

1. Introduction

Semiconductor photocatalysis is a promising solution for current environmental and energy-related issues. ZnO has received much attention for photocatalysis applications due to its similar band gap to TiO_2 , the most widely used and classical photocatalytic material. Considering the advantages of ZnO such as low cost, nontoxicity and high quantum yield, it should be a promising alternative to TiO_2 in photocatalysis [1, 2]. However, the wide application of ZnO is still limited due to its lower photocatalytic activity than TiO_2 in most cases [3]. Additionally, the limited number of studies on massive production of ZnO photocatalysts also restricts their large-scale commercialization. Therefore, to meet the needs for practical applications, the synthesis of ZnO photocatalyst should not only aim to achieve higher photocatalytic activity, but also lead to cost effectiveness and high yield.

Although some vapor or thermal approaches are capable of producing ZnO photocatalysts on a large scale at high temperatures [4, 5], solution-based methods are more favorable due to the mild conditions and low cost. To improve the activity of ZnO photocatalysts, most research efforts have been devoted to

1
2
3
4
5
6 controllable solution synthesis of ZnO with desired morphology, size/dimension or hierarchical/porous
7
8
9 structures [6-13]. Although such syntheses to tailor the micro-/nano-scale architectures were effective in
10
11 enhancing the structural-dependent photocatalytic performance, the produced ZnO micro-/nano-architectures
12
13 usually suffered from low efficiency of solar energy utilization, since the intrinsic wide band gap (~ 3.2 eV) of
14
15 ZnO can only absorb UV light (5–7% of the total sunlight [14]). On the other hand, these syntheses were
16
17 generally carried out in dilute solutions (typical zinc concentration: 1-100 mM) leading to very low yields of
18
19 the catalysts. In addition, many of these reported syntheses were rather complex, as they are associated with
20
21 either the high-temperature hydro-/solvo-thermal processes or the use of toxic and expensive
22
23 reagents/surfactants. The above factors will limit the practical application of ZnO photocatalysts.
24
25
26
27
28
29
30

31 By considering all of these limitations, the synthesis of band-engineered ZnO photocatalysts appear to be
32
33 a promising approach for practical application. By doping or introducing defects as “self-doping” to adjust the
34
35 band levels, ZnO photocatalysts with enhanced activity could be simply synthesized in large quantity with
36
37 low cost [15-19]. In particular, the oxygen vacancy (V_O)-rich ZnO is more attractive since no other elemental
38
39 impurities would be introduced, and it has been demonstrated as an efficient photocatalyst under both UV and
40
41 visible-light. For example, Lai et al. investigated the effects of several kinds of defects on ZnO nanocatalysts
42
43 and suggested that only V_O was highly related to the UV photocatalytic activity [19]. Both Wang et al. [20]
44
45 and Ansari et al. [21] reported the V_O -induced band-gap narrowing and enhanced visible-light photocatalytic
46
47 activity of ZnO. Our previous study also demonstrated the V_O -rich ZnO nanosheets as an efficient
48
49 visible-light photocatalyst [22]. However, it remains a big challenge for the large-scale production of V_O -rich
50
51 ZnO photocatalysts that work efficiently under both UV and visible light via a cost-effective method. One the
52
53
54
55
56
57
58
59
60
61
62
63
64
65

other hand, the photocatalytic mechanism of V_O -rich ZnO was still unclear from many of the previous studies.

It was previously proposed that the presence of V_O improved the light absorption and facilitated the charge separation [17, 19-21, 23, 24]. Nevertheless, the V_O -enhanced UV/visible-light activities of ZnO photocatalysts still remains as a controversial topic and needs more investigation.

In this work, we presented a cost-effective solution synthesis of ZnO photocatalyst in large quantity, via a facile phase conversion approach. The as-prepared ZnO photocatalyst with rich V_O exhibited superior activities to commercial ZnO and P25 TiO_2 powders under both UV and visible light. The mechanisms for V_O -enhanced UV/visible-light activities were also discussed on the basis of photoluminescence and reactive species detection.

2. Experimental

2.1. Synthesis

Commercial chemicals of analytical grade and deionized water with a resistivity $> 18 \text{ M}\Omega\cdot\text{cm}^{-1}$ were used in all the experiments. Commercial ZnO (denoted as ZnO-C, $>99.9\%$) and P25 TiO_2 powders were purchased from Sigma-Aldrich and Degussa, respectively.

ZnO photocatalysts were synthesized from $\epsilon\text{-Zn(OH)}_2$ precursor, which was prepared as follows:

$\epsilon\text{-Zn(OH)}_2$ was prepared by drop-wise addition of 200 ml of $2.0 \text{ mol}\cdot\text{L}^{-1}$ ZnSO_4 into 200 ml of $4.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH at 25°C under stirring. The precipitate was filtrated, washed and dried at 25°C for 24 h. 25.0 g of $\epsilon\text{-Zn(OH)}_2$ was dispersed in 100 ml of $4.0 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution, then the slurry was kept at 80°C for 2.0 h. The final ZnO product was filtrated, washed and dried at 60°C for 12 h.

2.2. Characterization

Powder X-ray diffraction (XRD) was used for phase identification using an X-ray powder diffractometer (PANalytical Empyrean, USA) with $\text{CuK}\alpha$ ($\lambda=0.154178$ nm) radiation. The morphology and microstructure of the samples were examined with a field emission scanning electron microscope (FESEM, Nova NanoSEM 630, FEI Company, USA) and a high-resolution transmission electron microscope (HRTEM, JEM-2010, JEOL, Japan). Electron-spin-resonance (ESR) measurements were performed on a JEOL-TE300 spectrometer operating at an X-band frequency of 9.4 GHz. Surface composition and valence band of the samples were characterized by X-ray photoelectron spectrometer (XPS, PHI-5300, PHI, USA). Photoluminescence (PL) spectra and PL decay curves of the samples were measured at room temperature on a FLS920 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) under the excitation of a LED lamp with an excitation wavelength of 325 nm. UV-visible diffuse reflectance spectra were recorded on a Perkin-Elmer Lambda 950 UV-vis-NIR spectrophotometer.

The photoelectrochemical experiments were performed in a three-electrode quartz cells with $0.1 \text{ mol}\cdot\text{L}^{-1}$ Na_2SO_4 electrolyte solution and recorded on an electrochemical system (CHI-660B, China). A UV lamp ($\lambda=254$ nm) and an Xe lamp equipped with an ultraviolet cutoff filter ($\lambda>420$ nm) were employed as the UV and visible-light source, respectively. The working electrodes were prepared by drop-casting the photocatalyst suspensions with a concentration of $10 \text{ mg}\cdot\text{mL}^{-1}$ onto Ti foil and drying at 60°C for 12 h. Platinum wire and Ag/AgCl were used as the counter and reference electrode, respectively.

2.3. Photocatalytic experiments

The photocatalytic activities were evaluated at 25°C by the degradation of rhodamine B (RhB) under light irradiation. UV and visible light were provided by a UV lamp ($\lambda = 254$ nm) and a Xe lamp equipped

with an ultraviolet cutoff filter ($\lambda > 420$ nm), respectively. In a typical run, 10 mg of the photocatalyst was dispersed in 50 mL of RhB aqueous solution ($10 \text{ mg} \cdot \text{L}^{-1}$). Before irradiating, the above suspension was stirred in the dark for 30 min to achieve the adsorption-desorption equilibrium. The suspension was then illuminated under UV/visible light, sampled at regular intervals and centrifuged to remove the catalysts at 5000 rpm for 10 min. The UV-vis absorption spectra of the centrifuged solutions were measured by a Perkin-Elmer Lambda 950 UV-vis-NIR spectrophotometer to determine the concentration of RhB. The initial concentration (C_0) was considered to be the RhB concentration after adsorption equilibrium.

5, 5-dimethyl-1-pyrroline N-oxide (DMPO) in methanol was used for the detection of superoxide radicals ($\text{DMPO} \cdot \text{O}_2^-$). 10 mg samples and 40 μL DMPO were dispersed in 0.5 mL methanol. After 30 s illumination, ESR signals of $\text{DMPO} \cdot \text{O}_2^-$ species were recorded with a JEOL-TE300 spectrometer. PL spectra were used to disclose the formation of $\cdot\text{OH}$ using terephthalic acid (TA) as a probe molecule. Photocatalyst (0.05 g) was dispersed in a 40 mL of the TA ($5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$) aqueous solution with NaOH ($2 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) at room temperature. The suspension was illuminated for 30 min, whose PL spectra were then measured using a FLS920 fluorescence spectrophotometer with an excitation wavelength of 365 nm.

3. Results and discussion

3.1. Large-scale synthesis of ZnO photocatalyst

The large-scale synthesis of ZnO photocatalyst was based on the conversion of $\epsilon\text{-Zn}(\text{OH})_2$ to ZnO in concentrated NaOH solutions. By aging 25 g $\epsilon\text{-Zn}(\text{OH})_2$ in 100 mL of $4 \text{ mol} \cdot \text{L}^{-1}$ NaOH solution at 80°C for only 1 h, complete conversion from $\epsilon\text{-Zn}(\text{OH})_2$ to ZnO was achieved, as demonstrated by XRD analyses (Fig. 1a). About 15.3 g ZnO was produced in a single batch with a zinc yield of ca. 75%. The obtained ZnO product

exhibited a nanorod morphology with diameters of 200-400 nm and lengths of 1-3 μm (SEM and TEM images in Fig. 1b and c). The SAED analysis (inset in Fig. 1c) indicated the c-axis oriented growth of the nanorods, while some irregular spots indicate the existence of lattice disorders. A few damaged domains (marked by dashed yellow circles) were also observed in the HRTEM image of the nanorods (Fig. 1d). Such a lattice deformation could be mainly caused by the surface reconstruction or the existence of defects [25].

According to our previous work, $\epsilon\text{-Zn(OH)}_2$ was converted to ZnO in concentrated NaOH solutions ($\geq 2 \text{ mol}\cdot\text{L}^{-1}$) mainly via the dissolution-precipitation mechanism [26]. This was confirmed in the current case by monitoring the variations of soluble zinc concentration and molar ratio of ZnO in solid products with reaction time, as shown in Fig. 2a. Three growth stages were identified according to the variation trend of soluble zinc concentration. The soluble zinc concentrations increased gradually in the initial time (stage I, 0-20 min) owing to the higher dissolution rate of $\epsilon\text{-Zn(OH)}_2$ than the formation rate of ZnO. Subsequently, the dissolution of $\epsilon\text{-Zn(OH)}_2$ and the formation of ZnO achieved an approximate equilibrium, resulting in the stable zinc concentration in stage II (20-45 min). The continuous dissolution of $\epsilon\text{-Zn(OH)}_2$ and formation of ZnO during stages I and II were evidenced by the gradually increased molar ratio of ZnO in the obtained solid products. The conversion of $\epsilon\text{-Zn(OH)}_2$ to ZnO completed in stage III (45-80 min), and ZnO was continuously precipitated from the supersaturated zinc alkaline solutions, leading to the fast decrease of zinc concentration until the dissolution and recrystallization equilibrium of ZnO was finally achieved.

The concentrated NaOH solutions ($4 \text{ mol}\cdot\text{L}^{-1}$) was critical for the rapid production of ZnO in large quantity. The effect of NaOH concentration on the formation of ZnO was investigated by monitoring the variation of amount of the produced ZnO with reaction time in 100 mL of suspensions, as shown in Fig. 2b.

The increase of NaOH concentration led to the accelerated formation of ZnO and shortened reaction time for complete phase conversion, however, the higher concentration of NaOH decreased the amounts of finally obtained ZnO products due to the increased solubility. The formation rate and final zinc yield were calculated based on the linear increasing part and the equilibrium part of the curves, respectively, and are presented in Fig. 2c. The increase of NaOH concentration from 2 to 4 mol·L⁻¹ led to the increase of formation rate from 0.13 to 0.25 g·min⁻¹, the decrease of conversion time from ca. 140 to 60 min and the decrease of zinc yield from ca. 93 to 76%. The increasing NaOH to 6 mol·L⁻¹ only led to a slight increase of the formation rate to 0.26 g·min⁻¹ but led to a significant decrease of zinc yield from 76 to 56%. Therefore, 4 mol·L⁻¹ NaOH solution was considered as an optimal condition in the current work for the rapid and high-yield synthesis of ZnO photocatalyst. It was notable that although the formation of ZnO nanorods from ε-Zn(OH)₂ precursor was widely achieved previously [26-29], such a rapid and high-yield production has not been reported until now.

The synthesis is also featured with solvent-recyclability. The conversion process could be expressed as:

which indicated that NaOH actually played the role of “solvent” and would not be consumed in the synthesis.

Therefore, after separation of ZnO products from solution at the end of one batch of synthesis, the solution containing NaOH and soluble zinc could be recycled to serve as “solvent” for the next batch of synthesis by simply replenishing the ε-Zn(OH)₂ precursor, as illustrated in Fig. 2d. Since water is the only byproduct, no salts will be accumulated in the cycled solutions, making it very convenient to recycle the solvent (note: extra water can be simply removed by evaporation after several batches). Our results indicated the robust

production of ZnO with unchanged properties even after tens of cycles. In addition, since the cycled solutions were saturated to ZnO, almost 100% zinc yields could be achieved in many cycles. The advantages of cost-effective and high-yield of the present method will benefit the potential large-scale production and low-cost applications of ZnO photocatalyst.

3.2. Structural and optical properties

As indicated above, ZnO was formed from highly-concentrated solution through a rapid dissolution-precipitation route. Such a non-equilibrium process may lead to the generation of high-concentration of defects. Fig. 3a shows the enlarged (100) diffraction peaks of ZnO NR, revealing a slight shift of the (100) peak to lower angles with a deviation of 0.029° compared to that of the standard (100) position (the dashed line), which may be connected with the defect-induced lattice expansion [30]. The structural properties of ZnO NR were further investigated by ESR and XPS spectra. The ESR spectra (Fig. 3b) displayed two kinds of paramagnetic signals. The peak intensity of ESR signal at $g \sim 1.96$ of ZnO NR was almost the same as that of ZnO-C, which was widely accepted to result from neutral shallow donor centers. However, a new significant signal with g -factor=2.01 was observed for ZnO NR, which was commonly attributed to an unpaired electron trapped in an oxygen vacancy site [31], indicating that ZnO NR had a high concentration of oxygen vacancies (V_O). Fig. 1c shows the high-resolution O1s spectra of the two samples. The species centered at ca. 530.2~530.3 eV originated from the lattice oxygen anions, whereas the species centered at 531.6~531.7 eV belonged to the O_x^- ions in the oxygen-defective regions caused by V_O on the surface [32]. The ratios of V_O -related species on the surface of ZnO NR and ZnO-C were 43.6 and 12.4%, respectively, confirming the high concentration of V_O in the ZnO NR. The valence band XPS spectra

(VB-XPS) were also measured (Fig. 3d). Both ZnO NR and ZnO-C samples displayed VB with the edge of the maximum energies around 2.5 eV, similar to that of bulk ZnO (~2.6 eV), indicating that the V_O did not affect the VB position of ZnO NR.

Photoluminescence (PL) analyses were performed to investigate the optical properties and band structures. As shown in Fig. 4a, ZnO NR shows a broad-band green emission centered at ca. 520 nm, while the C-ZnO sample exhibited an intrinsic UV emission located at 384 nm under 325 nm excitation. The visible luminescence emission from ZnO NR could be divided into two peaks, including mainly a green emission at ~520 nm and a weak orange emission at ~620 nm. The occurrence of visible luminescence implied the generation of defects-isolated energy levels between CB and VB of ZnO [33]. According to many previous studies on luminescent properties of ZnO [34-38], the green emission corresponding to an energy of ca. 2.4 eV could be attributed to the recombination of the photoexcited holes in VB with the photoexcited electrons that were trapped in the V_O -level of about 0.8 eV below the CB of ZnO, while the orange emission corresponding to an energy of ca. 2.0 eV should have originated from the recombination of the photoexcited electron in CB with the holes that were trapped in the oxygen interstitial (O_i)-level of about 1.2 eV above the VB of ZnO. This proposed band structure and PL emission mechanism of ZnO NR were summarized in Fig. 4c. The absence of intrinsic UV emission and week orange emission of ZnO NR implied that most of the photoinduced electrons were preferably trapped in the V_O -level. The roles as electron acceptor and trap of V_O -level under light illumination could also be evidenced by monitoring the time-resolved PL decay curve at 520 nm under 325 nm excitation. As can be seen in Fig. 4d, the emission decay data could be normalized and fitted by triexponential kinetics ($I = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$) for which three components were

derived and determined to be : $\tau_1=46.9 \mu\text{s}$, $A_1=2.8\%$; $\tau_2=1.9 \mu\text{s}$, $A_2=70.2\%$; $\tau_3=11.5 \mu\text{s}$, $A_3=27.0\%$). The intensity-average lifetime $\langle\tau\rangle$ was calculated to be $17.3 \mu\text{s}$ through the following equation [39]:

$$\langle\tau\rangle = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}$$

Notably, the decay lifetime corresponding to the green emission was much larger than the common lifetime for band to band UV emission in previous reports, which was of the order of nanosecond [40, 41]. Such long green emission lifetime ($\sim\mu\text{s}$) was also observed by Camarda et al. [34] and Das et al. [42] very recently, which was attributed to the defect-level induced by singly charged V_O . These results implied that the V_O -level could serve as an acceptor and trap for photoinduced electrons to facilitate the charge separation and inhibit the recombination process, which were beneficial for photocatalytic reactions.

The V_O -level would also affect the absorption and photocurrent properties of ZnO NR. The UV-visible diffuse reflectance spectra (DRS) in Fig. 5a revealed that ZnO-C only absorbed the light with $\lambda<420 \text{ nm}$ owing to the intrinsic wide band gap, while the absorption curve of ZnO NR exhibited an obvious red shift to longer wavelength. As ZnO is a direct semiconductor, the plots of $(\alpha h\nu)^2$ versus the energy of the absorbed light would give the band gap (Fig. 5b). The band gap of ZnO NR was determined to be 2.94 eV , slightly smaller than that of ZnO-C (3.13 eV). The large absorption tail occurring in the visible-light regions and narrowed band gap of ZnO NR should be attributed to the occurrence of V_O -level below the CB of ZnO, as suggested by photoluminescence analyses, which is consistent with some previous studies [17, 43]. Fig. 5c and d show the photocurrent responses of samples tested under UV ($\lambda\sim 254 \text{ nm}$) and visible light ($\lambda > 420 \text{ nm}$), respectively. Under UV light, ZnO NR electrode showed a photocurrent of about 1.5 times higher than that of ZnO-C, implying the V_O -enhanced charge generation and separation. Under visible light, ZnO-C electrode

showed very weak photocurrent responses, while the ZnO NR electrode showed an obvious larger photocurrent, about 7 times higher than that of ZnO-C, which should be attributed to the improved visible-light absorption and charge generation mediated by V_O -level.

3.3. UV/visible-light photocatalytic properties and mechanisms

The photocatalytic performances of ZnO NR were evaluated by degradation of RhB under both UV ($\lambda \sim 254$ nm) and visible light ($\lambda > 420$ nm), using commercial ZnO and P25 TiO_2 powders as references. Under UV light, the activity of ZnO NR was obviously higher than that of ZnO-C and even slightly higher than that of P25 (Fig. 6a). For example, the degradation ratios of RhB after 60 min of UV irradiation were 76.4, 63.2 and 82.1%, respectively for P25, ZnO-C and ZnO NR. Under visible light, only about 7.2 and 14.8 % of RhB was degraded after 360 min of irradiation by ZnO-C and P25, respectively, indicating their low visible-light activity. In contrast, in the presence of ZnO NR, over 92% of RhB was degraded after 360 min, resulting in the almost complete decolorization of the RhB solution (Fig. 7c). The apparent rate constants of the tested samples under UV and visible light were determined by the pseudo first-order kinetic equation and displayed in Fig. 7d. These results suggested that the rich V_O in ZnO NR not only improved the UV photocatalytic performance, but also made it highly active in visible-light. Moreover, the enhancement of photocatalytic performance of ZnO NR sample was more significant under visible-light than that under UV light, indicating the V_O -rich ZnO is particularly suitable for visible-light photocatalysis.

The presence of surface generated reactive species such as $\bullet O_2^-$ and $\bullet OH$ on the photocatalysts were employed to investigate the photocatalytic mechanism of ZnO NR under UV and visible light. DMPO in methanol was used for the detection of $\bullet O_2^-$ through ESR signals of DMPO- $\bullet O_2^-$ [44], as shown in Fig. 7a.

ZnO NR showed obvious signals under UV irradiation while weak signals upon visible light illumination, suggesting the formation of $\bullet\text{O}_2^-$ species was not preferable under visible light. On the other hand, generated $\bullet\text{OH}$ was also detected by PL spectra using terephthalic acid (TA) as a probe molecule, as shown in Fig. 8b. TA readily reacts with $\bullet\text{OH}$ to produce a highly fluorescent product (2-hydroxyterephthalic acid) with an emission at ca. 425 nm [45]. The results indicated that $\bullet\text{OH}$ could be produced on the VB of ZnO NR under both UV and visible light irradiation, but more $\bullet\text{OH}$ species were generated under UV irradiation. The contributions of reactive species to the photocatalytic reaction were also evaluated by introducing ammonium oxalate (AO), benzoquinone (BQ) and tertbutyl alcohol (TBA) as scavengers for h^+ , $\bullet\text{O}_2^-$ and $\bullet\text{OH}$, respectively [46], as shown in Fig. 8c. The photocatalytic activity of ZnO NR under UV light were greatly suppressed by the addition of the three scavengers, indicating h^+ , $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ were all involved in the photocatalytic processes. However, under visible light, the photocatalytic activity was only slightly suppressed with the addition of BQ while it was significantly inhibited in the presence of TBA and AO, suggesting that h^+ and $\bullet\text{OH}$ were the main active species in the visible-light photocatalytic reaction.

Based on the PL results and active species detection, the V_O -enhanced photocatalytic mechanisms of ZnO NR under UV and visible light are illustrated in Fig. 8d. According to PL results, a V_O level of about 0.8 eV below the CB of ZnO was generated. Under UV light, electrons and holes were generated on CB and VB of ZnO via direct band-to-band excitation, respectively, and further led to the formation of $\bullet\text{O}_2^-$ and $\bullet\text{OH}$. The photoinduced holes associated with active $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ species could trigger the oxidation of RhB molecules. The photoinduced electrons could also be trapped in the V_O -level, which would inhibit the recombination of electron-hole pairs and prolonging their lifetime. Therefore, in this case, V_O -level mainly played the role of

promoting the charge separation. On the other hand, under visible-light, direct band-to-band excitation was inhibited, electrons were excited to the V_O -level, while the holes leaving behind in the VB and subsequently generated $\bullet OH$ could both lead to the oxidation of RhB. However, the photoinduced electrons that were trapped in the V_O -level could not reduce the adsorbed O_2 molecules because the V_O -level potential (ca. 0.1 eV vs. NHE) is more positive than the standard redox potential $E(O_2/\bullet O_2^-)$ (-0.33 eV vs. NHE, pH=7 [47]), consistent with the DMPO trapping results. Therefore, in the case of visible-light photocatalysis, the V_O -level played the role of “band-gap narrowing”, i.e. mediating visible-light absorption and thereby facilitating the charge generation.

The initial pH value of the photocatalytic reaction solution was optimized for ZnO NR sample. Fig. 8a shows the variation of photocatalytic rate constants of ZnO NR with pH value in the range of 4-12 under UV and visible light. The increase of pH from 4 to 10 led to a gradually increase of the rate constants in both cases, which should be attributed to the more efficient formation of $\bullet OH$ from OH^- than from H_2O leading to a higher oxidation ability [48]. When pH exceeded 10, the accelerated dissolution of ZnO led to the decreased rate constants. Moreover, since the photocorrosion of ZnO was caused by the hole-induced self-oxidation ($ZnO + 2h^+ \rightarrow Zn^{2+} + 0.5O_2$) [49], the increase of pH to 10 would also suppress the dissolution of ZnO by promoting the consumption of photoinduced holes ($OH^- + h^+ \rightarrow \bullet OH$). As a result, the photostability of ZnO was highly improved at pH=10. As shown in Fig. 8b, under UV irradiation, the rate constant of ZnO dropped significantly from 0.0210 to 0.0176 min^{-1} after 6 cycles (a change of ~16.2%) at pH=7. In contrast, the rate constant of ZnO dropped slightly from 0.0302 to 0.0293 min^{-1} (a change of ~3.0%) at pH=10, implying the photocorrosion of ZnO was inhibited at higher pH. The ZnO NR also showed good stability under visible

light (Fig. 8c). Moreover, the representative XRD pattern and SEM image of the used ZnO photocatalyst after 6 cycles did not show any obvious difference compared to the original sample.

4 Conclusion

In summary, this work presented a cost-effective synthesis of ZnO photocatalyst with rich oxygen vacancies in large quantity. The large-scale high-yield synthesis was based on the rapid conversion of ϵ -Zn(OH)₂ to ZnO in concentrated NaOH solutions. The ZnO photocatalyst exhibited superior photocatalytic activities under both UV and visible light compared to those of commercial ZnO and P25 TiO₂ powders owing to the generation of V_O-level. Moreover, the enhancement of photocatalytic performance of ZnO NR sample was more significant under visible-light than that under UV light, indicating the V_O-rich ZnO is particularly suitable for visible-light photocatalysis. The superior UV activity was attributed to the enhanced charge separation, while the high visible-light activity should be related to the improved visible-light absorption and charge generation mediated by V_O-level.

Acknowledgements

This work was financially supported by the National Science Foundation of China (Nos. 51174125, 51234003 and 51374138), National Key Technology Research and Development Program of China (2013BAC14B02).

Jing Wang is grateful for the scholarship from China Scholarship Council (No. 201506210232).

References

[1] S. Sakthivel, B. Neppolian, M. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye comparison of photocatalytic efficiency of ZnO and TiO₂, Sol. Energy Mater. Sol. Cells 77 (2003) 65-82.

- [2] M.D. Hernández-Alonso, F. Fresno, S. Suárez, J.M. Coronado, Development of alternative photocatalysts to TiO₂: challenges and opportunities, *Energy Environ. Sci.* 2 (2009) 1231-1257.
- [3] K.M. Lee, C.W. Lai, K.S. Ngai, J.C. Juan, Recent developments of zinc oxide based photocatalyst in water treatment technology a review, *Water Res.* 88 (2016) 428-448.
- [4] C. Ma, Z. Zhou, H. Wei, Z. Yang, Z. Wang, Y. Zhang, Rapid large-scale preparation of ZnO nanowires for photocatalytic application, *Nanoscale Res. Lett.* 6 (2011) 1-5.
- [5] C. Tian, Q. Zhang, A. Wu, M. Jiang, Z. Liang, B. Jiang, H. Fu, Cost-effective large-scale synthesis of ZnO photocatalyst with excellent performance for dye photodegradation, *Chem. Commun.* 48 (2012) 2858-2860.
- [6] L. Fu, Z. Fu, *Plectranthus amboinicus* leaf extract–assisted biosynthesis of ZnO nanoparticles and their photocatalytic activity, *Ceram. Int.* 41 (2015) 2492-2496.
- [7] Y. Song, P. Shao, J. Tian, W. Shi, S. Gao, J. Qi, X. Yan, F. Cui. One-step hydrothermal synthesis of ZnO hollow nanospheres uniformly grown on graphene for enhanced photocatalytic performance. *Ceram. Int.* 42 (2016) 2074-2078.
- [8] J. Wang, S. Hou, L. Zhang, J. Chen, L. Xiang, Ultra-rapid formation of ZnO hierarchical structures from dilution-induced supersaturated solutions, *CrystEngComm* 16 (2014) 7115-7123.
- [9] Y. Hong, C. Tian, B. Jiang, A. Wu, Q. Zhang, G. Tian, H. Fu, Facile synthesis of sheet-like ZnO assembly composed of small ZnO particles for highly efficient photocatalysis, *J. Mater. Chem. A* 1 (2013) 5700-5708.
- [10] J. Liu, Y. Zhao, J. Ma, Y. Dai, J. Li, J. Zhang, Flower-like ZnO hollow microspheres on ceramic mesh substrate for photocatalytic reduction of Cr (VI) in tannery wastewater. *Ceram. Int.* 42 (2016) 15968-15974.
- [11] F. Xu, Y. Shen, L. Sun, H. Zeng, Y. Lu, Enhanced photocatalytic activity of hierarchical ZnO

nanoplate-nanowire architecture as environmentally safe and facilely recyclable photocatalyst, *Nanoscale* 3 (2011) 5020-5025.

[12] H. Lu, S. Wang, L. Zhao, J. Li, B. Dong, Z. Xu, Hierarchical ZnO microarchitectures assembled by ultrathin nanosheets hydrothermal synthesis and enhanced photocatalytic activity, *J. Mater. Chem.* 21 (2011) 4228-4234.

[13] C. Yu, K. Yang, Y. Xie, Q. Fan, C.Y. Jimmy, Q. Shu, C. Wang, Novel hollow Pt-ZnO nanocomposite microspheres with hierarchical structure and enhanced photocatalytic activity and stability, *Nanoscale* 5 (2013) 2142-2151.

[14] T. Bak, J. Nowotny, M. Rekas, C. Sorrell, Photo-electrochemical hydrogen generation from water using solar energy. Materials-related aspects, *Int. J. Hydrogen Energy* 27 (2002) 991-1022.

[15] I. Ganesh, Al and Li co-doping effects on structural, band-gap, and photocatalytic properties of pyro-hydrolyzed ZnO nano-powder. *Ceram. Int.* 42 (2016) 10410-10421.

[16] M.W. Kadi, D. McKinney, R.M. Mohamed, I.A. Mkhallid, W. Sigmund, Fluorine doped zinc oxide nanowires: Enhanced photocatalysts degrade malachite green dye under visible light conditions, *Ceram. Int.* 42 (2016) 4672-4678.

[17] S. Akir, A. Barras, Y. Coffinier, M. Bououdina, R. Boukherroub, A.D. Omrani, Eco-friendly synthesis of ZnO nanoparticles with different morphologies and their visible light photocatalytic performance for the degradation of Rhodamine B. *Ceram. Int.* 42 (2016) 10259-10265.

[18] S. Mukhopadhyay, P.P. Das, S. Maity, P. Ghosh, P.S. Devi, Solution grown ZnO rods synthesis, characterization and defect mediated photocatalytic activity, *Appl. Catal. B: Environ.* 165 (2015) 128-138.

- [19] Y. Lai, M. Meng, Y. Yu, X. Wang, T. Ding, Photoluminescence and photocatalysis of the flower-like nano-ZnO photocatalysts prepared by a facile hydrothermal method with or without ultrasonic assistance, *Appl. Catal. B: Environ.* 105 (2011) 335-345.
- [20] J. Wang, Z. Wang, B. Huang, Y. Ma, Y. Liu, X. Qin, X. Zhang, Y. Dai, Oxygen vacancy induced band-gap narrowing and enhanced visible light photocatalytic activity of ZnO, *ACS Appl. Mater. Interfaces* 4 (2012) 4024-4030.
- [21] S.A. Ansari, M.M. Khan, S. Kalathil, A. Nisar, J. Lee, M.H. Cho, Oxygen vacancy induced band gap narrowing of ZnO nanostructures by an electrochemically active biofilm, *Nanoscale* 5 (2013) 9238-9246.
- [22] J. Wang, Y. Xia, Y. Dong, R. Chen, L. Xiang, S. Komarneni, Defect-rich ZnO nanosheets of high surface area as an efficient visible-light photocatalyst, *Appl. Catal. B: Environ.* 192 (2016) 8-16.
- [23] J. Wang, P. Liu, X. Fu, Z. Li, W. Han, X. Wang, Relationship between oxygen defects and the photocatalytic property of ZnO nanocrystals in nafion membranes, *Langmuir* 25 (2008) 1218-1223.
- [24] Y. Zheng, L. Zheng, Y. Zhan, X. Lin, Q. Zheng, K. Wei, Ag/ZnO heterostructure nanocrystals synthesis, characterization, and photocatalysis, *Inorg. Chem.* 46 (2007) 6980-6986.
- [25] X. Xu, C. Xu, Y. Lin, J. Li, J. Hu, Comparison on Photoluminescence and Magnetism between Two Kinds of Undoped ZnO Nanorods, *J. Phys. Chem. C* 117 (2013) 24549-24553.
- [26] J. Wang, P. Ma, L. Xiang, Effects of NaOH on formation of ZnO nanorods from ϵ -Zn(OH)₂, *Mater. Lett.* 141 (2015) 118-121.
- [27] J. Wang, L. Xiang, Formation of ZnO rods with varying diameters from ϵ -Zn(OH)₂, *J. Cryst. Growth* 401 (2014) 279-284.

- [28] N.J. Nicholas, G.V. Franks, W.A. Ducker, The mechanism for hydrothermal growth of zinc oxide, *CrystEngComm* 14 (2012) 1232-1240.
- [29] P. Li, H. Liu, B. Lu, Y. Wei, Formation mechanism of 1D ZnO nanowhiskers in aqueous solution, *J. Phys. Chem. C* 114 (2010) 21132-21137.
- [30] H. Zeng, G. Duan, Y. Li, S. Yang, X. Xu, W. Cai, Blue luminescence of ZnO nanoparticles based on non-equilibrium processes defect origins and emission controls, *Adv. Funct. Mater.* 20 (2010) 561-572.
- [31] X. Zou, J. Liu, J. Su, F. Zuo, J. Chen, P. Feng, Facile synthesis of thermal- and photostable titania with paramagnetic oxygen vacancies for visible-light photocatalysis, *Chem. Eur. J.* 19 (2013) 2866-2873.
- [32] K. Kotsis, V. Staemmler, Ab initio calculations of the O1s XPS spectra of ZnO and Zn oxo compounds, *Phys. Chem. Chem. Phys.* 8 (2006) 1490-1498.
- [33] L. Schmidt-Mende, J.L. MacManus-Driscoll, ZnO-nanostructures, defects, and devices, *Mater. Today* 10 (2007) 40-48.
- [34] P. Camarda, F. Messina, L. Vaccaro, S. Agnello, G. Buscarino, R. Schneider, R. Popescu, D. Gerthsen, R. Lorenzi, F.M. Gelardi, Luminescence mechanisms of defective ZnO nanoparticles, *Phys. Chem. Chem. Phys.* 18 (2016) 16237-16244.
- [35] L. Zhang, L. Yin, C. Wang, N. Lun, Y. Qi, D. Xiang, Origin of visible photoluminescence of ZnO quantum dots defect-dependent and size-dependent, *J. Phys. Chem. C* 114 (2010) 9651-9658.
- [36] Y. Zheng, C. Chen, Y. Zhan, X. Lin, Q. Zheng, K. Wei, J. Zhu, Y. Zhu, Luminescence and photocatalytic activity of ZnO nanocrystals correlation between structure and property, *Inorg. Chem.* 46 (2007) 6675-6682.
- [37] K. Kodama, T. Uchino, Thermally activated below-band-gap excitation behind green photoluminescence

in ZnO, J. Appl. Phys. 111 (2012) 093525.

[38] X. Wu, G. Siu, C. Fu, H. Ong, Photoluminescence and cathodoluminescence studies of stoichiometric and oxygen-deficient ZnO films, Appl. Phys. Lett. 78 (2001) 2285-2287.

[39] Y.C. Chen, Y.C. Pu, Y.J. Hsu, Interfacial charge carrier dynamics of the three-component In_2O_3 - TiO_2 -Pt heterojunction system, J. Phys. Chem. C 116 (2012) 2967-2975.

[40] S. Chichibu, T. Onuma, M. Kubota, A. Uedono, T. Sota, A. Tsukazaki, A. Ohtomo, M. Kawasaki, Improvements in quantum efficiency of excitonic emissions in ZnO epilayers by the elimination of point defects, J. Appl. Phys. 99 (2006) 93505-93505.

[41] T. Koida, A. Uedono, A. Tsukazaki, T. Sota, M. Kawasaki, S. Chichibu, Direct comparison of photoluminescence lifetime and defect densities in ZnO epilayers studied by time-resolved photoluminescence and slow positron annihilation techniques, Phys. Status Solidi A 201 (2004) 2841-2845.

[42] S. Das, C.K. Ghosh, R. Dey, M. Pal, Novel green phosphorescence from pristine ZnO quantum dots tuning of correlated color temperature, RSC Adv. 6 (2016) 236-244.

[43] H. L. Guo, Q. Zhu, X.L. Wu, Y.F. Jiang, X. Xie, A.W. Xu, Oxygen deficient ZnO_{1-x} nanosheets with high visible light photocatalytic activity, Nanoscale 7 (2015) 7216-7223.

[44] L. Yu, W. Chen, D. Li, J. Wang, Y. Shao, M. He, P. Wang, X. Zheng, Inhibition of photocorrosion and photoactivity enhancement for ZnO via specific hollow ZnO coreZnS shell structure, Appl. Catal. B: Environ. 164 (2015) 453-461.

[45] J. Yu, W. Wang, B. Cheng, B.L. Su, Enhancement of photocatalytic activity of mesoporous TiO_2 powders by hydrothermal surface fluorination treatment, J. Phys. Chem. C 113 (2009) 6743-6750.

- 1
2
3
4
5
6 [46] X. Zheng, D. Li, X. Li, J. Chen, C. Cao, J. Fang, J. Wang, Y. He, Y. Zheng, Construction of ZnO/TiO₂
7
8
9 photonic crystal heterostructures for enhanced photocatalytic properties, Appl. Catal. B: Environ. 168 (2015)
10
11 408-415.
12
13
14 [47] X. Li, J. Yu, M. Jaroniec, Hierarchical photocatalysts, Chem. Soc. Rev. 45 (2016) 2603-2636.
15
16
17 [48] N. Daneshvar, D. Salari, A. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO
18
19 as an alternative catalyst to TiO₂, J. Photochem. Photobiol. A 162 (2004) 317-322.
20
21
22 [49] C. Han, M.Q. Yang, B. Weng, Y.J. Xu, Improving the photocatalytic activity and anti-photocorrosion of
23
24 semiconductor ZnO by coupling with versatile carbon, Phys. Chem. Chem. Phys. 16 (2014) 16891-16903.
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Fig. 1. XRD patterns of the precursor and ZnO product (a); SEM (b), TEM (c) (inset: SAED pattern) and HRTEM images of the ZnO nanorods (denoted as ZnO NR).

Fig. 2. (a) Variations of soluble zinc concentration and molar ratio of ZnO in solid products with reaction time; three regions were indexed by colors according to different growth stages; (b) variation of amount of the produced ZnO with reaction time in 100 mL of suspensions in different NaOH solutions; (c) variation of formation rate and yield of ZnO with NaOH concentration; (d) illustration of the solvent-recyclable process.

Fig. 3. Characterizations of ZnO NR using commercial ZnO powder (ZnO-C) as a reference. Enlarged (100) diffraction peak (a), ESR spectra (b), high-resolution O1s XPS spectra (c) and VB-XPS spectra (d).

Fig. 4. (a) Steady-state PL measurements of ZnO NR and ZnO-C under 325 nm excitation; (b) Gaussian-Lorentz fitting curves of the visible emission of ZnO NR; (c) proposed band structure and PL emission mechanism of ZnO NR; (d) time-resolved PL decay and its fitting curves (inset: semi-logarithmic plots) monitored at 520 nm under 325 nm excitation.

Fig. 5. UV-Vis DRS (a) and the energy band gap (b) of ZnO NR and ZnO-C; photocurrent responses of ZnO NR and ZnO-C under UV-light ($\lambda \sim 254$ nm) (c) and visible-light ($\lambda > 420$ nm) (d).

Fig. 6. Photocatalytic degradation of RhB by ZnO-C, ZnO NR and P25 under UV-light ($\lambda \sim 254$ nm) (a) and visible-light irradiation ($\lambda > 420$ nm) (b); (c) variation of adsorption curves of RhB in aqueous solution with irradiation time in the presence of ZnO NR under visible-light; (d) apparent rate constants (k , min^{-1}) of the tested samples.

Fig. 7. (a) ESR signals for DMPO-•O₂⁻ of ZnO NR in methanol dispersion upon UV and visible light irradiation for 30 s; (b) •OH trapping as detected by PL spectra of ZnO NR with TA solution upon UV and visible light irradiation for 30 min; (c) photocatalytic degradation of RhB by ZnO NR under UV and visible light in the presence of different scavengers; (d) schematic illustration of photocatalytic mechanism of ZnO NR under UV and visible light.

Fig. 8. (a) variation of photocatalytic rate constants of ZnO NR with pH value under UV and visible light; (b) cycle performances of ZnO NR under UV-light irradiation at pH=7 and 10; (c) cycle performance of ZnO NR under visible light at pH=10; (d) XRD pattern and SEM image of the used ZnO photocatalyst after 6 cycles.