Influence of Defects on the Photocatalytic Activity of ZnO

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Supporting Information

ABSTRACT: The influence of defects on the photoactivity of ZnO has been revealed. The defects can be formed via ball-milling treatment, and part of the defects can be repaired via annealing treatment. The photocatalytic activity of the ZnO sharply decreased as the ball-milling speed and milling time increased. After the annealing treatment, the photocatalytic activity recovered partly but could not return to the activity of the pristine ZnO. The bulk defects such as oxygen vacancies (V_{O}), zinc vacancies (V_{Zn}) and a lot of nonradiative defects were formed after the milling treatment. The annealing treatment can only repair part of the bulk defects and nonradiative defects. Thus, only part of the photoactivity was recovered. The species trapping experiments showed that the introduction of the bulk defects did not change the photocatalytic mechanism. The main oxidative species for the pristine ZnO, the milled ZnO, and the annealed ZnO are photogenerated holes and hydroxyl radicals.

1. INTRODUCTION

ZnO is a direct band gap semiconductor with a wide band gap of 3.3 eV. It is one of the most widely used photocatalysts due to its high catalytic efficiency, low cost, and environmental sustainability.1–3 Some researches showed that ZnO had even better photocatalytic activity than TiO2.4 However, ZnO still exhibits low photoenergy conversion efficiency probably because of their relatively low charge separation efficiency and fast recombination of charge carriers, and further modification is indeed needed.4–6

It is well-known that the property of one material is determined by its structures including particle size, crystal structure, morphology, surface defect, and so on. Among these factors, intrinsic defects in metal oxides have drawn much interest because not only is a defect effective in modulating the activity of the photocatalyst but also it is prevailing in materials.7 For example, some research showed that introduction of surface oxygen vacancies in ZnO was an effective way to produce visible response and enhance photocatalytic activity.8–10 Many methods such as hydrogen reduction, high-temperature calcination, and vacuum deoxidation11–13 were employed to create defects and consequently improve the photocatalytic activity. It is generally accepted that surface defects are beneficial to the photocatalytic activity, whereas bulk ones only have bad effects on the photocatalytic activity.14–16 However, contradictory effects of native defects have been reported, with higher and lower concentrations having beneficial effects.17 In addition, ZnO has rich defect chemistry and many kinds of defects exist in ZnO nanocrystals such as zinc vacancy (V_{Zn}), oxygen vacancy (V_{O}), zinc interstitial (Zn\text{I}), oxygen interstitial (O\text{I}), or antisite oxygen (O\text{Zn}).18–20 The presence of different defects could result in either improvement or worsening of the photocatalytic activity, depending on the type and location of native defects. Therefore, the formation of the defects and the relationship between these defect structures and photocatalytic activity are likely to be inherently complex and still controversial. Furthermore, since bulk defects commonly exist in the ZnO crystal and generally worsen the photocatalytic activity of ZnO, it is significantly important to find an effective method to repair these defects.

In our work, high-energy ball-milling was employed to treat the commercial ZnO sample in order to form defects. Then annealing method was used to repair the structural defects of ZnO. Many kinds of defects can be formed via ball-milling treatment, and part of these defects can be repaired via annealing treatment. The photocatalytic activity of the milled ZnO was sharply decreased due to the formed bulk defects. After the annealing treatment, the photocatalytic activity recovered partly. The effect of the defects on the photocatalytic activity and the mechanism of defects reparation are deeply discussed. It is hoped that the present work may open a strategy for the defects reparation for photocatalyst and provide a new insight into the role of defect in certain positions over photocatalytic activity.

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2. Experimental Section

2.1. Materials Preparation. A commercial ZnO with the particle diameter of 30–50 nm and surface area of 9.654 m$^2$g$^{-1}$ was obtained from Nanjing Haitai Nanometer Materials Corp., Jiangsu, People’s Republic of China. All other reagents used in the experiments were analytically pure and used without further purification. The purchased ZnO sample was first milled in the planetary ball-mill under the different treatment times and rotating speeds in order to produce the defect structure. The mill consists of a cylindrical agate bowl with a volume of 50 cm$^3$ and 15 agate balls with the diameter sizes of 10–20 mm. The mass ratio of the ball to powder was about 8:1. After ball-milling treatment, the obtained ZnO sample was annealed under different temperatures or times in a muffle furnace in order to repair the defects produced by the ball-milling.

2.2. Characterization. X-ray diffraction (XRD) was performed on a Bruker D8-Advance diffractometer using Cu K$\alpha$ radiation ($\lambda = 1.5418$ Å). High-resolution transmission electron microscopy (HRTEM) images were obtained by a JEOL JEM-2011F field emission transmission electron microscope with an accelerating voltage of 200 kV. The UV–vis diffuse reflection spectra (UV-DRS) of the samples were obtained in the range from 200 to 800 nm by using a Hitachi U-3010 UV–vis spectrophotometer, which is equipped with an integrated sphere attachment and used BaSO$_4$ as the reference sample.

The electron spin resonance (ESR) signals of radicals spin-trapped by spin-trap reagent 5,5$’$-dimethyl-1-pirriline-N-oxide (DMPO; purchased from Sigma Chemical Co.) were examined on a Bruker model ESR JES-FA200 spectrometer equipped with a Quanta-Ray Nd:YAG laser system as the irradiation source ($\lambda = 365$ nm). Magnetic parameters of the radicals detected were obtained from direct measurements of magnetic field and microwave frequency. Raman measurements were recorded using a HORIBA JY HR800 confocal microscope Raman spectrometer employing an Ar-ion laser ($514.5$ nm). All spectra were calibrated with respect to silicon wafer at $520.7$ cm$^{-1}$. The room-temperature photoluminescence (PL) spectra of the samples were investigated utilizing the PerkinElmer LSS5 luminescence spectrophotometer equipped with a xenon (Xe) lamp with an excitation wavelength of 325 nm.

Electrochemical and photo-electrochemical measurements were performed in three-electrode quartz cells with a 0.1 M Na$_2$SO$_4$ electrolyte solution. Platinum wire was used as the counter electrode, and saturated calomel electrodes (SCE) were used as the reference electrodes. The as-prepared photocatalyst film electrodes on ITO served as the working electrode. The photocurrent was measured on an electrochemical system (CHI-660B, Shanghai Chenhua Instruments, Shanghai, China). UV light was obtained from an 11 W germicidal lamp. The intensity of light was 1 mW-cm$^{-2}$. Potentials were given with reference to the SCE. The photoresponses of the photocatalysts as UV light on and off were measured at 0.0 V. Electrochemical impedance spectra (EIS) were measured at 0.0 V. A sinusoidal alternating current (ac) perturbation of 5 mV was applied to the electrode over the frequency range of 0.05–10$^5$ Hz.

2.3. Photocatalytic Tests. The photocatalytic activities were evaluated by the degradation of methylene blue (MB) under UV light ($\lambda = 365$ nm) obtained from a 100 W mercury lamp. A 25 mg sample of photocatalyst was totally dispersed in an aqueous solution of MB ($50$ mL, $2 \times 10^{-5}$ mol/L). The suspensions were magnetically stirred for 60 min in the dark to get absorption–desorption equilibrium between MB and the photocatalyst before irradiation. Then, 3 mL aliquots were sampled and centrifuged to remove the particles at certain time intervals. The concentration of the MB was tested by recording the absorbance at the characteristic band of 663 nm by using a Hitachi U-3010 UV–vis spectrophotometer.

3. Results and Discussion

3.1. Influence of Defects on Photocatalytic Activity of ZnO. The photocatalytic activities of the pristine ZnO and the milled ZnO samples treated with various times and rotating speeds were evaluated by the photodegradation of MB in solution under UV light irradiation. The degradation process is fitted to pseudo-first-order kinetics, and the values of the rate constant $k$ are shown in Figure 1a,b, respectively. The photocatalytic activities of the milled ZnO samples gradually decrease with the increase of the ball-milling time or rotating speed. It is well-known that the ball-milling treatment might cause the ZnO particles to become small and consequently increase the surface area of the photocatalyst. The specific surface area of the pristine ZnO is 10.5 m$^2$/g. After milling treatment, it increases to 13.0 m$^2$/g. This fact can also be confirmed by the transmission electron microscopy (TEM) result (see Supporting Information, Figure S1). In general, the larger surface area of the photocatalyst is favorable to the photocatalytic activity because it increases the contact between the catalyst and the dye.

However, in our experiment, the photocatalytic activities of all milled ZnO samples decrease compared with the pristine ZnO. The probable reason is that a large amount of structural defects, especially the many bulk defects in commercial ZnO crystals, would be produced by ball-milling, which lead to the decrease of the photocatalytic activity.

Figure 1. Apparent rate constants for the photocatalytic degradation of MB under UV light irradiation ($\lambda = 365$ nm) over (a) ZnO and the ZnO samples milled at the rotating speed of 300 rpm for different times and (b) ZnO and the ZnO samples with different rotating speeds of ball-milling for 1 h.
In order to repair the structural defects produced by ball-milling, the milled ZnO samples were treated using the annealing method. Parts a and b of Figure 2 show the photocatalytic activities of the pristine ZnO, the milled ZnO sample, and the ZnO samples annealed with different temperatures and times, respectively. In Figure 2a, compared with the milled ZnO sample (300 rpm, 1 h), the UV photocatalytic activities of all of the annealed ZnO samples are enhanced and it gradually increases with the increase of the annealing temperature. When the temperature attains 350 °C, the photocatalytic activities achieve the maximum. This fact suggests that the annealing temperature of 350 °C is optimum to repair the structural defects of the milled ZnO sample. In Figure 2b, the photocatalytic activities of the annealed ZnO samples increase with prolonging of the annealing time, and it reaches the maximum at 16 h treatment. Further increasing the annealing time, the photocatalytic activity will change only a little. Therefore, it can be deduced that annealing method is an effective method to repair the structural defects of the milled ZnO sample, and consequently improve the photocatalytic activity. Although the photocatalytic activity of the milled ZnO samples is enhanced through the annealing treatment, however, it is still lower than that of the pristine ZnO. This fact shows that the annealing treatment cannot repair all of the bulk defects produced by ball-milling.

The photocurrent analysis is commonly used to study the separation of electrons and holes and the migration process of the photocatalyst. The UV photocurrent responses of the pristine ZnO, the milled ZnO sample, and the annealed ZnO samples treated at 350 °C with different times after deposition on indium tin oxide (ITO) electrodes are provided in Figure 3. A fast and stable photocurrent response is observed for each switch-on and switch-off event in both electrodes. The UV photocurrent of the milled ZnO sample is only one-fifth as high as that of the pristine ZnO. After the milled ZnO sample is treated by annealing, the photocurrent is enhanced and it gradually increases with the annealing time. When the annealing time is 16 h, the photocurrent achieved the maximum. However, it is still lower than that of the pristine ZnO. This result is in agreement with the tendency of photocatalytic activity of the ZnO samples in Figure 2b. The improvement of UV photocurrent of the annealed ZnO sample verifies that the charge separation efficiency improves greatly through the annealing treatment.

### 3.2. Formation and Recovery of ZnO Defects

In order to confirm the presence of defects in the ZnO crystal, HRTEM images of the pristine ZnO, the milled ZnO sample (350 rpm, 1 h), and the annealed ZnO sample (350 °C, 16 h) are shown in Figure 4a–c, respectively. It can be seen that these three kinds of ZnO samples are structurally uniform with a lattice spacing...
of about 0.281 nm corresponding to the (100) plane of cubic ZnO, which indicates that both the ball-milling and annealing treatment cannot change the crystal structure of the ZnO sample, while the lattice spaces of the milled ZnO sample and annealed ZnO sample become slightly smaller than that of the pristine ZnO sample through the calculation of the average distance of 30–50 lattice fringes. This might be the crystal contraction due to the formed vacancies in the ZnO lattice. However, this fact is absurdist with the XRD result. The peak locations in the XRD pattern hardly have any shift for all ZnO samples. The reason might be that the high-resolution TEM (HRTEM) image can only reflect the local position and cannot show the situation of the whole sample. Only parts of the lattice spaces became smaller after ball-milling treatment. The pristine ZnO is highly crystallized, as seen from perfect lattice features shown in HRTEM Figure 4a. After ball-milling treatment, many lattice fringes of the ZnO crystal (Figure 4b) become indiscernible, which indicates that some regions in the ZnO crystal become disordered due to the formation of defects. Furthermore, except for the formed surface defect, a lot of bulk defects can be clearly observed in the milled ZnO samples. It is commonly accepted that the bulk defects can become the recombination center of the photogenerated charges and thus worsen the photocatalytic activity. After the milled ZnO sample was treated by the annealing method, the lattice fringes of ZnO (Figure 4c) became clearer compared with those of the milled ZnO sample, suggesting that part of the defects, especially bulk defects, have been repaired. However, the lattice fringes of the annealed sample are still not as clear as those of primeval ZnO. Some bulk defects can be found in the annealed ZnO sample. This phenomenon indicates that some defects, especially some bulk defects, cannot be repaired through the annealing treatment.

The result of HRTEM can be confirmed by the XRD result. The peak intensities of the milled ZnO sample are obviously lower than those of the pristine ZnO (see Supporting Information, Figure S2), which indicates that the crystallization and structure orderliness decrease due to the formation of defects by the ball-milling. After annealing treatment, the peak intensities increase slightly, suggesting that the crystallization and structure orderliness are improved.

UV-DRS spectra of the pristine ZnO, the milled ZnO sample (350 rpm, 1 h), and the annealed ZnO samples (350 °C) for different annealing times are shown in Figure 5. As expected, ZnO has a fundamental absorption edge at 400 nm. The absorbance edge of the milled ZnO sample exhibits an obvious red shift, and it even has a broad long tail extended to 650 nm, which might be induced by the formed defects. However, after the milled ZnO sample was treated by the annealing, the absorption edge has a little blue shift, and the absorption intensity of the long tail decreases. This fact means the decrease of the defects by the annealing treatment. With annealing time increasing, the absorption edge of the annealed ZnO sample hardly has any change, which suggests that prolonging the annealing time does not have a great effect on the bulk defects reparation. Although the absorption edge of the annealed ZnO sample shifts to short wavelength, it cannot completely recover to the position of the pristine ZnO absorption edge, which indicates that some bulk defects cannot be repaired through the annealing method.

ESR is a useful tool to monitor various behaviors of the present native defects, such as oxygen vacancies and zinc vacancies. To further confirm the existence and properties of defects, ESR analyses of the pristine ZnO, the milled ZnO sample (350 rpm, 1 h), and the annealed ZnO sample (350 °C, 16 h) were performed, which are shown in Figure 6. A strong signal at g = 1.9580 can be observed in the ESR spectra of these three ZnO samples. Although the origin of this peak is still highly controversial, most works proved the g = 1.9580 signal to be the shallow donor caused by the surface O vacancy (V_{O}) and interstitial Zn (Z_n)\textsuperscript{21,22}. For the milled ZnO sample, the peak intensity at g = 1.9580 was sharply decreased compared with that of the pristine ZnO. Meanwhile, four new signals at g = 2.0190, 2.0165, 2.0024, and 1.9948 can be observed. Based on the literature, the signals at g = 2.0165 and 2.0023 are attributed to the Zn vacancy (V_{Zn})\textsuperscript{23,24} and the signal at 2.0190 is related to the Zn vacancy–interstitial Zn complex (V_{Zn}-Z_{n}). The signal with g = 1.9948 is reported to be associated with interstitial oxygen (O_{i}).\textsuperscript{25} From the preceding analysis, it can be inferred that the ball-milling treatment can damage the crystal structure to some extent and produce a large amount of defects, especially many bulk defects in the ZnO crystal. For the annealed ZnO sample, however, the signals attributed to the V_{Zn}, V_{Zn}-Z_{n}, and O_{i} almost disappeared. Furthermore, the signal intensity at g = 1.9580 due to the surface vacancy was slightly enhanced compared with that of the milled sample, while it was not as strong as that of the pristine ZnO. This fact shows that the annealing treatment can repair part of the ZnO
two Raman-active modes of a wurtzite structure ZnO are detected in all of the ZnO samples, which are \( E_2 \) mode at around 99 cm\(^{-1} \) and \( A_1(LO) \) mode at around 437 cm\(^{-1} \).\(^{26} \) Normally, the low-frequency Raman peaks are assigned to lattice vibrations. So the band observed at 144 cm\(^{-1} \) can be attributed to lattice vibration and the band around 184 cm\(^{-1} \) due to deformation mode.\(^{27} \) The band at 331 cm\(^{-1} \) belongs to the phonon scattering peak of the process, which is the overlap of \( E_2 (H) \) and \( E_2 (L) \).\(^{28} \) It can be seen that the peak intensities of the ZnO sample obviously decrease after the ball-milling treatment, while they have a slight increase after the milled ZnO sample was annealed. The decrease of the ZnO crystallinity is attributed to a large amount of defects produced during the ball-milling, and then a slight increase is due to the reparation of some defects by the annealing treatment. It is noted that the pristine ZnO has no peak between 500 and 600 cm\(^{-1} \). However, two peaks at 560 and 584 cm\(^{-1} \) can be observed in the milled ZnO sample, which are identified as the defects of Zn\(^{29,30} \) and oxygen vacancy (\( V_O \)).\(^{31-33} \) respectively. For the annealed ZnO samples, the intensities of these two peaks decrease due to reparation of some defects through the annealing treatment. It can be observed that the lattice vibration peak at 141 cm\(^{-1} \) disappears when the ZnO was treated by ball-milling. Meanwhile, the lattice deformation vibration peak at 184 cm\(^{-1} \) increases by ball-milling and then decreases by the annealing treatment. This fact further confirms that ball-milling can damage the crystal structure of ZnO slightly and annealing can make the crystal more perfect.

PL investigation is a convenient method to study the native defect in ZnO.\(^{37,34} \) The PL spectra of the pristine ZnO, the milled ZnO sample (350 rpm, 1 h), and the annealed ZnO sample (350 °C) were investigated at wavelength 325 nm excitation, which are shown in Figure 8. It can be seen that there are several emission peaks for the pristine ZnO. The relatively weak UV emission band at about 395 nm, corresponding to the near band edge (NBE) emission, is responsible for the recombination of the free excitons of ZnO. The blue luminescence at 406 nm\(^{35} \) and 411 nm\(^{36} \) have been attributed to the surface zinc vacancy. The emission at 420 nm has been attributed to the transition between defects (interphase traps) at grain boundaries and the valence bands, lattice defects that are related to oxygen vacancy,\(^{37-39} \) zinc vacancy,\(^{40} \) and interstitial oxygen.\(^{37,38} \) The emission at 438 nm is caused by the transitions of excited electrons from the level of Zn, to the valence band.\(^{42} \) The 446 nm blue emission peak in ZnO implies that electrons are trapped at interfaces lying within the depletion regions located at ZnO–ZnO grain boundaries.\(^{42} \) The green yellow emission band at 454 nm originates from deep level defect emission associated with oxygen vacancies in ZnO lattices.\(^{33} \) The 485 nm emission is attributed to a transition between the \( V_O \) and \( O_\text{int} \), and lattice defects related to oxygen and zinc vacancies.\(^{40} \) The green emission at 527 nm for the samples is nearly in concordance with the energy gap between the level of \( V_O \) and the valence band (VB).\(^{44} \) Although the origin of these emissions is still in controversy, it is widely accepted that they are highly related to the different kinds of defects in ZnO, such as \( V_O \), \( V_{\text{Zn}} \), \( O_\text{int} \), and Zn. For the milled ZnO sample, the PL peak intensities sharply decreased and became indistinguishable. In general, the strong PL means high recombination of photogenerated carriers, suggesting the low photocatalytic activity. However, in our experiment, the PL peak intensity of the pristine ZnO is much stronger than those of the milled and annealed ZnO samples. On the contrary, the photocatalytic activity of the pristine ZnO is much higher than those of the milled and annealed ZnO samples. There might be two reasons: one is due to the decrease of crystallinity of the pristine ZnO after the ball-milling treatment. This fact can be confirmed by the XRD and TEM results previously shown. The other reason is that PL can only detect the light energy that is dissipated as the radiation; thus, many nonradiative transitions cannot be observed. It is well-known that the recombination of the photogenerated electrons and holes would release the chemical energy and further transform to heat or light energy. The increase of the nonradiative transitions leads to the decrease of the PL peak intensity. Therefore, the decrease of PL peak intensity in the milled ZnO sample certified that a lot of nonradiative defects with different energy levels have been formed during the ball-milling treatment and a certain amount of chemical energy might be released via heat. It has been reported that nonradiative recombination centers have significant negative impact on the photocatalytic activity, since higher concentration of nonradiative defects would result in higher losses of photogenerated carriers.\(^{45} \) The significant decrease of the PL intensity of the milled ZnO sample shows that a lot of the nonradiative defects were formed after the ZnO was milled. The nonradiative defects which can become the recombination
centres of the photogenerated charges make the photocatalytic activity decrease.

Meanwhile, compared with other peaks in PL of the milled ZnO sample (350 rpm, 1 h), the decrease tendency of the peak intensity at 454 nm, coming from the deep level defect emission of oxygen vacancies in ZnO lattices, is relatively smaller. This fact shows that the milling treatment produced a lot of bulk oxygen defects. For the annealed ZnO sample (350 °C, 16 h), the peak intensities are relatively higher than those of the milled ZnO sample. The reason is that the number of the bulk defects in the ZnO crystal was decreased by the annealing, which causes the radiative transitions to increase. At the same time, the relatively high peak intensity of the emission band at 454 nm in the annealed ZnO sample (350 °C, 16 h) shows that the bulk defect is also the main defect in this annealed sample.

3.3. Mechanism of the Effects of Defects on Photocatalytic Activity. It is well-accepted that degradation of pollutants can occur via either direct oxidation by photogenerated holes or reaction with generated intermediate oxygen species. The main oxidative species in the photocatalytic process could be detected through trapping experiments of radicals and holes by using isopropyl alcohol (IPA; hydroxyl radical scavenger) and disodium salt of ethylenediaminetetra-acetic acid (EDTA-2Na; photogenerated hole scavenger), respectively. As shown in Figure 9a, the photocatalytic activity of the pristine ZnO could be greatly suppressed by the addition of a scavenger for holes (EDTA-2Na) or radicals (IPA), suggesting that both the photogenerated holes and the hydroxyl radicals are the main oxidative species of the pristine ZnO system. Nevertheless, the reduction speed of the photocatalytic activity by adding the EDTA-2Na is faster than that by adding the IPA. This shows that the photogenerated holes play a more important role in the MB degradation than the radicals do. The trapping experiments of active species during the photocatalytic reaction of the milled ZnO sample (350 rpm, 1 h) and annealed ZnO sample (350 °C, 16 h) are shown in Figure 9b,c, respectively. It can be found that the milled and annealed ZnO samples have the same photodegradation mechanism as that of pristine ZnO. MB degradation can occur either via direct transfer of photogenerated holes or via reactions with the generated hydroxyl radicals as intermediate species.

As discussed previously, the crystal phase structure (Supporting Information Figure S2) and the degradation mechanism are not evidently changed before and after the treatment, and the difference of the specific surface area and the particle size cannot account for the change of the photocatalytic activity. In our work, the main factor to influence photocatalytic activity is the separation efficiency of photoinduced electron–hole pairs.

It is well-known that, while different mechanisms of photocatalytic dye degradation have been proposed, it is commonly accepted that the separation efficiency of photoinduced electron–hole pairs is the key factor in the photocatalytic process. The interface charge separation efficiency of photogenerated electrons and holes was investigated by the typical EIS (presented as Nyquist plots). The radius of the arc on the EIS spectra reflects the interface layer resistance occurring at the surface of electrode. The smaller arc radius implies higher efficiency of charge transfer. Figure 10a gives the EIS Nyquist plots of the pristine ZnO and the milled ZnO samples (300 rpm) with different ball-milling times in the case of UV light irradiation. The arc radius of the pristine ZnO is smaller than those of the milled ZnO samples, demonstrating that ball-milling treatment can dramatically decrease the separation and transfer efficiency of the photogenerated electron–hole pairs. The reason might be that the bulk defects formed by the ball-milling treatment act as the recombination centers of the photogenerated charges. With prolonging the ball-milling time, the arc radius increases. This indicates that prolonging the ball-milling time can induce the
formation of more bulk defects and consequently increase the recombination centers of the photogenerated charges. Therefore, the photocatalytic activity of the milled ZnO sample sharply decreased due to the decrease of the charge separation efficiency. The XRD, TEM, and PL analyses show the pristine ZnO has good crystalline quality and many surface defects exist on the surface of the ZnO crystal, such as $V_{O}$, $V_{Zn}$, $O_{2}$ and $Zn_{2}$. After ball-milling treatment, the crystal structure of the pristine ZnO is damaged to some extent. The crystallinity decrease and many deep level defects especially many $V_{O}$ and $V_{Zn}$ and a lot of nonradiative defects are produced in the bulk of ZnO. In general, surface defects can serve as active sites, which are favorable to the photocatalytic activity, while bulk defect is often regarded as the recombination sites, which result in worsening of the photocatalytic activity.

Figure 10b shows the EIS Nyquist plots of the pristine ZnO, the milled ZnO sample (350 rpm, 1 h), and the annealed ZnO sample (350 °C, 16 h). The pristine ZnO has the smallest arc radius among the three samples, followed by the annealed ZnO sample (350 °C, 16 h) and milled ZnO sample (350 rpm, 1 h) in order. This fact suggests that the charge separation efficiency decreased when the ZnO was treated by the ball-milling and then increased through the annealing treatment. Therefore, the decrease of the UV photocatalytic activity of the milled ZnO sample is mainly due to the formation of large amounts of bulk defects through ball-milling treatment, while the increase of the UV photocatalytic activity of the annealed ZnO sample is mainly ascribed to the reduction of the bulk defects by the annealing treatment. The bulk defects produced by the ball-milling can form the new energy levels between the forbidden band of the ZnO sample, which can become the recombination centers of electron–hole pairs and will result in the decrease of photocatalytic activity. It can be seen that the arc radius of the annealed sample is not as small as that of the pristine ZnO, which further confirms that the bulk defects produced by ball-milling cannot be repaired completely by annealing treatment.

4. CONCLUSION

In summary, a large amount of bulk defects have been produced by the ball-milling treatment. These bulk defects can become the recombination centers of the photogenerated charges and cause the photocatalytic activity to decrease significantly. After annealing treatment, the photocatalytic activity increased to some degree since part of the bulk defects are repaired. The species trapping experiments showed that the introduction of the bulk defects did not change the photocatalytic mechanism. The main oxidative species for the pristine ZnO, the milled ZnO, and the annealing ZnO were photogenerated holes and the hydroxyl radicals.

ASSOCIATED CONTENT

Supporting Information

TEM images of materials (a) ZnO; (b) the ZnO sample milled at the rotating speed of 350 rpm for 1 h, and (c) the annealed ZnO sample treated at 350 °C for 16 h; XRD spectra of ZnO, the ZnO sample milled at the rotating speed of 350 rpm for 1 h and the annealed ZnO samples treated at 350 °C with different times. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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