

Optical properties and photocatalytic activity of Nd-doped ZnO powders

Zhen ZHAO¹, Ji-ling SONG¹, Jia-hong ZHENG^{1,2}, Jian-she LIAN¹

1. Key Laboratory of Automobile Materials, Ministry of Education, Jilin University, Changchun 130022, China;

2. Key Laboratory of Preparation and Applications of Environmental Friendly Materials,
Ministry of Education, Jilin Normal University, Siping 136000, China

Received 18 June 2013; accepted 6 September 2013

Abstract: To improve the photocatalytic activity of zinc oxides, ZnO powders doped with different neodymium (Nd) concentrations were prepared via hydrothermal method. X-ray diffraction (XRD) together with X-ray photoelectron spectroscopy (XPS) patterns revealed that Nd atoms were successfully incorporated into the ZnO lattice. XRD pattern also showed some anisotropy of the powders. The photoluminescence (PL) spectrum demonstrated a strong and broad peak in the visible light region, and the intensity of visible light emission was enhanced by Nd-doping. The photocatalytic activity was evaluated by the degradation of methyl orange solution. It is shown that doping of Nd into ZnO induces an increase of the photocatalytic activity and it attains to optimum at 3% (mole fraction) doping concentration. The intense visible light emission and the enhanced photocatalytic activity were explained by the increase in electron hole pairs and induced defects like antisite oxygen O_{Zn} and interstitial oxygen O_i , due to the doping of Nd.

Key words: Nd-doped ZnO; photoluminescence; photocatalysis

1 Introduction

Various metal oxide semiconductors, such as TiO_2 , ZnO, WO_3 and SnO_2 , have been studied and applied as photocatalysts. Among them, TiO_2 is considered the most efficient photocatalyst due to its abundant availability, cost-effectiveness and chemical stability. However, recent researches have shown that ZnO can be used as a more efficient photocatalyst compared with TiO_2 [1,2], as it is also a wide bandgap (3.37 eV) semiconductor of abundant availability, cost-effectiveness and no secondary environmental pollution. An important characteristic is that ZnO contains various intrinsic defects. Introducing defects into ZnO structure can not only narrow the band gap to increase the solar light harvesting capability, but also bring many split energy gaps to set up a possible catalytic systems which sense and shoot environmental contaminants [3,4].

Doping of metal and nonmetal elements is an effective way to introduce defects to modify the optical property of ZnO [5,6]. Rare-earth (RE) ions [7,8] have been recognized as excellent candidates for

luminescence centers of the doped ZnO nanocrystals due to their optical advantages. Doping [9] can effectively improve the photocatalytic performance of the semiconductors, through extending the light absorption wavelength. Nd as one element of lanthanide has gained focus of numerous investigations because of its particular optical properties [10,11] and promising applications in optoelectronic [12,13] and magnetic devices [14]. In the present work, Nd-doped ZnO particles were prepared by hydrothermal method. The effects of Nd-doping and its concentration on the the photoluminescence (PL) and photocatalysis properties were investigated.

2 Experimental

The $Zn_{1-x}Nd_xO$ powders ($x=0$, 1%, 3%, and 5%; mole fraction) were prepared via the hydrothermal method. All the chemical reagents used in the experiment were in analytical grade without further purification. The mixture of zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$) and neodymium nitrate ($Nd(NO_3)_3 \cdot 6H_2O$) of 0.55 mol/L were dissolved into deionized water with vibration in a magnetic stirrer to get the solution A. 0.55 mol/L

hexamethylene tetramine (HTMA) was dissolved into deionized water in the same way to form solution B. Then solution A was dissolved into solution B to form the final reagent solution in a sealed Teflon-lined stainless steel autoclave which was then heated at 95 °C for 16 h in an oven and cooled to room temperature. The obtained product was washed with deionized water and centrifuged several times and dried at 50 °C in the oven to become white powder, which was then further sintered at 600 °C for 2 h in a furnace to form the final $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powders.

X-ray diffraction was applied to determining the phase structure, performed on a D/max-Rigaku XRD diffraction spectrometer with a $\text{Cu K}\alpha$ line of 1.5417 Å and a monochromator at 50 kV and 300 mA. XPS spectra of the ZnO powders were obtained by an ESCALABMk II (Vacuum Generators) spectrometer using un-monochromatic Al $\text{K}\alpha$ X-rays (240 W). Cycles of XPS measurements were done in a high vacuum chamber with a base pressure of 1.33×10^{-6} Pa. The PL spectra were measured by a fluorescence spectrophotometer using a He–Cd laser with a wavelength of 325 nm as the excitation light source at room temperature.

UV-Vis spectrophotometer was employed to examine the absorption spectrum and to analyze the photocatalysis degradation of the powder. Photocatalysis experiment was done by catalyzing the 30 mL solution containing 15 mg/L methyl orange. 30 mg of the as-synthesized $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powder was put as catalysis into the solution and the degradation was realized under a UV-Vis light source. The degradation efficiency was estimated by the light absorption of the solution measured by the UV-Vis spectrophotometer by the following equation:

$$\eta = (c_0 - c_t) / c_0 \times 100\% = (A_0 - A_t) / A_0 \times 100\%$$

where c_0 , A_0 and c_t , A_t are the concentration and absorption of methyl orange solution at original moment (0) and instant time (t), respectively.

3 Results and discussion

3.1 Characterization of $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powder

Figure 1 shows the XRD patterns of the as-synthesized $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ ($x=0, 1\%, 3\%$ and 5%). All diffraction peaks match with those of wurtzite structure ZnO (JCPDS: 36–1451) and no extra peaks of other substance are detected, indicating the synthesis of $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ as expected. As random powder, it should hold isotropy XRD spectrum. For the isotropy polycrystalline wurtzite structure ZnO powder, the (101) plane has the maximum diffraction, and the (100) and (002) planes are the second and third (see JCPDS:

36–1451). However, the present samples show that the (002) plane has the maximum diffraction peak, namely, the powders show anisotropy, that is, more c -axis planes than random are exposed to the X-ray in a heap of the ZnO powder.

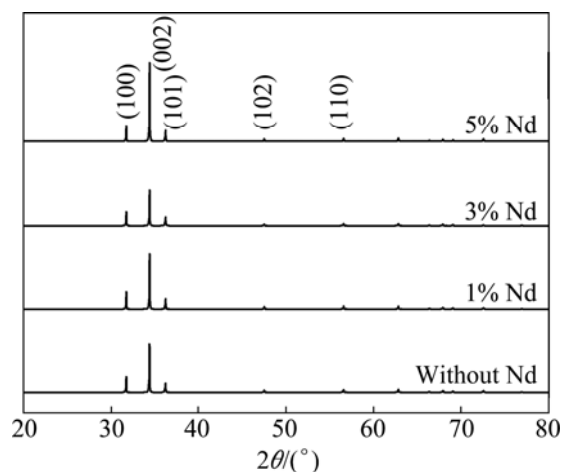


Fig. 1 XRD patterns of $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powders with different Nd concentrations

Figure 2 shows the FESEM images of $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powder samples ($x=1\%$ and $x=5\%$). Many plate-like ZnO crystals are observed and the plate surface should be the (002) plane of wurtzite structure ZnO, according to the XRD patterns shown in Fig. 1. As the Nd concentration increases, the ZnO crystals tend to reunite with each other. Meanwhile, the quantity of plate-like crystals (with (002) plane as the surface) decreases, which is also proved by the relative reduction of the diffraction intensity of the (002) plane with Nd concentration increasing as shown in Fig. 1.

Figure 3 shows the XPS survey spectra of the as-obtained $\text{Zn}_{0.95}\text{Nd}_{0.05}\text{O}$ particles. Figure 3(a) shows the whole spectrum where the bind energies of Zn, Nd, O and C elements are labeled. Figures 3(b), (c) and (d) show the amplificatory spectra of Zn 2p, O 1s and Nd 3d peaks, respectively. In the XPS spectra, the binding energies have been calibrated by taking the C 1s peak (285.0 eV) [15] as reference. Figure 3(b) shows the Zn 2p_{3/2} (1021.4 eV) peak and Zn 2p_{1/2} (1044.5 eV) peak, respectively. They are assigned to the lattice zinc in zinc oxide [16–18]. The O 1s can be fitted through Lorentzian–Gaussian by two peaks located at 530.2 eV and 531.8 eV. The former with lower banding energy corresponds to the intrinsic O^{2-} in ZnO, i.e., the Zn–O bonds. The peak at 531.8 eV is attributed to the chemisorbed oxygen of the surface hydroxyl, $-\text{CO}_3$, absorbed H_2O , absorbed O_2 or mainly due to the surface contamination [19,20]. The spectrum of Nd 3d region is depicted in Fig. 3(d). The peaks of 976.4 eV and 1011.6

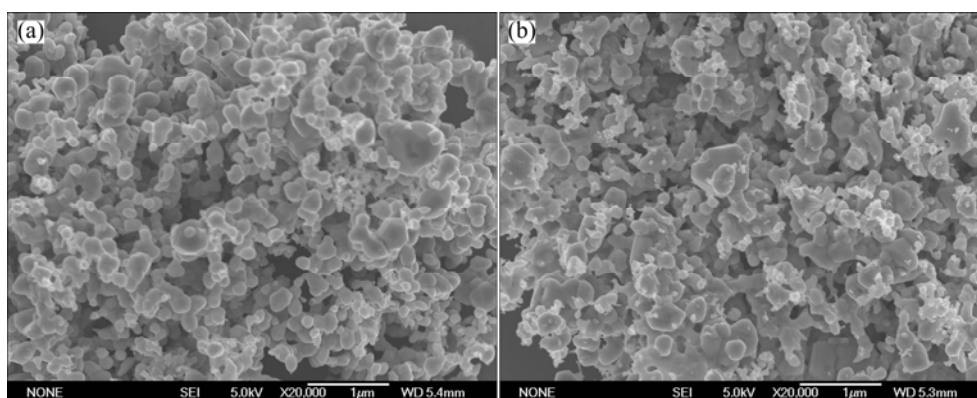


Fig. 2 FESEM images of $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ particles with $x=1\%$ (a) and $x=5\%$ (b)

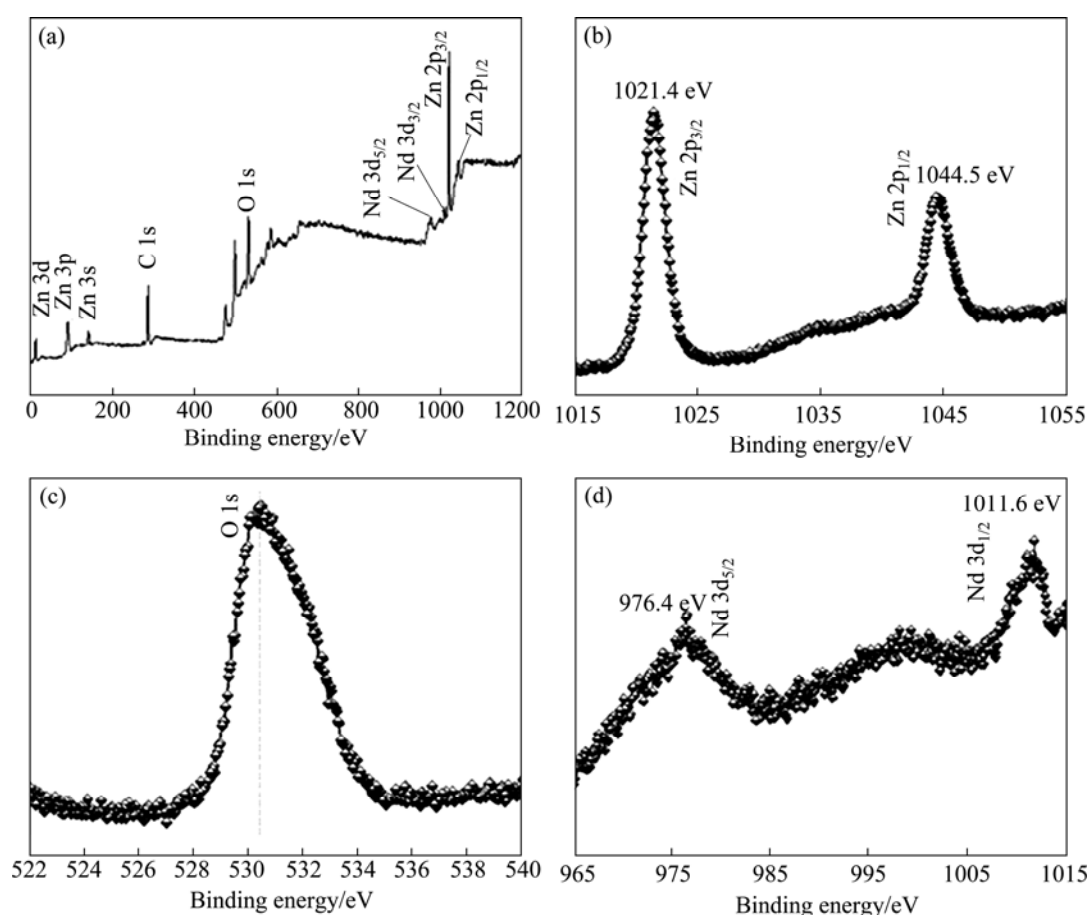


Fig. 3 XPS spectra of Nd-doped ZnO particles (a), Zn 2p (b), O 1s (c) and Nd 3d (d) for $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ at $x=5\%$

eV represent 5/2 and 3/2 spin-orbit double components of Nd 3d core level photoemission respectively, which reveals that Nd ions exist in trivalent state in comparison with Nd ions in Nd_2O_3 [21,22]. So, Nd atoms were successfully incorporated into the ZnO lattice, and they would cause the local oxygen deficiency as every two Nd atoms combined three oxygen atoms.

3.2 Photoluminescence and photocatalysis of $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powder

Figure 4 shows the photoluminescence (PL) spectra

of $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powders at room temperature with different concentrations as well as the pure ZnO ($x=0$) for comparison. These powders show relatively weak UV emission, but enhanced deep level (DL) emission, which is obviously different from other samples synthesized by sol-gel method [23]. The intensity of the DL emission first increases as the concentration of Nd in the $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powder increases, reaching a maximum at the concentration of $x=3\%$, which is about 21.8 times the intensity of UV emission, namely, the ZnO powder becomes a photoluminescent visible emission source,

which is quite different from the common ZnO. With further increasing the Nd concentration, the DL emission intensity decreases.

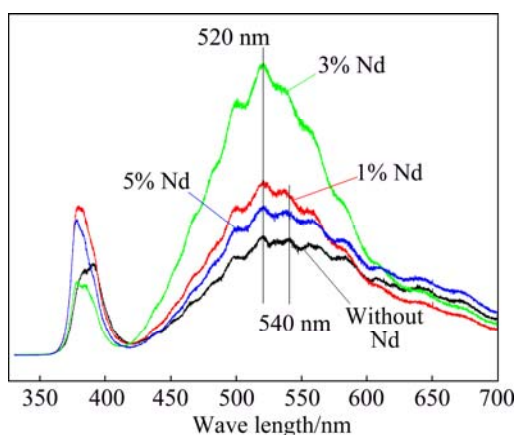


Fig. 4 PL spectra of $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powders with different concentrations measured at room temperature

Figure 5 shows the photocatalytic performance of as-synthesized $\text{Zn}_{1-x}\text{Nd}_x\text{O}$. The ZnO powder without doping also has an acceptable photocatalytic activity as it degrades about 85% of methyl orange in 45 min. Doping of Nd in ZnO improves the photocatalytic activity, while the $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ with $x=3\%$ has the best degradation as it degrades all the methyl orange in 45 min. The $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ with more Nd doping (for example, $x=5\%$) has decreased photocatalytic activity, although it is still better than that without Nd doping. It is interesting to note that the intensity of PL in deep level emission reaches the maximum and the photocatalytic degradation of methyl orange reaches the best both at the Nd doping concentration of 3%, which implies that similar effects should be dominant on the two properties.

The visible light emission illustrates that there are impurities and defects in the negative-charged interstitial oxygen ion state [24]. The highest decomposed peaks

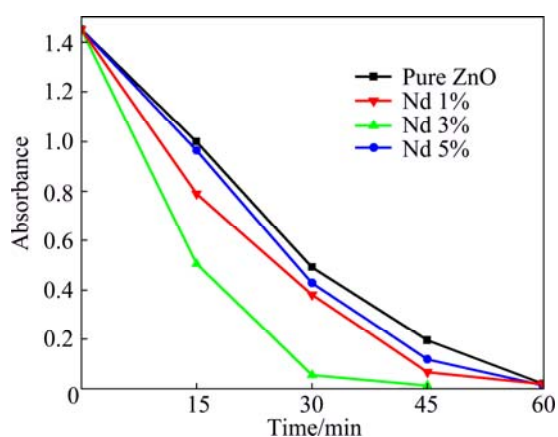


Fig. 5 Absorption and degradation efficiency spectra of $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powders

located at about 520 nm and 540 nm should be aroused by the intrinsic defects of antisite oxygen O_{Zn} (2.385 eV or 520 nm) and interstitial oxygen O_i (2.296 eV or 540 nm) [25]. Doping Nd atoms would attract more oxygen atoms around them as a pair of Nd atoms need three oxygen atoms according to the above XPS analysis; while in ZnO lattice, each Zn atom needs only one O atom. So, there should be more interstitial oxygen O_i or antisite oxygen O_{Zn} nearby doping Nd atoms in ZnO lattice, which induces the enhanced visible emission at 520–540 nm. Meanwhile, the lattice distortion and other defects would split the energy gaps to make the emission spread in a broad wavelength range as shown in Fig. 4.

For semiconductor materials with wide band gap, the recombination of electron-hole pairs in the redox processes usually reduces the photocatalytic activity considerably [26], which is one of the main reasons limiting the photocatalytic performance of semiconductor materials like ZnO and TiO_2 . Doping of Nd induces pretty much defects like interstitial oxygen O_i and antisite oxygen O_{Zn} , which play important roles in trapping the charge carriers to prevent them recombination, and hence enhance the photocatalytic activity of ZnO. Doping of trivalence Nd in ZnO lattice (where Zn is bivalence ion) would also provide more electrons and holes, to promote the photocatalytic activity.

Over-doping of Nd will not further increase the visible emission and the photocatalytic activity. It was reported that the photocatalytic activity of ZnO depends on the crystalline plane [27]; the exposure of a greater portion of polar faces ((002) plane) leads to greater photocatalytic activity as the (002) face has the intrinsically highest energy among all the faces and could adsorb OH^- ions on it. It is seen from Fig. 1 that the primary ZnO has good photocatalytic activity. However, the over-doping of Nd decreases the crystal size, reunites the particles and reduces the portion of exposed (002) plane. So, the photocatalytic activity of $\text{Zn}_{0.95}\text{Nd}_{0.05}\text{O}$ cannot be further increased.

4 Conclusions

1) Nd-doped ZnO ($\text{Zn}_{1-x}\text{Nd}_x\text{O}$) powders were prepared by the hydrothermal method and the XRD with XPS analyses confirmed the doping of Nd into ZnO lattice.

2) The as-synthesized $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powders show an intense and broad visible light (DL) emission centered at 520–540 nm and a relative weak UV emission. The DL emission peak reaches the maximum for the $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powder with 3% Nd doping ($x=3\%$). The enhanced visible emission can be explained by the induced defects like antisite oxygen O_{Zn} and interstitial oxygen O_i , due to

the doping of Nd.

3) The as-synthesized $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powders show enhanced photocatalytic activity tested by the photocatalytic degradation of methyl orange solution, and the photocatalytic activity also reaches optimum for the $\text{Zn}_{1-x}\text{Nd}_x\text{O}$ powder with 3% Nd doping. The improved photocatalytic activity can be attributed to the increased electrons and hole pairs and the introduce of intrinsic defects by Nd doping.

References

- [1] AHMAD M, AHMAD E, ZHANG Y W, KHALID N R, XU J F, ULLAH M, HONG Z L. Preparation of highly efficient Al-doped ZnO photocatalyst by combustion synthesis [J]. *Curr Appl Phys*, 2013, 13: 697–704.
- [2] ZHONG Jun-bo, LI Jian-zhang, XIAO Zheng-hua, HU Wei, ZHOU Xiao-bei, ZHENG Xing-wen. Improved photocatalytic performance of ZnO prepared by sol–gel method with the assistance of CTAB [J]. *Mater Lett*, 2013, 91: 301–303.
- [3] KAMATH P V, HUEHN R, NICOLAESSU R. A “sense and shoot” approach for photocatalytic degradation of organic contaminants in water [J]. *J Phys Chem B*, 2002, 106: 788–794.
- [4] LIN Bi-xia, FU Zhu-xi, JIA Yun-bo. Green luminescent center in undoped zinc oxide films deposited on silicon substrates [J]. *Appl Phys Lett*, 2001, 79: 943–945.
- [5] BA-ABBAD M M, KADHUM A A H, MOHAMAD A B, TAKRIFF M S, SOPIAN K. Visible light photocatalytic activity of Fe^{3+} -doped ZnO nanoparticle prepared via sol–gel technique [J]. *Chemosphere*, 2013, 91: 1604–1611.
- [6] PENG Xiao-yan, YANG Bo-qian, CHU Jin, FENG Peter. Effects of nitrogen pressure during pulsed laser deposition on morphology and optical properties of N-doped ZnO nanostructures [J]. *Surf Sci*, 2013, 609: 48–52.
- [7] ARMELAO L, HEIGL F, JURGENSEN A, BLYTH RIR, REGIER T, ZHOU X T, SHAM T K. X-ray Excited optical luminescence studies of ZnO and Eu-doped ZnO nanostructures [J]. *J Phys Chem C*, 2007, 111: 10194–10200.
- [8] DUARTE F J. Tunable laser applications [M]. 2nd ed. New York: CRC, 2009.
- [9] CHEN Y, XU X L, ZHANG G H, XUE H, MA S Y. Blue shift of optical band gap in Er-doped ZnO thin films deposited by direct current reactive magnetron sputtering technique [J]. *Physica E*, 2010, 42: 1713–1716.
- [10] ZENG Xiao-yan, YUAN Jun-lin, WANG Zhen-yang, ZHANG Li-de. Nanosheet-based microspheres of Eu^{3+} -doped ZnO with efficient energy transfer from ZnO to Eu^{3+} at room temperature [J]. *Adv Mater*, 2007, 19: 4510–4514.
- [11] MEHTA A, THUNDAT T, BARNES M D, CHHABRA V, BHARGAVA R, BARTKO A P, DICKSON R M. Size-correlated spectroscopy and imaging of rare-earth-doped nanocrystals [J]. *Appl Opt*, 2003, 42: 2132–2139.
- [12] CHEN Pei-lang, MA Xiang-yang, YANG De-ren. ZnO:Eu thin-films: Sol–gel derivation and strong photoluminescence from $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition of Eu^{3+} ions [J]. *J Alloys Compd*, 2007, 431: 317–320.
- [13] WANG Xin, KONG Xiang-gui, YU Yi, SUN Ya-juan, ZHANG Hong. Effect of annealing on upconversion luminescence of ZnO:Er^{3+} nanocrystals and high thermal sensitivity [J]. *J Phys Chem C*, 2007, 111: 15119–15124.
- [14] SUBRAMANIAN M, THAKUR P, GAUTAM S, CHAE K H, TANEMURA M, HIHARA T, VIJAYALAKSHMI S, SOGA T, KIM S S, ASOKANAND K, JAYAVEL R. Investigations on the structural, optical and electronic properties of Nd doped ZnO thin films [J]. *J Phys D: Appl Phys*, 2009, 42: 105410–105415.
- [15] ARMELAO L, BOTTARO G, PASCOLINI M, SESSOLO M, TONDELLO E, BETTINELLI M, SPEGHINI A. Structure–luminescence correlations in europium-doped sol–gel ZnO nanopowders [J]. *J Phys Chem C*, 2008, 112: 4049–4054.
- [16] WANG Yi, SUN Lei, KONG Ling-gang, KANG Jin-feng, ZHANG Xing, HAN Ru-qi. Room-temperature ferromagnetism in Co-doped ZnO bulk induced by hydrogenation [J]. *J Alloys Compd*, 2006, 423: 256–259.
- [17] SINGHAL A. Study of electronic and magnetic properties of vacuum annealed Cr doped ZnO [J]. *J Alloys Compd*, 2012, 515: 12–15.
- [18] CAGLARA M, YAKUPHANOGLU F. Structural and optical properties of copper doped ZnO films derived by sol–gel [J]. *Appl Surf Sci*, 2012, 258: 3039–3044.
- [19] ISLAM M N, GHOSH T B, CHOPRA K L, ACHARYA H N. XPS and X-ray diffraction studies of aluminum-doped zinc oxide transparent conduction films [J]. *Thin Solid Films*, 1996, 280(1–2): 20–25.
- [20] MAJOR S, KUMAR S, BHATNAGAR M, CHOPRA K L. Effect of hydrogen plasma treatment on transparent conducting oxides [J]. *Appl Phys Lett*, 1986, 49(7): 394–396.
- [21] RIVERA L F, MARIANO P. X-ray photoelectron spectroscopy: Surface and depth profiling studies of glasses doped with Nd and Yb ions [J]. *Surf Interface Anal*, 2012, 44: 927–930.
- [22] ZHANG Z H, ZHONG X L, LIAO H, WANG F, WANG J B, ZHOU Y C. Composition depth profiles of $\text{Bi}_{3.15}\text{Nd}_{0.85}\text{Ti}_5\text{O}_{12}$ thin films studied by X-ray photoelectron spectroscopy [J]. *Appl Surf Sci*, 2011, 257: 7461–7465.
- [23] ZHENG Jia-hong, SONG Ji-ling, ZHAO Zhen, JIANG Qing, LIAN Jian-she. Optical and magnetic properties of Nd-doped ZnO nanoparticles [J]. *Cryst Res Technol*, 2012, 47: 713–718.
- [24] GAO Y F, NAGAI M, MASUDA Y, SATO F, KOUMOTO K. Electrochemical deposition of ZnO film and its photoluminescence properties [J]. *J Cryst Growth*, 2006, 286: 445–450.
- [25] BHARGAVA R, SHARMA P, DUTTA R K, KUMAR C, AVINASH C P, KUMAR N. Influence of Co-doping on the thermal, structural, and optical properties of sol–gel derived ZnO nanoparticles [J]. *Mater Chem Phys*, 2010, 120: 393–398.
- [26] MOHAN R, KRISHNAMOORTHY K, KIM S J. Enhanced photocatalytic activity of Cu-doped ZnO nanorods [J]. *Solid State Commun*, 2012, 152: 375–380.
- [27] MCLAREN A, VALDES-SOLIS T, LI G Q, TSANG S C. Shape and size effects of ZnO nanocrystals on photocatalytic activity [J]. *J Am Chem*, 2009, 131: 12540–12541.

钕掺杂氧化锌粉末的光性能和光催化性能

赵 真¹, 宋季岭¹, 郑佳红^{1,2}, 连建设¹

1. 吉林大学 汽车材料教育部重点实验室, 长春 130022;

2. 吉林师范大学 环境友好材料制备及应用省部共建教育部重点实验室, 四平 136000

摘 要: 为了提高氧化锌(ZnO)的光催化性能, 通过水热法制备了不同钕(Nd)掺杂量的 ZnO。X 射线衍射分析(XRD)和光电子能谱(XPS)测试说明钕原子成功地掺杂进入了 ZnO 晶格。XRD 图谱还说明了粉末具有各向异性。光致发光(PL)图谱在可见光区域出现较宽范围的强峰。Nd 掺杂使得可见光发射强度增强。光催化性能通过降解甲基橙溶液进行测试。研究发现 Nd 掺杂使得氧化锌的光催化性能得到提高, 当掺杂 Nd 的摩尔分数为 3%时, 其光催化性能最佳。Nd 掺杂引起的电子空穴对的增加以及诱导产生的置换氧缺陷(O_{Zn})和间隙氧缺陷 (O_i)使得可见光发射增强和光催化性能得到提高。

关键词: 钕掺杂氧化锌; 光致发光; 光催化

(Edited by Hua YANG)