

Blue luminescence from carbon modified ZnO nanoparticles

Z.G. WANG

Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu, 610054, People's Republic of China

X.T. ZU*

Department of Applied Physics, University of Electronic Science and Technology of China, Chengdu, 610054, People's Republic of China; International Center for Material Physics, Chinese Academy of Sciences, Shengyang, 110015, People's Republic of China
E-mail: xiaotaozu@yahoo.com or xtzu@uestc.edu.cn

S.Z. YANG

School of Physics and Electronics Information, China West Normal University, Nanchong, 637002, China

L.M. WANG

Department of Nuclear Engineering and Radiological Sciences, University of Michigan, Ann Arbor, MI48109, USA

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In this work, a novel method was used to prepare carbon modified ZnO nanoparticles. The nanoparticles were coated with a layer of poly(methyl methacrylate) by γ radiation firstly, and then the coated nanoparticles were annealed in air. The polymer was burned and carbon was left on the surface of ZnO nanoparticles. A stable blue luminescence peak (~ 420 nm) can be observed for the carbon modified ZnO nanoparticles. The carbon modified ZnO nanoparticles were also investigated by X-ray photoelectron spectroscopy. The origin of the blue emission was discussed. The blue PL is related to the left carbon. This novel method also can be used to prepare other carbon modified nanoparticles. © 2006 Springer Science + Business Media, Inc.

1. Introduction

Nanoparticles possess many special characteristics that can be used in many fields such as optics, electricity, magnetism and catalysis [1]. However, nanoparticles aggregate easily because of their extremely high specific surface energy, so preparing nanocomposites becomes an economical and effective method for using nanoparticles. Surface modification of nanoparticles has attracted much attention and extensive investigation [2–4]. The modification not only can change the surface characterization of nanoparticles, but also can induce some new characteristics.

ZnO is a direct wide bandgap II-VI semiconductor (3.36 eV) that is suitable for short wavelength optoelectronic applications. In spite of a number of studies that were performed on the photoluminescence of ZnO, there is no consensus in the literature on the positions of the

peaks in PL spectrum of ZnO nanostructures and thin films or their origin. In addition to the most commonly observed violet and green luminescence, blue luminescence from ZnO thin films, nanoparticles, and whiskers were reported before. Among the peaks reported are 405 nm [5], ~ 420 nm [5–8], 446 nm [9], 450 nm [10], 465 nm [11], 466 nm [12], and ~ 485 nm [5, 7]. The blue luminescence at 405 nm has been attributed to the zinc vacancy [13]. According to the calculations, 405 nm transition corresponds to the Zn vacancy, 427 nm transition to interstitial zinc, and 544 nm to interstitial oxygen [14]. Blue emission at ~ 413 nm was observed in ZnO films that were grown under oxygen rich conditions, and it was attributed to the possible existence of cubic ZnO [15]. The emission at ~ 420 nm has been attributed to the interstitial oxygen [7, 8], transition between defects at grain boundaries and the valence band, and lattice defects that are related to

*Author to whom all correspondence should be addressed.

oxygen and zinc vacancies [5]. So the position of the blue emission is not consensus and the origin is not clear.

Non-metal atoms such as N, C or S can change the optical properties of TiO₂ and ZnO, such as N, C or S doping shifts the optical absorption edge of TiO₂ to lower energies, thereby increasing the photocatalytic activities in the visible region [16–18]. Nitrogen related photoluminescence at about 450 and 890 nm has been observed in the nitrogen-doped ZnO films [19]. There is no report on the effect of carbon on the optical properties of ZnO. In this paper, we report a novel method which was used to prepare carbon modified ZnO nanoparticles. The modified ZnO nanoparticles emit blue luminescence at ~420 nm.

2. Experimental methods

The investigation had been carried out on commercial ZnO nanoparticles which were purchased from Zhejiang Zhoushan Mingri Nano Materials Co Ltd. The average size of the nanocrystals was about 20 nm calculated using Scherrer's equation. Methyl methacrylate (MMA), which was purchased from Chinese Shanghai First Chemical Work of Reagent, was purified by vacuum distillation and preserved at 4° before using. All other reagents were analytical pure and were used without further purification.

The ZnO nanoparticles were heated at 120°C for 20 h in order to eliminate the possible adsorbed water on the surface of the particles. The treated ZnO nanocrystals were fully mixed with prepared MMA solution (20% in volume) and were put into the ampoule, and then sealed. The solvent of MMA solution was the mixture of n-heptane/chloroform (2:3 in volume). The samples were radiated to doses of 30, 60, 90 and 120 kGy by γ radiation from a ⁶⁰Co source at a dose rate 10 kGy/h. The purpose of the γ radiation is to induce polymerization of MMA, i.e. MMA polymerized into PMMA after the radiation. Then the nanoparticles were coated with a layer of PMMA.

After the radiation the synthesized nanoparticles/polymer composites were annealed for 1, 2 and 5 min in a quartz boat at air atmosphere heated by alcohol blast burner with a annealing temperature of 800°C. The polymethyl methacrylate was oxidized and carbon was left on the surface of ZnO nanoparticles. The modified ZnO nanoparticles were examined by photoluminescence and X-ray photoelectron spectroscopy.

Steady state photoluminescence studies were carried out on the dispersion of nanopowder in purified water. For the optical measurements, nanopowders were first suspended in purified water. The solutions were dispersed with a 50W KQ-50B ultrasonic irradiation cleaner. Photoluminescence was recorded on a Shimadzu RF-5301PC fluorometer employing a 150 W Xe lamp as the light source.

Some samples were analyzed by X-ray photoelectron spectroscopy (XPS). XPS were performed using a XSAM 800 Flexo electron spectrometer with monochromatic

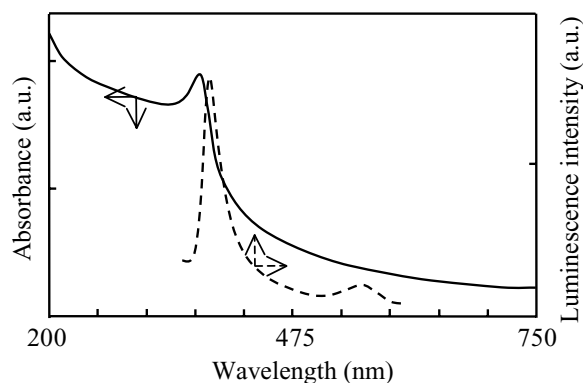


Figure 1 Optical absorption spectra and PL spectra of the as received ZnO nanoparticles.

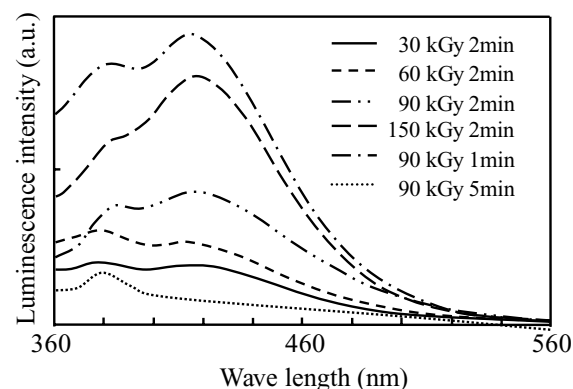


Figure 2 The PL spectra of the carbon modified ZnO nanoparticles.

Al-K _{α} X-ray radiation ($h\nu = 1486$ eV). The instrument was standardized against the C1s spectral line at 285 eV, and the spectra were interpreted and deconvoluted using the KRATOS computer software package.

3. Results and discussion

3.1. Optical properties of the as received ZnO nanoparticles

Fig.1 shows the optical absorption spectra and PL spectra (excitation wavelength = 305 nm). A strong exciton absorption peak at 373 nm owing to the relatively large exciton binding energy (~60 meV) can be observed in the optical absorption spectra. Two emission bands for the ZnO nanoparticles: one is at ~380 nm and the other is at ~550 nm. UV luminescence at about 380 nm (3.25 eV) is produced by exciton annihilation [20, 21]. The green emission at ~550 nm originates from oxygen vacancy defects or antisite defects (O_{Zn}) [22, 23].

3.2. Photoluminescence properties of the carbon modified ZnO nanoparticles

There is no visible emission from the PMMA coated ZnO nanoparticles, which was not shown in this paper. Fig.2 shows the PL spectra of the carbon modified ZnO nanopar-

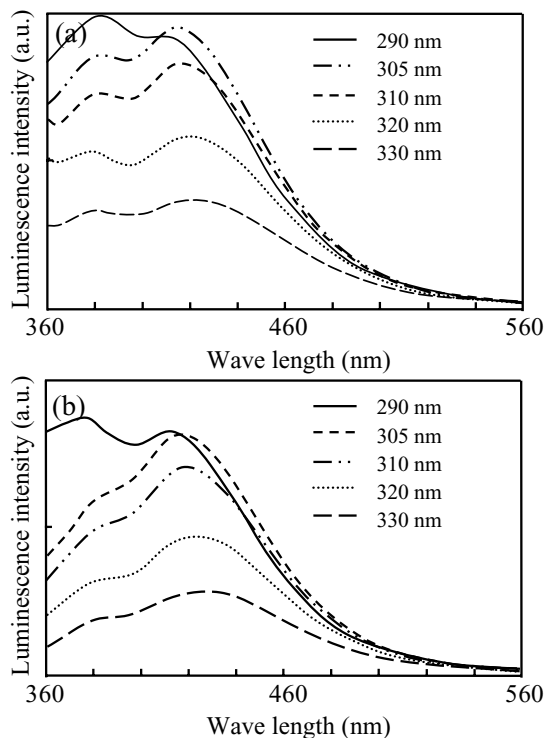


Figure 3 The excitation wavelength dependence of photoluminescence for the ZnO + MMA radiated to a dose of 90 kGy and annealed for 1 min (a) and the ZnO + MMA radiated to a dose of 150 kGy and annealed for 2 min (b).

ticles, and the experiment conditions (radiation dose and annealing time) have been shown in the figure. The excitation wavelength used is 305 nm. The UV emission at wavelength of 380 nm can be observed for all of the samples. A new emission bands for the modified ZnO nanoparticles can be found at ~ 420 nm. The UV emission depends on the annealing time, the UV PL peak disappears for the ZnO+MMA was radiated to a dose of 90 kGy and annealed for 5 min.

The excitation wavelength dependence of photoluminescence for the ZnO+MMA radiated to a dose of 90 kGy and annealed for 1 min and the ZnO+MMA radiated to a dose of 150 kGy and annealed for 2 min are shown in Figs 3a and b, respectively. The positions of the UV peak at different excitation wavelength are shown in Table I. Red shift of the emission band at ~ 420 nm with the increase of excitation wavelength can be observed.

3.3. X-ray photoelectron spectroscopy analysis

Fig. 4 shows the XPS surveys between binding energies of 0–1000 eV for the as received ZnO samples

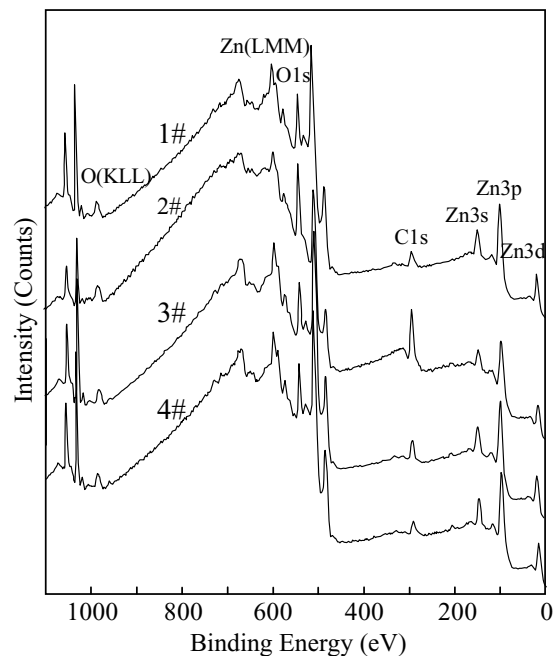


Figure 4 The XPS surveys between binding energies of 0–1000 eV for the as received ZnO (1#) samples and ZnO + MMA radiated to a dose of 90 kGy (2#) and ZnO + MMA radiated to a dose of 90 kGy (3#) and annealed for 1 min and 5 min (4#).

and ZnO+MMA radiated to a dose of 90 kGy and ZnO+MMA radiated to a dose of 90 kGy and annealed for 1 min and 5 min. The dominant signals are C, O, and Zn. Comparing the XPS survey of the four samples, it is evident the C signal increases after ZnO+MMA radiated to a dose of 90 kGy, and decreases with annealing time. The C signal recovers to original value as the received sample. This indicates that carbon must be left on the surface of ZnO nanoparticles after annealing for a short time.

High-resolution XPS collections of the O_{1s} , Zn_{2p} and C_{1s} binding energy regions have been shown in Figs 5a–c, respectively. In the Zn_{2p} region there are two peaks at 1021.941 and 1044.978 eV which correspond to the binding energies of $Zn_{2p_{3/2}}$ and $Zn_{2p_{1/2}}$, respectively. There are no changes of the Zn_{2p} peaks after the radiation and annealing treatment. For the as received ZnO nanoparticles, the photoelectron spectra of O_{1s} curve can be fitted by two peaks centered at 530.461 eV and 532.169 eV, respectively. The high-binding energy component is usually attributed to the presence of loosely bound oxygen on the surface of ZnO nanocrystals [24]. The low binding energy component is attributed to O^{2-} ions on the wurtzite structure of the hexagonal Zn^{2+} ion array, surrounded by Zn

TABLE 1 Position of UV PL peak as a function of excitation wavelength (nm)

Excitation wavelength (nm)	290	305	310	320	330
ZnO + MMA radiated to a dose of 90 kGy and annealed for 1 min	410	416	419	420	422
ZnO + MMA radiated to a dose of 150 kGy and annealed for 2 min	412	418	418	421	427

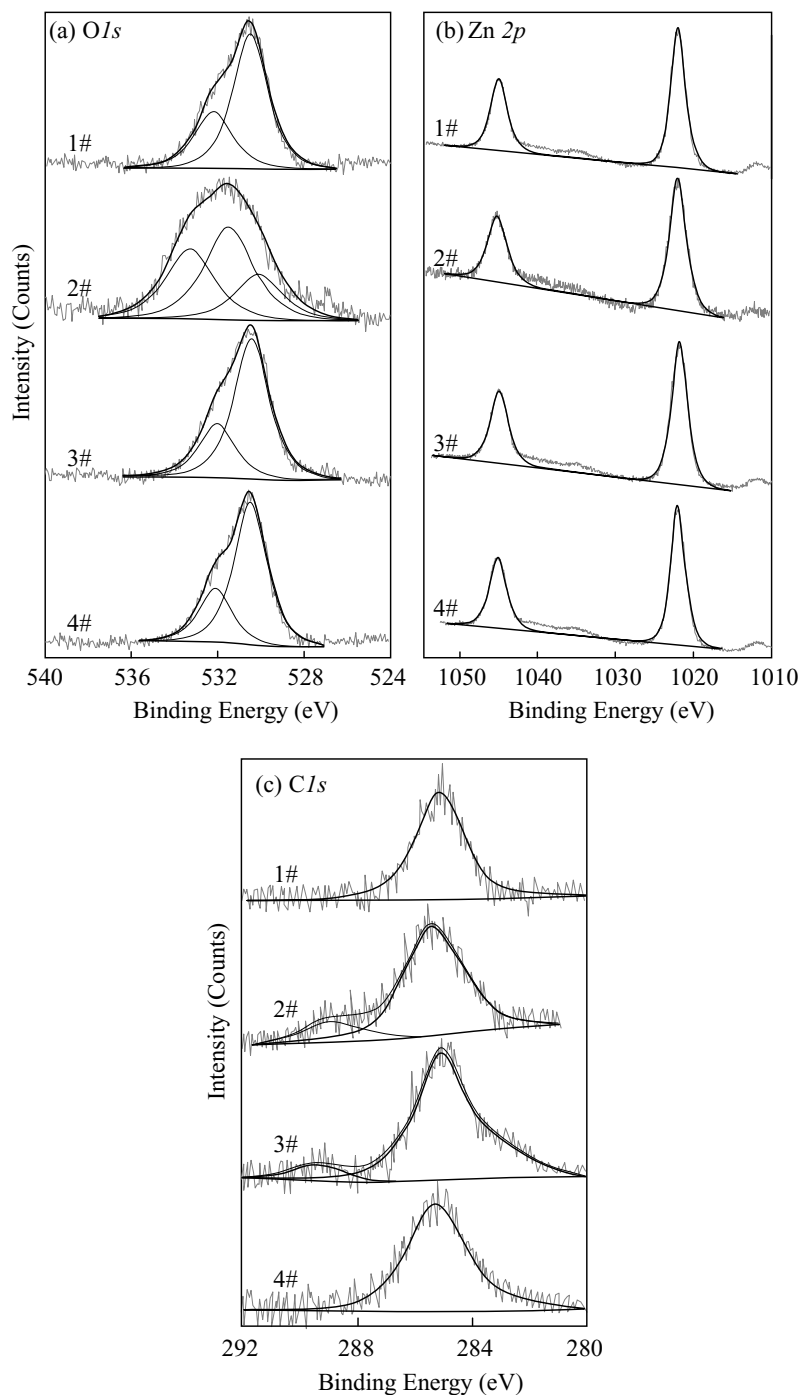


Figure 5 High-resolution XPS collections of the O_{1s} (a) , Zn_{2p} (b) and C_{1s} (c) binding energy for the as received ZnO (1#) samples and ZnO+MMA radiated to a dose of 90 kGy (2#) and ZnO+MMA radiated to a dose of 90 kGy (3#) and annealed for 1 min and 5 min (4#).

atoms [25, 26]. For the ZnO+MMA radiated to a dose of 90 kGy, the photoelectron spectra of O_{1s} curve can be fitted by three peaks centered at 530.080 eV, 531.4460 eV and 533.249 eV, respectively. The high binding energy component attributed to the carbonyl groups C=O, which indicates that the MMA polymerized after the radiation. For the annealed samples, the O 1s curve can be fitted by two peaks at 530.433 eV and 532.020 eV for sample annealed for 1 min, and 530.481 eV and 532.110 eV for sample annealed for 5 min, respectively. The binding en-

ergy of 533.249 eV disappears and the O_{1s} recovers to its original value. For the as received ZnO nanoparticles, the photoelectron spectra of C_{1s} curve can be fitted by one peak at 285.015 eV which is attributed to the diffusion pump oil representing C-C. For the ZnO+MMA radiated to a dose of 90 kGy, the photoelectron spectra of C_{1s} curve can be fitted by two peaks centered at 285.035 eV and 289.04 eV, respectively. The new peak at 289.04 eV is corresponding to carbonyl groups C=O [27]. For the annealed samples, the C_{1s} curve can be fit-

ted by two peaks at 284.921 eV and 289.5 eV for sample annealed for 1 min, and one peak at 285.200 eV for sample annealed for 5 min, respectively. The results of C_{1s} consist with those of the O_{1s} . MMA is polymerized by the radiation, and PMMA disappears after a long time annealing, and carbon is left on the surface of the ZnO nanoparticles.

XPS results show that carbon was left on the surface of ZnO nanoparticles when the PMMA coated particles were annealed in air for a short time (1–2 min). And the PMMA was burned out after annealing for a long time. The PL results show that there is no visible emission from the PMMA coated ZnO nanoparticles. However, the ~ 420 nm luminescence can be observed for the PMMA coated ZnO nanoparticles annealed for a short time (1–2 min), and the visible emission disappears after a long annealing time. We can see that the ~ 420 nm visible PL is related to the left carbon. Much O^{2-} vacancies exist on the surface of ZnO nanoparticles [22, 23], the carbon maybe absorbed at the O^{2-} vacancies as a substitution of O. Carbon is an acceptor in GaN when substituting nitrogen and the blue luminescence from the carbon doping has been observed [28]. In this work, the blue emission band maybe originates the recombination of the electron in the conduction band or in shallow donors (such as interstitial) with the carbon acceptors. More experiments are needed to confirm the above-proposed mechanism for the carbon-related luminescence. The red shift of the emission band with the increase of excitation wavelength indicates that a series of trapped states exist. The formation of these rapped states, due to the interaction between interfacial oxygen vacancies and carbon. This phenomenon has been observed in nanometer-sized SnO_2 capped with stearic acid [29]. But further investigation is needed to confirm the proposed mechanism.

4. Conclusions

The surface of ZnO nanoparticles were modified by carbon prepared through a novel method. The nanoparticles were coated a layer of poly(methyl methacrylate) by γ radiation firstly, then the coated nanoparticles were annealed in air, the polymer were burned and carbon was left on the surface of ZnO nanoparticles. A stable blue luminescence peak (~ 420 nm) can be observed for the carbon modified ZnO nanoparticles.

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