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# Photoluminescence of ZnO nanoparticles loaded into porous anodic alumina hosts

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## Abstract

The photoluminescence (PL) of ZnO nanoparticles loaded into porous anodic alumina (PAA) hosts has been investigated. These ZnO/PAA composites are synthesized by soaking the PAA films in an aqueous solution of zinc acetate and then annealing them at 500 °C. An intense blue PL emission peaked around 450 nm was observed after ZnO nanoparticles were loaded into the blank PAA hosts. Investigation results reveal that the singly ionized oxygen vacancies of ZnO nanoparticles are responsible for the 450 nm PL emission. This stable photoluminescent system with the blue emission wavelength (450 nm) shows promise for use in the field of light-emitting devices.

## 1. Introduction

The engineering of materials on the nanometre scale is an emerging interdisciplinary field based on solid-state physics, chemistry and materials science. ZnO is a wide-band-gap ( $E_g \approx 3.37$  eV) semiconductor and has promising electronic and optical properties. The preparation and characterization of ZnO materials at nanometre dimensions—including nanowires [1–6], nanobelts [7] and nanoparticles [8–11]—have recently attracted considerable attention owing to their novel physical properties and potential applications such as in short-wavelength light-emitting nanodevices.

The dependence of physical properties of materials on their grain size is a well-known phenomenon [12, 13]. Due to their small size (1–100 nm), nanoparticles exhibit novel materials properties that differ considerably from those of the bulk solid state and many efforts have been made to set up new appropriate synthesis approaches. Use of the nanosized pores of such host materials as zeolite [14], MCM-41 [10], mesoporous SiO<sub>2</sub> [9, 11] and porous anodic alumina (PAA) films [15, 16] to confine the growth of the guest materials (semiconductors, metals

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or compounds) has been adopted widely as an attractive method. For example, by putting ZnO nanoparticles into a mesoporous SiO<sub>2</sub> host, enhanced photoluminescence (PL) has been achieved and investigated previously [9].

PAA films prepared in various acid electrolytes have been widely investigated [17–19]. In particular, the pore diameters and interpore spacings of PAA films depend on the preparation conditions [18, 19], which makes PAA films attractive hosts in which to prepare nanostructures with different materials [20, 21]. The enhanced luminescence of semiconductors such as siloxenes [15], Tb-doped titania xerogel [16] and ZnO nanoparticles [22] loaded into PAA hosts has also been investigated previously. We present herein a simple and low-cost route for producing stable light-emitting systems by loading photoluminescent ZnO nanoparticles into PAA hosts. An intense 450 nm PL emission, which is different from the finding in the previous work reported by Shi *et al* [22], has been found for the ZnO/PAA composites obtained; a probable PL mechanism is proposed and discussed in this paper.

## 2. Experimental procedures

The PAA films used in this work were prepared by a two-step process of anodizing aluminium foils as described previously [19]. Briefly, the aluminium foils were anodized in a 0.3 M sulfuric acid solution under a constant voltage of 25 V at 10 °C to obtain sulfuric PAA films. After anodization, the remaining aluminium substrate at the bottom of the PAA films was removed by using a saturated SnCl<sub>4</sub> solution. Then the PAA films were cleaned with de-ionized water several times and finally dried at 120 °C for 5 h.

The PAA hosts obtained were immersed in aqueous solutions of zinc acetate with different concentrations at room temperature for two weeks. Then the soaked PAA films were washed with de-ionized water to get rid of the zinc acetate on the surface of the samples; this was followed by calcining at 500 °C in air for 5 h to cause the zinc acetate to decompose and to remove the organic components [11]. Thus, ZnO/PAA composites were obtained. The as-prepared samples with a high loading level (0.1 M zinc acetate solution) and a low loading level (0.05 M zinc acetate solution) are called samples A and B, respectively, in this work.

PL spectra of the ZnO/PAA composites were collected using a visible–ultraviolet (Vis–UV) spectrophotometer (Hitachi 850) with a Xe lamp as the excitation light source. Optical absorption data were collected on a Cary 5E UV–Vis–NIR photometer. X-band electron paramagnetic resonance (EPR; EPR-200) spectra were also measured. All these experiments were carried out at room temperature.

## 3. Results and discussion

The sulfuric PAA films obtained in our experiment have typical thicknesses and pore diameters of about 30 μm and 20 nm, respectively. Figure 1 is a schematic diagram of the nanopore structures of PAA films produced on the basis of the various existing viewpoints [17, 22]. Assuming an average number of 10<sup>10</sup> pores cm<sup>-2</sup>, a PAA film of 1 cm<sup>2</sup> size, 30 μm thick, with 20 nm pores would have an inner surface of about 200 cm<sup>2</sup>. Furthermore, it has been widely reported that PAA films possess highly ordered nanopore arrays arranged in a close-packed hexagonal pattern, whose pore diameters and interpore spacings depend on the preparation conditions [18, 19]. These properties make the PAA films good hosts for preparing guest materials of nanometre dimensions [15, 16].

Room temperature PL spectra of the as-prepared samples A and B are shown in figure 2. After the ZnO nanoparticles were loaded, the ZnO/PAA composites obtained exhibited intense

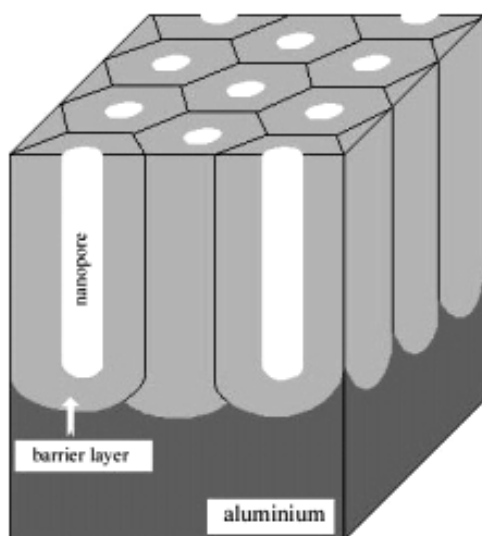


Figure 1. A schematic diagram of the nanopore structures of PAA films.

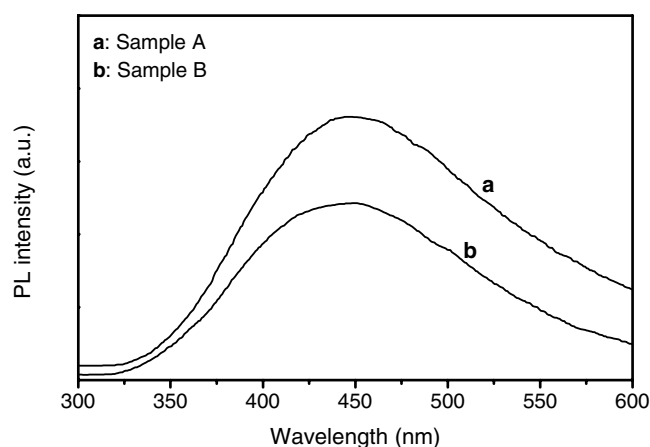
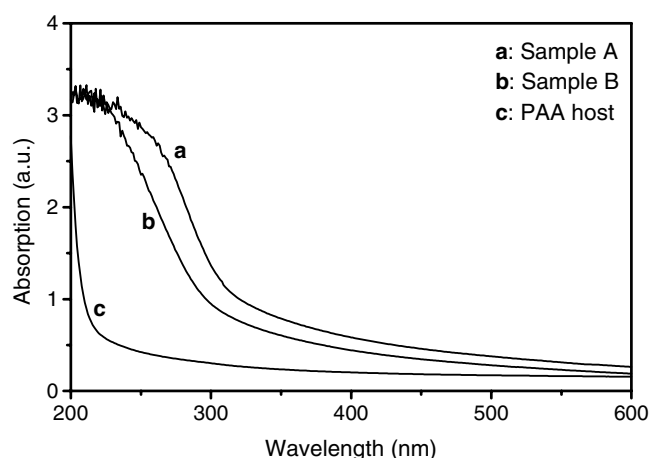


Figure 2. PL spectra of the ZnO/PAA composites. The excitation wavelength and filter are 250 and 310 nm, respectively.

and broad PL emission with the peak position around 450 nm, for which the wavelengths of the excitation and filter were 260 and 310 nm, respectively. Figure 2 also reveals that the 450 nm emission intensities increase with the ZnO loading level. The PL emission characteristics of ZnO nanoparticles loaded into sulfuric PAA hosts are similar to those of ZnO nanoparticles in MCM-41 hosts [10]. After storing all the ZnO/PAA composites in air for more than a month, their 450 nm PL emission peak positions and intensities were checked and they were found to show no obvious changes, revealing that this photoluminescent system is very stable.

Previously, Shi *et al* [22] have reported an enhanced green luminescence band with the peak position at 485 nm for the ZnO/PAA assembly, using PAA films anodized in oxalic acid as host materials. It should be noted that the luminescence characteristics of PAA films formed in different acid solutions, however, were different [23, 24]. For example, the PAA films prepared in oxalic acid have a PL emission around 470 nm, while the luminescence of



**Figure 3.** Optical absorption spectra of the ZnO/PAA composites at room temperature.

PAA films obtained in sulfuric acid is very weak [23]. In our work, the PAA hosts annealed at 500 °C in air for 5 h show no obvious luminescence. This means that the 450 nm emission has resulted from ZnO nanoparticles rather than the PAA host itself in this work. Similar conclusions were also reported previously in the cases of photoluminescent siloxenes [15] and Tb-doped titania xerogel [16] loaded into PAA films. Why there exist some differences in the case of ZnO nanoparticles loaded into different PAA hosts (i.e. the PAA films formed in different acid solutions) compared with the findings in previous work [22] is still under discussion. However, our stable photoluminescent system with a shorter emission wavelength (450 nm) than the previous one (485 nm in [22]) shows promise for use in the field of light-emitting devices.

To understand the origin of the 450 nm emission, we have characterized all the samples by using optical absorption. Figure 3 illustrates the optical absorption spectra for ZnO/PAA composites. As a reference, that for the pure PAA host annealed at 500 °C in air for 5 h was also measured. It can be seen that the ZnO/PAA composites are transparent over a larger wavelength range and show only the absorption edges of ZnO nanoparticles, which were also observed in the cases of ZnO nanoparticle/mesoporous silica composites [9, 11]. The absorption spectrum for the doped PAA hosts is quite different from that of the unloaded one (curve **c** in figure 3). The sulfuric PAA hosts annealed at 500 °C in air for 5 h start to absorb near 220 nm and show little absorption from 300 to 600 nm. After the ZnO nanoparticles were loaded in, the spectra of samples A and B featured an absorption edge near 340 and 320 nm, respectively. The absorption edges for both sample A (340 nm) and sample B (320 nm) show some blue-shifts compared to that for bulk ZnO (370 nm). These blue-shifts in the absorption spectra reveal an increasing band gap when ZnO nanoparticles are loaded into PAA hosts [25]. Various possible causes could be suggested. Firstly, the cause could be the large band gap of PAA films, which is about 5.6 eV [17], and similar results have been obtained in the case of ZnO/Al<sub>2</sub>O<sub>3</sub> films [25]. Secondly, the band gap increase could result from the size quantization effect [10, 14] due to the small sizes of ZnO nanoparticles confined in the nanopores of the host materials [9–11]. It is true that the electronic properties of the nanoparticles have a hybrid character—between those of molecules and bulk materials—and they turn into molecule-like ones as the size of the nanoparticles decreases [14]. We suggest that the ZnO nanoparticles loaded within sample A have larger sizes than those of sample B, resulting in different absorption behaviours of the two samples. This assumption is reasonable, since the concentration of the zinc acetate solutions

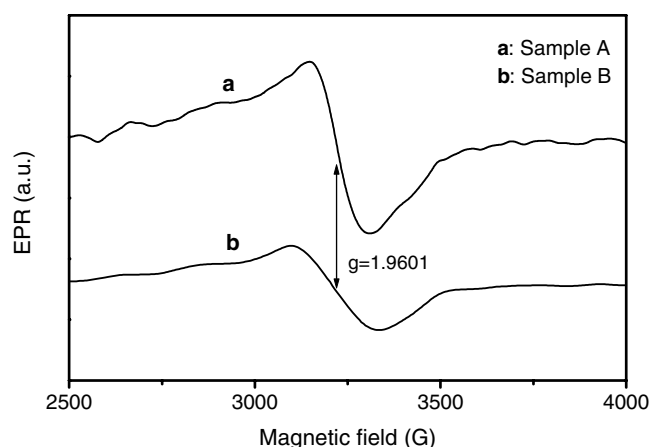


Figure 4. X-band (9.46 GHz) EPR traces of the ZnO/PAA composites at room temperature.

used for sample A is higher than that used for sample B, leading to large ZnO nanoparticles in sample A after the decomposition of zinc acetate [14, 26].

From figures 2 and 3, it can be seen that the PL emissions of the ZnO-containing samples have the same peak positions and Stokes shift as the absorption spectra. Consequently, the 450 nm PL emission would arise from mid-gap states of ZnO nanoparticles. It is well known that ZnO is a direct semiconductor of wide band gap and that the recombination of free excitons through an exciton–exciton collision process would cause near-band-edge emissions. For the different synthesis approaches, the near-band-edge emission is peaked around 380 nm [1–4]. Clearly, the PL emissions observed in our case would not be related to the free excitons but to a deep-level or defect luminescence. Previously, a 450 nm PL emission observed for ZnO nanoparticles loaded into MCM-41 hosts was thought to have resulted from the oxygen vacancy in ZnO nanoparticles [10] and a similar assumption was made in the case of a ZnO/PAA assembly [22]. However, no direct evidence was presented in the previous references.

Figure 4 shows the X-band EPR traces of the ZnO/PAA composites measured at room temperature. The PAA hosts were also characterized and showed no EPR signals. However, an obvious EPR signal with a  $g$ -factor of 1.9601 appeared after the PAA films were loaded with ZnO nanoparticles. It can be seen that sample A has a more intense EPR signal than sample B, while their  $g$ -values are same. This EPR signal with a  $g$ -factor of about 1.9601 has commonly been attributed to the singly ionized oxygen vacancies,  $F^+$  centres, in ZnO phosphor powders [27] and ZnO nanoparticles in irregular mesoporous silica aerogels [9]. On the basis of these data, we suggest that there were many  $F^+$  centres in ZnO nanoparticles loaded into PAA hosts. Therefore, the 450 nm PL emission resulted from the radiative recombination of a photogenerated hole with an electron occupying the singly ionized oxygen vacancy, the  $F^+$  centre. Figure 4 also reveals that the concentration of  $F^+$  centres in sample A is higher than that in sample B (about 1.53:1), which is in good agreement with sample A showing a more intense PL emission than sample B (about 1.51:1; see figure 2). This result also provides strong evidence that the 450 nm PL emission appeared in the case of ZnO nanoparticles loaded within MCM-41 [10] and that the 485 nm PL from the ZnO/PAA assembly [22] resulted from the oxygen vacancy in ZnO nanoparticles.

However, the visible luminescence characteristics of ZnO particles with reduced dimensions are controversial [6, 8–11, 22]. The PL mechanism of ZnO nanoparticles is very complex and influenced by many factors. Firstly, it can be assumed that the physical properties

of ZnO nanoparticles are strongly affected by their sizes. Secondly, the surface states of ZnO nanoparticles would have influences on their optical properties, such as the luminescence [8]. The sizes and the surface states of ZnO nanoparticles are both strongly sensitive to their preparation methods, which could possibly be why there exist some different PL characteristics and controversial explanations of the visible luminescence of ZnO nanoparticles [8–11]. On the basis of the experimental results obtained in our work, however, it is not possible to suggest any other detailed microscopic PL mechanism than the  $F^+$  centres of ZnO nanoparticles loaded into PAA hosts.

In summary, photoluminescent ZnO nanoparticles loaded into PAA host materials have been prepared by immersing PAA films in an aqueous solution of zinc acetate and then annealing them at high temperature. A large blue-shift of the absorption edge compared to that of bulk ZnO in the absorption spectra has been observed and a band-gap increase can be expected. PL and EPR investigations reveal that the singly ionized oxygen vacancies,  $F^+$  centres, are responsible for the green/blue emission (450 nm) of ZnO nanoparticles loaded into PAA hosts. Furthermore, the photoluminescent system obtained, ZnO/PAA composite, is very stable, which holds promise as regards use in the field of light-emitting devices.

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### References

- [1] Huang M H, Wu Y, Feick H, Tran N, Weber E and Yang P 2001 *Adv. Mater.* **13** 113
- [2] Kong Y C, Yu D P, Zhang B, Fang W and Feng S Q 2001 *Appl. Phys. Lett.* **78** 407
- [3] Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P 2001 *Science* **292** 1897
- [4] Tang Z K, Wong G K L, Yu P, Kawasaki M, Ohtomo A, Koinuma H and Segawa Y 1998 *Appl. Phys. Lett.* **72** 3270
- [5] Lakshmi B B, Patrissi C J and Martin C R 1997 *Chem. Mater.* **9** 2544
- [6] Li Y, Meng G W, Zhang L D and Phillipp F 2000 *Appl. Phys. Lett.* **76** 2011
- [7] Pan Z W, Dai Z R and Wang Z L 2001 *Science* **291** 1947
- [8] Zou B S, Volkov V V and Wang Z L 1999 *Chem. Mater.* **11** 3037
- [9] Mo C M, Li Y H, Liu Y S, Zhang Y and Zhang L D 1998 *J. Appl. Phys.* **83** 4389
- [10] Zhang W H, Shi J L, Wang L Z and Yan D S 2000 *Chem. Mater.* **12** 1408
- [11] Yao B, Shi H, Bi H and Zhang L 2000 *J. Phys.: Condens. Matter* **12** 6265
- [12] Li J and Nazer L F 2000 *Chem. Commun.* 1749
- [13] Aronson B J, Blanford C F and Stein A 1997 *Chem. Mater.* **9** 2842
- [14] Stucky G D and Dougall J E M 1990 *Science* **247** 669
- [15] Heilmann A, Jutzi P, Klipp A, Kreibitz U, Neuendorf R, Sawitowski T and Schmid G 1998 *Adv. Mater.* **10** 398
- [16] Balandin A, Wang K L, Kouklin N and Bandyopadhyay S 2000 *Appl. Phys. Lett.* **76** 137
- [17] Diggle J W, Downie T C and Goulding C W 1969 *Chem. Rev.* **69** 365
- [18] Li A P, Müller F, Birner A, Nielsch K and Gösele U 1998 *J. Appl. Phys.* **84** 6023
- [19] Masuda H and Satoh M 1996 *Japan. J. Appl. Phys.* **35** L126
- [20] Martin C R 1994 *Science* **266** 1961
- [21] Huczko A 2000 *Appl. Phys. A* **70** 365
- [22] Shi G, Mo C M, Cai W L and Zhang L D 2000 *Solid State Commun.* **115** 253
- [23] Du Y, Cai W L, Mo C M, Chen J, Zhang L D and Zhu X G 1999 *Appl. Phys. Lett.* **74** 2951
- [24] Yamamoto Y, Baba N and Tajima S 1981 *Nature* **289** 572
- [25] Meng X Q, Zhen W, Guo J P and Fan X J 2000 *Appl. Phys. A* **70** 421
- [26] Cai W P and Zhang L D 1997 *J. Phys.: Condens. Matter* **9** 7257
- [27] Vanheusden K, Warren W L, Seager C H, Tallant D R, Voigt J A and Gnade B E 1996 *J. Appl. Phys.* **79** 7983