

# The enhanced photoluminescence of zinc oxide and polyaniline coaxial nanowire arrays in anodic oxide aluminium membranes

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Paper

Received 6th February 2002, Accepted 26th February 2002

Published on the Web 1st March 2002

A novel nanomaterial, an array of zinc oxide (ZnO) and polyaniline (PANI) coaxial nanowires, was synthesized using an anodic aluminum oxide (AAO) membrane as the template. The morphology of these coaxial nanowires was observed with transmission electron microscope (TEM). The experiments on photoluminescence (PL) of coaxial nanowires and their array in AAO membrane show that the visible emission band of ZnO shifts from 530 to 400 nm for the coaxial nanowires array in AAO membrane, and to a lower wavelength (385 nm) for coaxial nanowires in NaOH solution. When compared with the PL spectrum of ZnO nanowires array in AAO membrane, an about 100 times PL enhancement was found in the PL spectrum of ZnO and PANI coaxial nanowires array in AAO membrane. The possible explanations for these two blue shifts of visible emission band of ZnO and the PL enhancement were presented.

ZnO has been known as a luminescent material for a century because of its unique properties and nowadays it is used for various applications. The direct band-gap of ZnO (3.37 eV) at room temperature makes it suitable for blue optoelectronic applications. The large bond strength with large exciton binding energy ( $E_b = 60$  meV) of ZnO makes itself a good candidate for laser materials. Nanomaterials constructed from ZnO have been extensively studied. ZnO thin films for UV laser were synthesized by Mitra *et al.*<sup>1</sup> Shi *et al.* found that ZnO nanoparticles in AAO membrane may cause luminescence enhancement.<sup>2</sup> Monticone *et al.* have investigated the UV and visible fluorescence of colloidal ZnO particles by time-resolved spectroscopy and discussed the mechanism of these two emission bands.<sup>3</sup> Dijken *et al.* also discussed the mechanism of the two emission bands by measuring the steady-state luminescence of nanocrystalline ZnO particles with different size.<sup>4</sup> Due to a wide range of potential applications in micro-electronics, display technologies, catalysis, sensors, interests in the development of new inorganic-organic hybrid materials with composition modulated on the nanometer scale have grown exponentially in recent years. And nanostructured multilayer ZnO-PANI films were studied by Kovtyukhova *et al.*<sup>5</sup> The luminescence spectrum of the composite film (ZnO-PANI)<sub>5</sub>ZnO displays a blue shift in the visible emission band of ZnO. Recently, Huang *et al.* have reported room-temperature ultraviolet nanolasers using  $\langle 0001 \rangle$  oriented ZnO nanowires grown on sapphire substrates.<sup>6</sup>

In our previous work,<sup>7</sup> ZnO film and ZnO-PANI composite film were prepared on ITO substrates by electrochemical assembly (ECA) and sol-gel technique. The ZnO-PANI composite film shows excellent luminescent performance and high photoelectrochemical conversion efficiency.

In this work, a novel nanomaterial, an array of zinc oxide (ZnO) and polyaniline (PANI) coaxial nanowires, was synthesized using anodic aluminum oxide (AAO) membrane as the template. The PL spectrum of ZnO and PANI coaxial

nanowires array in AAO membrane displays a blue shift and a 100 times PL enhancement of the visible emission band of ZnO (from 440 to 400 nm). The PL spectrum of ZnO and PANI coaxial nanowires in 0.5 M NaOH shows a greater blue shift from 440 to 385 nm of the visible emission band of ZnO.

The AAO membrane was obtained by a two-step process, which was introduced by Masuda and co-workers.<sup>8,9</sup> An adhesion layer of Ti and an Au film were sputtered onto a piece of mica as a conducting layer of the AAO membrane. The AAO membrane with a conducting layer acts as the working electrode in the process of the electrochemical synthesis of PANI nanotubules, a platinum sheet as the counter electrode and a saturated calomel electrode (SCE) as reference electrode. The electrode potential was cycled between  $-0.2$  and  $0.7$  V (scan rate  $100$  mV s<sup>-1</sup>) for 1000 cycles in 1 M HClO<sub>4</sub> solution containing 0.5 M aniline.<sup>10</sup> ZnO sols and its ethanolic dispersion were prepared and purified according to the method developed by Meulenkamp.<sup>11</sup> An AAO membrane was dipped in the ZnO colloidal solution for 30 min. After that it was washed with ethanol to remove the ZnO particles on the surface. Then, the AAO membrane was heated at 150 °C for 10 min and the ZnO nanowires array in an AAO membrane was prepared. To prepare a ZnO-PANI coaxial nanowire array in AAO membrane, the AAO membrane with a PANI nanotubule array was used as the template, ZnO colloidal solution was dropped on the template, and then was filled into the PANI nanotubules and the intervals between the PANI nanotubules and the walls of the pores in the AAO membrane under a negative pressure. Finally, the AAO membrane was washed with ethanol.

The PANI nanotubule array in an AAO membrane was characterized by SEM and TEM respectively, which was shown in Fig. 1. It can be seen from Fig. 1a, which is a SEM image with top view, that the diameter of the pores in AAO membrane is about 60 nm. Fig. 1b is a TEM cross-section view of PANI nanotubules in an AAO membrane. It shows

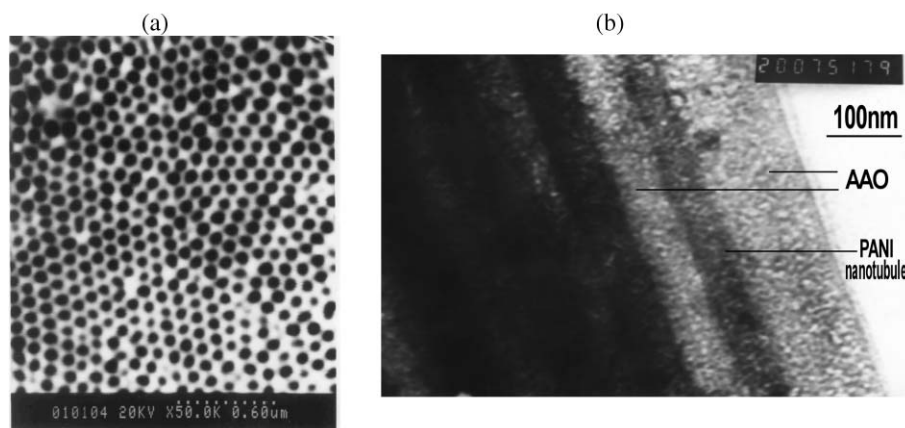


Fig. 1 (a) SEM top view and (b) TEM cross-section view of PANI nanotubules array in AAO membrane.

that the PANI nanotubules were not in contact with the walls of the pores in an AAO membrane. Fig. 2 is a TEM micrograph of one PANI nanotubule in NaOH solution. It shows that the outer diameter of the PANI nanotubule is less than 30 nm and the inner diameter less than 10 nm, which is in consistent with diameter of PANI nanotubules in AAO membrane showed in Fig. 1b. Obviously, the PANI nanotubules do not grow against the walls of pores in the AAO membrane and there is an interval between them.

The TEM images of ZnO and PANI coaxial nanowires (ZnO/PANI/ZnO) are shown in Fig. 3. Fig. 3a shows the diameter of ZnO and PANI coaxial nanowire is about 60 nm, the same as the diameter of the pores in AAO membrane. In Fig. 3b, several coaxial nanowires, some are overlapped, are shown. In the center of Fig. 3b, the PANI nanotubule (A) surrounded by ZnO nanoparticles (B) can be seen. Comparing

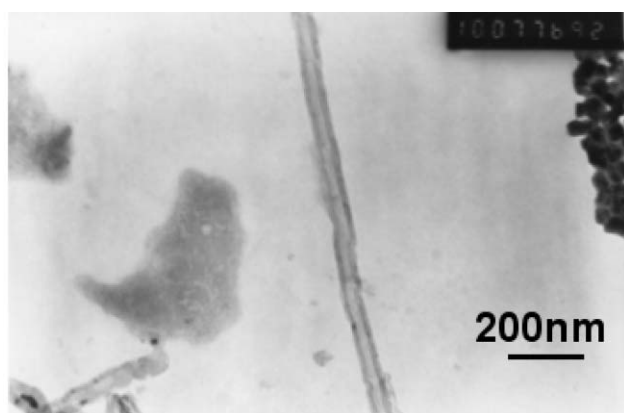


Fig. 2 TEM image of a PANI nanotubule.

with Fig. 1 and Fig. 2, it may be concluded that the ZnO particles have been filled in the intervals between the PANI nanotubules and the walls of AAO membrane. The existence of ZnO and PANI coaxial nanowire can also be proved by PL experiments (Fig. 5).

The PL spectra of ZnO film and ZnO-PANI composite film on ITO substrates are shown in Fig. 4. There is a relatively weak and narrow UV emission band at around 375 nm (3.30 eV), this band is due to the radiative annihilation of excitons. A much stronger and broader emission band is situated in the visible spectrum, with a maximum at about 530 nm, it is assigned to the radiative recombination of an electron from a level close to the conduction band edge and a surface fluorescence center located in the forbidden band.<sup>3</sup> The

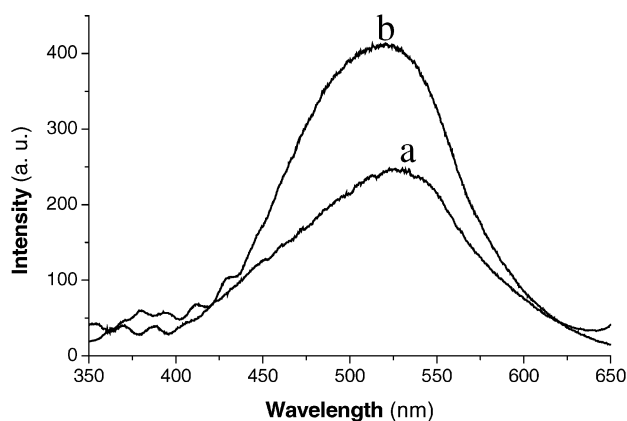


Fig. 4 Photoluminescence spectra of ZnO film (a) and ZnO-PANI composite film (b) on ITO substrates, excited at 330 nm.

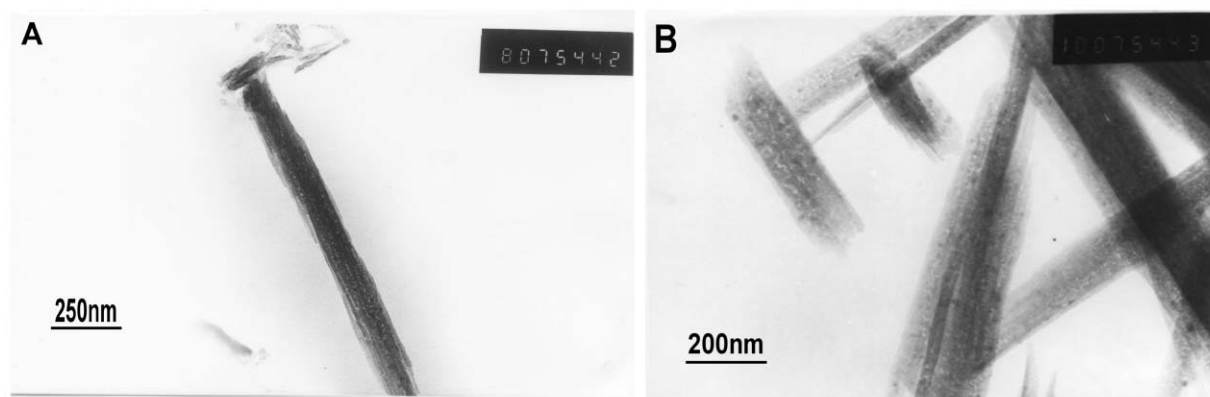
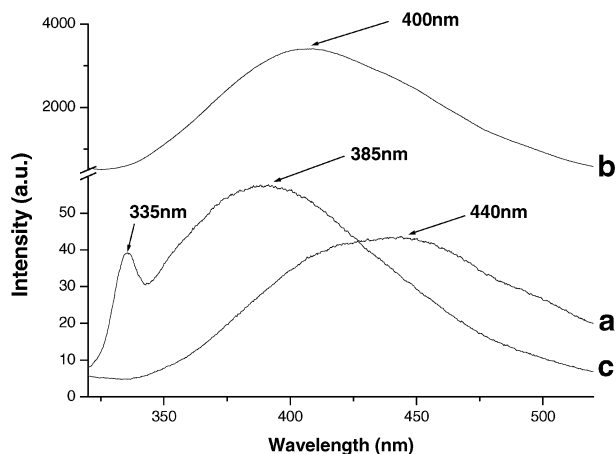


Fig. 3 TEM images of a ZnO and PANI coaxial nanowire (A) and several coaxial nanowires (B).



**Fig. 5** Photoluminescence spectrum of ZnO nanowires array in AAO membrane (a), ZnO and PANI coaxial nanowires array in AAO membrane (b), ZnO and PANI coaxial nanowires in  $0.5 \text{ mol l}^{-1}$  NaOH (c), excited at 300 nm.

PL spectrum of ZnO–PANI composite film indicates that the PANI film causes a significant photoluminescence enhancement and a blue shift of the visible emission band of ZnO film (from 530 to 520 nm). A possible reason for the PL enhancement may be the concentration of ZnO particles and the transfer of some energy absorbed by PANI to ZnO particles. The blue shift may be caused by the chemical interaction between NH groups of the PANI chains and surface  $\text{Zn}^{2+}$  ions.<sup>5</sup>

The PL spectrum of ZnO and PANI coaxial nanowires array in AAO membrane displays a broad UV and visible band. And the visible emission band peaks at 400 nm (Fig. 5b). The band has a blue shift of 40 nm and a great PL enhancement (about 100 times) compared with the PL spectrum of the ZnO nanowires array in the AAO membrane (Fig. 5a). The blue shift of the visible emission band of ZnO is greater than the one caused by the PANI film in the ZnO–PANI composite film (Fig. 4). One possible explanation for it is that PANI nanotubules make more of the NH groups in the PANI chains interact with surface  $\text{Zn}^{2+}$  ions. The great PL enhancement can be also assigned to the existence of PANI nanotubules. These results also proved the existence of ZnO and PANI coaxial nanowires.

The PL spectrum of ZnO and PANI coaxial nanowires in 0.5 M NaOH (Fig. 5c) shows that the visible emission band of ZnO has a greater blue shift of 55 nm than the one caused by

the array (Fig. 5b). Kanaev found the analogous blue shift effect when the colloidal ZnO nanoparticles were prepared in the solution with excess  $\text{OH}^-$  ions.<sup>3</sup> Obviously, apart from the chemical interactions between NH-groups and surface  $\text{Zn}^{2+}$  ions, the  $\text{OH}^-$  ions adsorbed on the surface may be responsible for this greater blue shift.

In our work on the PL spectrum of ZnO nanoparticles, it is found that when there is an excess of  $\text{Zn}^{2+}$  ions during the preparation process, the band-edge emission peak in the UV region is too weak to show. And if there is an excess of  $\text{OH}^-$  ions, the band-edge emission peak will appear relatively strong. The PL spectra shown in Fig. 5 are consistent with these results. In Fig. 5c, the band-edge emission band peaks at 335 nm. It also has a blue shift of 40 nm.

## Acknowledgement

The support of this work by the National Nature Science Foundation of China (29833060, 20023001 and 20173044), Ministry of Education (99177) and Fujian Science Foundation for Young Scientist Innovation (2001J031) are gratefully acknowledged. The authors acknowledge Yang Hong from the Institute of the Aluminum Factory, Wulumuqi, Xinjiang for his kind offer of the Al plate (>99.99%). The authors also acknowledge Teacher Ni Hongjing, Xue Ru and Dr Zai from the Center of Analysis and Test for their work on SEM and TEM.

## References

- 1 A. Mitra, R. K. Thareja, V. Ganesan, A. Gupta, P. K. Sahoo and V. N. Kulkarni, *Appl. Surf. Sci.*, 2001, **174**, 232.
- 2 G. Shi, C. M. Mo, W. L. Cai and L. D. Zhang, *Solid State Commun.*, 2000, **115**, 253.
- 3 S. Monticone, R. Tufeu and A. V. Kanaev, *J. Phys. Chem B.*, 1998, **102**, 2854.
- 4 A. Dijken, E. A. Meulenkaamp, D. Vanmaekelbergh and A. Meijerink, *J. Lumin.*, 2000, **87–89**, 454.
- 5 N. I. Kovtyukhova, A. D. Gorchinskiy and C. Waraksa, *Mater. Sci. Eng.*, 2000, **B69–70**, 424.
- 6 M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo and P. D. Yang, *Science*, 2001, **292**, 1897.
- 7 Z. X. Zheng, Y. Y. Xi, H. G. Huang, L. L. Wu and Z. H. Lin, *PhysChemComm*, 2001, 21.
- 8 H. Masuda and M. Satoh, *Jpn. J. Appl. Phys.*, 1996, **35**, L126.
- 9 H. Masuda and K. Fukuda, *Science*, 1995, **268**, 1466.
- 10 J. Luo, H. G. Huang, H. P. Zhang, L. L. Wu, Z. H. Lin and M. Hepel, *J. New Mater. Electrochem. Syst.*, 2000, **3**, 249.
- 11 E. A. Meulenkaamp, *J. Phys. Chem.*, 1998, **102**, 5566.