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Nghiên cứu chế tạo và tính chất quang của cấu trúc nano phân nhánh ZnO/NiO

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TÓM TẮT

Vật liệu ZnO/NiO có cấu trúc nano phân nhánh được tổng hợp bằng việc kết hợp giữa các phương pháp phun tĩnh điện, thủy nhiệt và lắng đọng hỗ trợ quang. Ban đầu, sợi ZnO nano được tổng hợp bằng phương pháp phun tĩnh điện rồi oxy hóa nhiệt. Sau đó, ZnO cấu trúc nano phân nhánh được tổng hợp bằng phương pháp thủy nhiệt. Cuối cùng, ZnO/NiO cấu trúc nano phân nhánh được tổng hợp bằng phương pháp lắng đọng hỗ trợ quang nhờ tia cực tím. Đặc trưng về hình thái, cấu trúc và tính chất của vật liệu được xác định nhờ ảnh hiển vi điện tử quét (SEM), phổ tán sắc theo năng lượng (EDS), phổ nhiễu xạ tia X (XRD), phổ quang điện tia X (XPS), phổ huỳnh quang (PL). Kết quả cho thấy vật liệu thu được có cấu trúc nano phân nhánh, tinh thể ZnO có cấu trúc lục giác và không có sự hình thành pha mới của NiO. Phổ huỳnh quang của vật liệu cho thấy có sự dịch chuyển đỉnh phát xạ về phía bước sóng dài hơn trong vùng nhìn thấy khi lắng đọng NiO.

Từ khóa: *ZnO/NiO, cấu trúc nano phân nhánh, tính chất quang.*

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Fabrication and optical properties of NiO/ZnO hierarchical nanostructures

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ABSTRACT

NiO/ZnO hierarchical nanostructures were synthesized by a combination of electrospinning, hydrothermal and ultraviolet (UV)-assisted deposition. Initially, ZnO nanofibers were synthesized by electrospinning method following thermal oxidation. Subsequently, ZnO hierarchical nanostructures were synthesized by hydrothermal method using ZnO nanofibers as templates. Finally, NiO nanoparticles were deposited on ZnO surface by UV-assisted deposition method. Morphology and characteristics of the material were determined by scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectrum (XPS) and photoluminescence spectrum (PL). The results showed that the NiO/ZnO hierarchical nanostructures with high open space were obtained. NiO/ZnO crystals showed hexagonal structure of ZnO without phase formation of NiO. PL spectra of the NiO/ZnO material showed emission peaks shift towards longer wavelengths in the visible region with increasing the content of NiO nanoparticles.

Keywords: *ZnO/NiO, hierarchical nanostructure, optical properties.*

1. INTRODUTION

Semiconductor materials in general and metal-semiconductor oxides (SMOs) in particular have been attracting great interest due to their advantages such as relatively simple fabrication, good stability, low cost, small size... Therefore, over the past decades, SMOs materials such as SnO_2, ZnO, CuO, V_2O_5, WO_3, In_2O_3, TiO_2... have been widely studied for the development of electronic, sensitive components gas.[1] Among SMOs, ZnO is preferred in many studies because of its advantages such as simple syntheses, low cost and low crystallization temperature.[2] In addition, the surface modification of ZnO materials by other materials results in improvement of the optical properties of the material. Recently, the optical properties, conductivity and surface catalytic properties of ZnO nanomaterials have been changed thanks to the surface modification of ZnO with other components such as metal nanoparticles (Au, Ag, Pt, Pd...) or metal oxides (NiO, CuO...).[2-6] R. Elilarassi *et al.* synthesized Ni-doped ZnO nanoparticles by "explosive method" at low temperature. The PL spectra of Ni doped ZnO showed a shift from the blue emission peak to the red emission peak.[7] Y. Wang *et al.* fabricated spherical Ni-doped ZnO material with an average diameter of 3 µm by heating a mixture of ZnO and Nickel citrate at 500 °C for 2 hours. The results showed that ZnO/Ni material had higher photocatalytic activity compared to pure ZnO.[8]

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W. Wang *et al.* synthesized ZnO/Ni nanorods on Si substrate by magnetic sputtering combined with hydrothermal at 100 °C. PL spectra of ZnO/Ni nanorods showed a narrow band in the UV region with an emission peak at 370 nm and a wide band in the yellow-green region with a peak at 560 nm. Compared with the pure ZnO, the emission peak intensity of ZnO/Ni in the UV region decreases as the concentration of doped Ni increases.[9]

Currently, there were several ways to fabricate ZnO nanostructure materials such as physical vapor deposition (PVD), chemical vapor deposition (CVD), solution method, electrospinning method, hydrothermal method, etc. In this paper, the NiO/ZnO hierarchical nanostructures were fabricated by combining electrospinning following oxidation, hydrothermal and UV-assisted deposition.

2. EXPERIMENTAL

2.1. Synthesis of ZnO nanofibers

ZnO nanofibers were synthesized by electrospinning method on Al_2O_3 sensing substrate, zinc acetatedihydrate (ZnAc) and polyvinylpyrrolidone (PVP) were dissolved in a solvent N-dimethylformamide (DMF) and ethanol. The solution was stirred during 6 hours. The solution was injected into a syringe and sprayed at a rate of 0.01 mL/hour. Al_2O_3 substrate was heated at 90°C using DC power supply; Nozzle and sample holders were connected to a DC voltage of 12 kV at distance of 12 cm. ZnAc/PVP nanofibers formed on the Al_2O_3 substrate were oxidized in an air environment at 500°C for 2 hours at a heating rate of 1°C/min to remove PVP and form ZnO nanofibers on the sensing substrate.

2.2. Synthesis of ZnO hierarchical nanostructure

ZnO hierarchical nanostructure was synthesized by hydrothermal method. The substrates containing ZnO nanofibers were placed in a mixture of zinc nitratehexahydrate ($Zn(NO_3)_2.6H_2O$) and hexamethylenetetramine (HMTA) in a 1:1 ratio that was hydrated at 90°C for 4 hours. ZnO nanofibers act as the seed for ZnO nanorods to grow around the ZnO nanofiber. After the hydrothermal process, ZnO hierarchical nanostructure on the substrate was obtained.

2.3. Synthesis of ZnO/NiO hierarchical nanostructure

NiO/ZnO hierarchical nanostructures were synthesized by UV-assisted deposition in Ni salt solution. Nickel acetate (NiAc) salts were dissolved in an ethanol solvent at room temperature. The sensing substrates containing the ZnO hierarchical nanostructure were placed in the NiAc salt solution under UV irradiation at different times of 2, 4, 8, 16 and 24 minutes. Next, samples were taken out following dry process naturally and oxidation at 350 °C for 30 minutes at a heating rate of 5°C/min. Finally, samples were cooled to room temperature naturally to obtain NiO/ZnO hierarchical nanostructures.

2.4. Morphology and Characterization

The morphological, structural and optical properties of the fabricated samples were studied by field emission scanning electron microscopy (FE-SEM; JSM 700F; JEOL), Energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD; D8 DISCOVER; Bruker AXS, Germany, with a Cu K radiation), X-ray photoelectron spectroscopy (XPS; VG Multilab 2000; ThermoVG Scientific, UK) and photoluminescence measurements using an FP-6500 spectrofluorometer (JASCO, Tokyo, Japan) utilizing an excited wavelength of 325 nm.

3. RESULTS AND DISCUSSION

Figure 1 shows SEM images with a magnification of × 100k of ZnO nanofiber (a) and hierarchical structures of ZnO (b) and NiO/ZnO with Ni deposition time of 16 min (c). Figure 1a shows the relatively uniform distribution of ZnO nanofibers, which was formed by the ZnO nanoparticles. The space between the nanofibers

is quite large. Figure 1b shows radial, symmetrical ZnO rods around ZnO fibers, with an average length of ~ 1μm and a relatively smooth surface. Figure 1c shows that the hierarchical structure of ZnO remains unchanged but the ZnO nanorods surface is slightly rough due to the deposition of NiO particles.

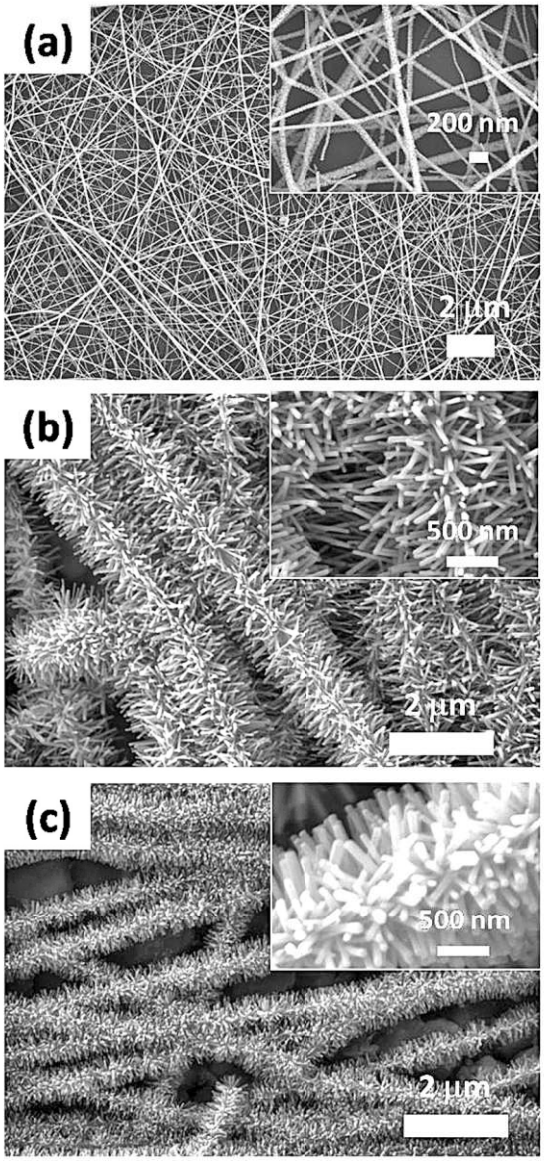

Figure 1. SEM images of ZnO nanofibers (a), ZnO hierarchical structures of pure ZnO (b) and NiO/ZnO with Ni deposition time of 16 minutes (c).

Figure 2 shows the spatial distribution of Zn, O, Ni elements and EDS spectrum of the NiO/ZnO hierarchical nanostructure with a NiO deposition time of 16 minutes. NiO/ZnO materials contain only the elements Zn, O and Ni. The elements Zn, O, Ni are distributed relatively evenly throughout the space of the material. This proves that the synthetic material is completely pure. The percentage content of O, Ni, Zn atoms in the sample are 48.56%, 0.61% and 50.83%, respectively. On another hand, the Ni content in the fabricated nanostructure is low in compared to Zn and O.

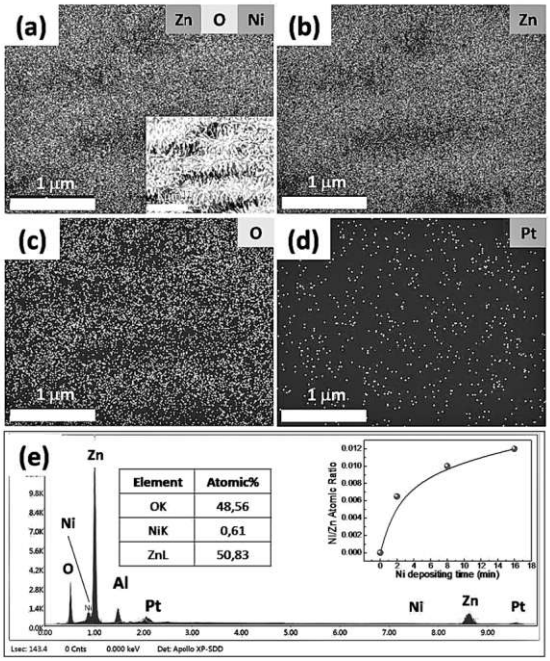

Figure 2. Distribution of the elements Zn, Ni and O (a), Zn (b), O (c), Ni (d) and EDS spectrum (e) of NiO(16)/ZnO nanostructure. Insert in (a) is the corresponding SEM image. Insert in (e) shows the dependence of the Ni/Zn atom ratio on the Ni deposition time determined from the EDS spectrum.

Figure 3 shows total XPS spectrum (a) and high magnification Ni2p (b) of NiO/ZnO hierarchical structure with Ni deposition time of 16 minutes. The composition and chemical states of the elements present in the NiO/ZnO sample show that the fabricated material contains only Zn, O, Ni and C. There are two peaks with strong strength at binding energies of 1020 eV and 1040 eV corresponds to the 2p3/2 and 2p1/2 state of Zn. Two peaks at the binding energies were located at 856 eV and 873 eV corresponding to the 2p3/2 and 2p1/2 states of Ni.

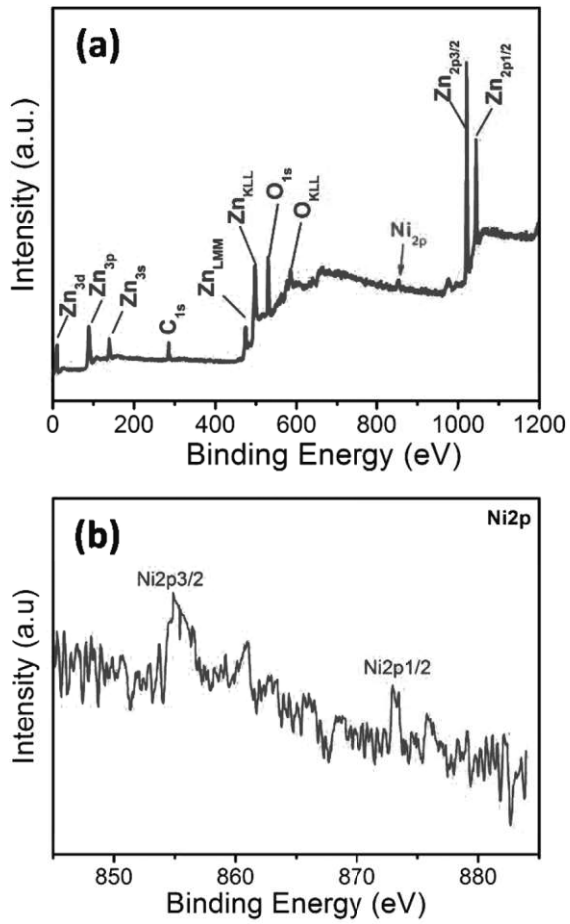

Figure 3. The total XPS spectrum (a) and high manification of Ni2p (b) in NiO(16)/ZnO structure.

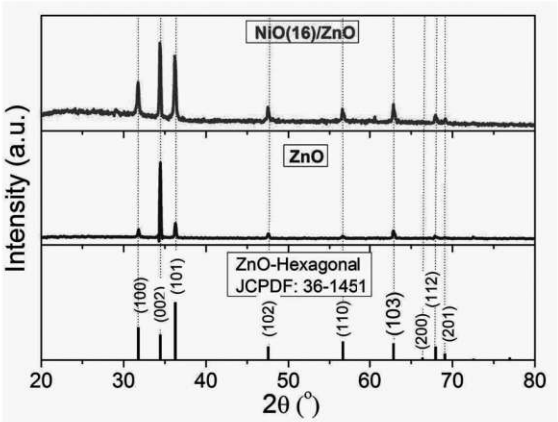

Figure 4. XRD spectrum of ZnO and NiO(16)/ZnO materials.

Figure 4 shows the X-ray diffraction spectrum (XRD) of ZnO and NiO/ZnO with a Ni deposition time of 16 minutes. Hierarchical structures of ZnO and NiO/ZnO showed the diffraction peaks corresponding to diffraction plans of (100), (002), (101), (102), (110), (103), (200), (112) and (201) (file JCPDF No. 36-1451). This result shows that ZnO has hexagonal structure with lattice constants of a = 3,294 Å and c = 5,206 Å. The fabricated structures show the diffraction peak with the strongest intensity at 2θ = 34,5°. This indicates that the growth of ZnO is highly oriented in the direction <002>. The NiO/ZnO structure did not see the diffraction peak of NiO. This can be explained by the low NiO concentration of this sample which is not enough to cause appearance of the diffraction peaks.

Figure 5 shows the PL spectra of ZnO and NiO/ZnO nanostructures with NiO deposition times of 2 minutes, 8 minutes and 16 minutes under the 325 nm excitation wavelength at 300 K. PL spectra of ZnO and NiO/ZnO materials include a narrow emission band in the ultraviolet region and a wide emission band in the visible light. The emission peak at 380 nm is considered to be the characteristic emission peak of ZnO related to the band - band recombination. At the wavelength value of this emission peak, we can estimate the band gap of ZnO and NiO/ZnO materials to be about 3.26 eV. Emission in the visible region is believed to originate from lattice defects such as: vacancy oxygen (V_O), interstitial oxygen (O_i), vacancy zinc (V_{Zn}), interstitial zinc (Zn_i)...

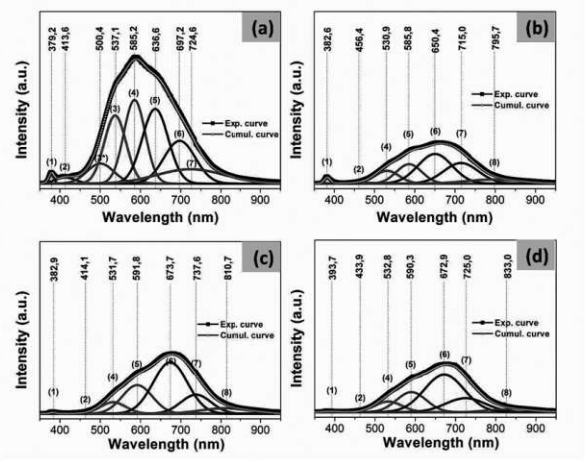

Figure 5. PL spectrum of ZnO (a), NiO(2)/ZnO (b), NiO(8)/ZnO (c) and NiO(16)/ZnO (d) materials.

The PL intensity of NiO/ZnO hierarchical structures is lower than that of the ZnO hierarchical structure. This is explained by the deposition of NiO particles (p-type semiconductor) on the surface of the ZnO rods (n-type semiconductor) forming a p-n junction, which prevents the recombination of photogenerated electrons and holes. The results show that the NiO deposition time prolong causing the decreasing of the intensity of emission peak in the UV region. Moreover, the spectral peak in the visible region is reduced and shifted towards longer wavelengths. The emission peaks is located at 650.4 nm, 673.7 nm and 672.9 nm for structures of NiO(2)/ZnO, NiO(8)/ZnO and NiO(16)/ZnO. NiO(8)/ZnO shows the strongest emissive peak intensity in the visible light region. This is explained by the increasing of donor impurity levels due to the formation of oxygen vacancies on the ZnO surface during NiO deposition.

4. CONCLUSION

NiO/ZnO hierarchical nanostructures were synthesized by electrospinning, hydrothermal and UV-assisted deposition. The study results showed that when ZnO was decorated by NiO nanoparticles, the morphology and structure of the material were not changed compared to pure ZnO nanostructure but the optical properties of the material changed significantly. The emission peaks shifted towards longer wavelengths in the visible light region with increasing the NiO deposition time on the ZnO surface. The emission peak intensity in visible region is the highest as NiO deposition time of 8 minutes. This opens up the application direction of NiO/ZnO materials for optoelectronic devices.

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