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Electrochemical Properties of Nickel Oxide Nanoparticles Loaded Poly(o-toluidine) Composites

Shanmugasundaram Komathi[†], Pothum Selvi[†], Paramasivam Manisankar[†], Anantha Iyengar Gopalan*, and Kwang-Pill Lee*

Department of Chemistry Graduate School, Kyungpook National University, Daegu 702-701, South Korea
[†]Department of Industrial Chemistry, Alagappa University, Karaikudi, India

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Abstract : New nanocomposites, composed of poly(o-toludine) (POT) and nickel oxide nanoparticles (NiO-NPs), were prepared through oxidative polymerization of o-toludine (OT) in the presence of NiO-NPs. Films of NiO/POT were prepared with different amount of NiO-NPs (x) and different concentrations of OT (y) and designated as NiO(x)/POT(y) nanocomposites (x = amount of NiO-NPs (mg), y = concentration of OT (mM)). Field emission scanning electron microscopy images revealed that NiO-NPs have nanorod like morphology. The two peaks, 0.39 V and 0.77 V, are attributed to the redox conversion of leucoemeraldine to emeraldine and emeraldine to fully oxidized forms of POT, respectively. Electroactivity of the NiO(x)/POT(y) films showed dependence on x and y. Efficient electrocatalysts could be obtained by tuning x and y.

Keywords : Nickel oxide, Poly(o-toluidine), Nanocomposite, Conductivity, Electrochemistry

1. Introduction

Polyaniline (PANI) received considerable attention due to its special doping mechanism, high environmental stability, ease of processability and low cost. Nanocomposites based on PANI with transition metal oxides have been intensively investigated as the composites can have improved magnetic, electrical and optical properties over the individual components.[1-3] Generally, three methods were adopted for the synthesis of such composites. The first one involves the intercalation of the monomer into the host (metal oxide) matrix followed by polymerization using an external oxidizing agent.[4] In the second method, the redox properties of the host ensure in-situ polymerization as well as interacalation of PANI.[5] The third method consists of direct intercalation of PANI or polymer chains inside the host particles.[6] Importantly, PANI-inorganic oxide nanocomposites are effective electrocatalysts for many reactions and find applications in sensors.[7,8] PANI/WO_3 composites have been prepared and used as humidity sensor.[9] Phosphomolybidic acid doped PANI/V_2O_5 composite has been proved to be an effective electrocatalyst for oxygen reduction in weakly acidic solution.[10] Metal oxides such as MOO_3 and VO_2 offered electrocatalytic properties when incorporated into PANI matrix.[11-13]

Xia *et al.*[14] reported the preparation of porous NiO and used as a template to synthesize porous materials. However, reports on the synthesis of NiO/PANI composites and studies on their electrochemical properties are scarce. NiO/PANI nanobelt and NiO/PANI rectangular tube powders have been prepared through chemical polymerization.[15,16] NiO_x/PANI composite films were prepared by electro-deposition and used as a catalyst towards electro-oxidation of polyhydroxyl compounds.[17]

In this article, we report the preparation and electrochemical properties of NiO/poly(o-toludine) (NiO/POT) nanocomposite. Briefly, NiO nanoparticles (NiO-NPs) were prepared by hydrothermal process and subsequently converted into NiO/POT nanocomposite through oxidative polymerization of o-toludine (OT) in the presence of NiO-NPs. Sodium dodecyl benzenesulfonate (SDS) was used as medium for polymerization to disperse the NiO-NPs.

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*E-mail: kplee@knu.ac.kr (K.P. lee),
algopal99@gmail.com (A.I. Gopalan)

2. Experimental

2.1. Chemicals

O-Toludine (OT), sodium dodecyl benzene sulphonate (SDS), nickel chloride, silver nitrate ($AgNO_3$), potassium peroxodisulphate (PDS) were obtained from Sigma Aldrich (S.Korea). Solvents such as hydrochloric acid (HCl) and N,N dimethyl formamide (DMF) are of analytical grade.

2.1.1. Preparation of NiO nanparticles

NiO-NPs were prepared from $Ni(OH)_2$ by thermal annealing process. $NiCl_2·6H_2O$ was used for the preparation of NiO. A mixed solution containing urea and $NiCl_2$ $6H_2O$ (with a molar ratio of 2 : 1) was prepared in water and kept at 50°C for 80 min. The reaction was stopped by the addition of ice water into the mixture. The precipitate, $Ni(OH)_2$, was filtered through a G4 sintered crucible and was washed with water till the filtrate was free from Cl^- ions. The filtrate was checked by the addition of 0.1 M $AgNO_3$ solution. The precipitate was calcined at 500°C for 2 h. NiO-NPs (dusky green color) were collected.

2.2. Preparation of NiO/POT nanocomposites

NiO/POT nanocomposites were prepared through in situ polymerization of OT in the presence of NiO-NPs. Polymerization was carried out as follows. NiO-NPs (20 mg) and OT (40 mM) were dispersed in 1 M HCl solution containing 0.05 M SDS with stirring. The solution temperature was maintained at 5°C. To the above dispersion, a pre-cooled solution of PDS (40 mM) was added drop wise. The solution was allowed to stir for another 12 h. The precipitate (dark green color) was filtered, washed with distilled water and dried in vacuum oven. The NiO/POT nanocomposites were also prepared using (i) fixed loading of OT (40 mM) with different amount of NiO-NPs (40 mg, 60 mg) and (ii) fixed loading of NiO-NPs (20 mg) with different concentrations of the monomer (10 mM, 20 mM, 30 mM). The nanocomposites were designated as NiO(x)/POT(y) (where x represents the amount (mg) of NiO-NPs used in the nanocomposite preparation and y represents the concen- tration (mM) of OT used for the preparation of nanocomposite).

2.3. Characterization and electrochemical properties of NiO(x)/POT(y) nanocomposites

Morphology of the NiO and NiO(x)/POT(y) nanocomposites were analyzed by Field emission scanning electron microscopy (FESEM, Hitach-530). UV-visible spectrum of NiO(x)/POT(y) nanocomposites were recorded using the UV- 2401 PC spectrophotometer in absorbance mode by dissolving the nanocomposites in N,N dimethyl formamide (DMF) solvent (UV- 2401 PC spectrophotometer). Conductivity measurements of NiO(x)/POT(y) nanocomposites were made through a four-probe resistivity setup (Concord Instruments). For the conductivity measurements, the NiO(x)/POT(y) nanocomposites films were prepared by drop casting method. 0.1 g of the nanocomposite was dissolved in DMF and sonicated for 15 min to form a colloidal solution. 50 μL of the colloidal solution of the nanocomposite was dropped onto the surface of a glass plate (area : 2 × 2 cm) and dried at room temperature to obtain the film on the surface of glass plate. Electrochemical measurements were carried out in Bas100 Electrochemical analyzer using three electrode cell set up. Saturated calomel electrode was used as reference electrode, Pt wire served as auxiliary electrode and NiO(x)/POT(y) nanocomposite film modified indium tin oxide coated glass plate (ITO) as working electrode respectively.

3. Results and Discussion

3.1. Characteristics of NiO(x)/POT(y) nanocomposites

3.1.1. Morphology

Fig. 1 shows the FESEM images of pristine NiO (a) and NiO/POT nanocomposites (b). Pristine NiO-NPs, prepared from $Ni(OH)_2$, showed nanorod morphology with diameters in the range of 40-50 nm (Fig. 1(a)). However, the particles of NiO(20)/POT(40) nanocomposites were irregular shaped with aggregation. The morphological changes between pristine NiO (Fig. 1(a)) and NiO(20)/POT(40) nanocomposite (Fig. 1(b)) could be due to polymerization of OT at the surface of NiO-NPs.

3.1.2. UV-visible Spectroscopy

UV-visible absorption spectra of NiO(x)/POT(y) nanocomposites, prepared with fixed amount of NiO(x) and different concentration of POT(y), are presented in Fig. 2(a). Typically, spectra of NiO(20)/POT(10) (Fig. 2(a), spectrum a), NiO(20)/POT(20) (Fig. 2(a), spectrum b), NiO(20)/POT(30) (Fig. 2(a), spectrum c), NiO(20)/POT(40) (Fig. 2(a), spectrum d), are displayed. Fig. 2(b)

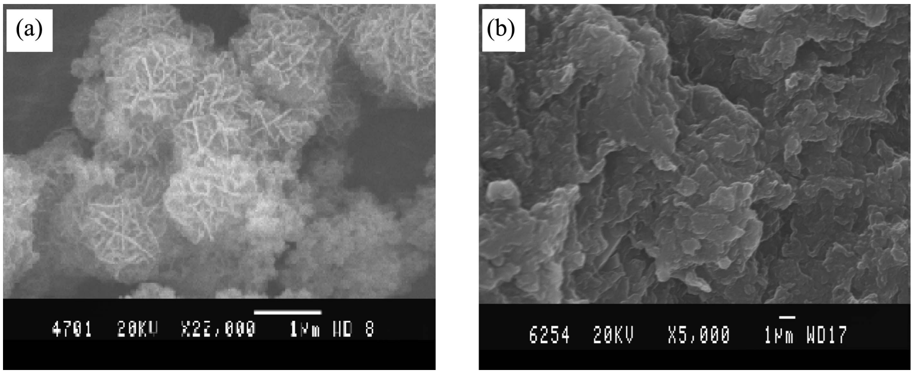

Fig. 1. FESEM images of (a) NiO nanorods, (b) NiO(x)/POT(y) nanocomposites (20 mg/40 mM).

represents the UV-visible spectra of NiO(x)/POT(y) nanocomposites prepared with different amount of NiO(x) and fixed concentration of POT(y). UV-visible spectra of NiO(20)/POT(40) (Fig. 2(b), spectrum a), NiO(40)/POT(40) (Fig. 2(b), spectrum b), NiO(60)/POT(40) (Fig. 2(b), spectrum c), are presented. The two electronic bands observed around 345 nm and 435 nm and 570 nm correspond to the doped states of POT.[19] The band around 345 nm is assigned for π-π* electronic transition of the benzenoid ring.[20] The peak around 435 nm is assigned to the localized emeraldine form.[21,22] The additional band around 570 nm may be due to π-π transition in N - phenyl para - phenylenediamine.

3.1.3. Electrical conductivity

Table 1 shows the conductivity values of NiO(x)/POT(y) nanocomposites films. The conductivity of NiO(x)/POT(y) nanocomposite showed an increasing trend with increasing loading of NiO-NPs. Also, the conductivity showed an increasing trend for the composites with increasing amount of POT.

3.1.4. Electrochemical properties of NiO(x)/POT(y) nanocomposites

Cyclic voltammograms (CVs) of NiO(20)/POT(10) (a), NiO(20)/POT(20) (b), NiO(20)/POT(30) (c), NiO(20)/POT(40) (d), were recorded in the potential range from -100 mV to 1100 mV (Fig. 3(a)). Two anodic peaks (around 0.39 V and 0.77 V) and a small shoulder around 0.52 V were observed for NiO(x)/POT(y) nanocomposite films. The two peaks, 0.39 V and 0.77 V are attributed to the redox conversion of leucoemeraldine to emeraldine and emeraldine to fully oxidized forms of POT. The

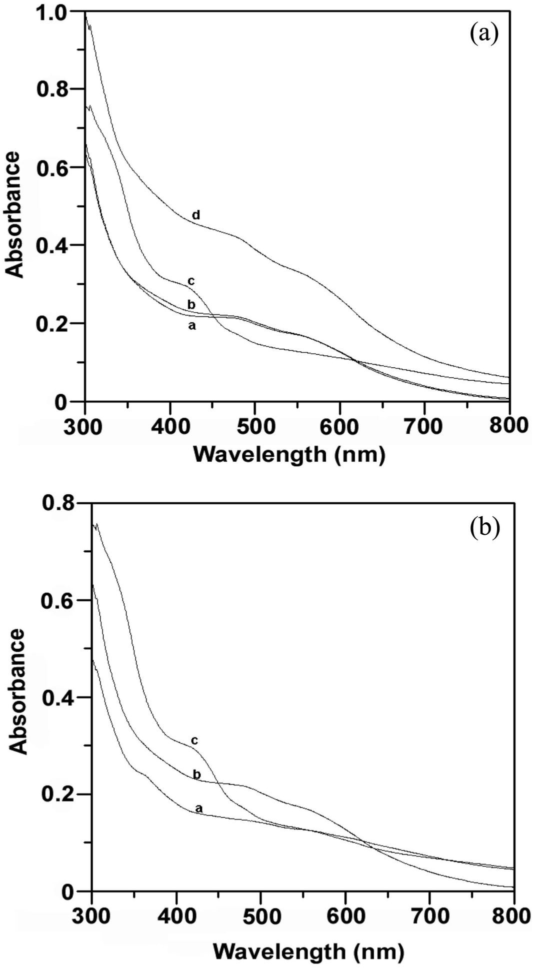

Fig. 2. UV-visible spectra of NiO(x)/POT(y) nanocomposite (A) NiO(20)/POT(10) (a), NiO(20)/POT(20) (b), NiO(20)/POT(30) (c), NiO(20)/POT(40) (d); (B) NiO(20)/POT(40) (a), NiO(40)/POT(40) (b), NiO(60)/POT(40) (c).

Table 1. Conductivity values of NiO(x)/POT(y) nanocomposites.

NiO(x)/POT(y) nanocomposite		Conductivity (mS/cm^2)
NiO(20)/POT(y)	y = 10	1.3
	y = 20	1.7
	y = 30	2.3
	y = 40	2.1
NiO(x)/POT(20)	x = 40 mg	2.5
	x = 60 mg	3.3

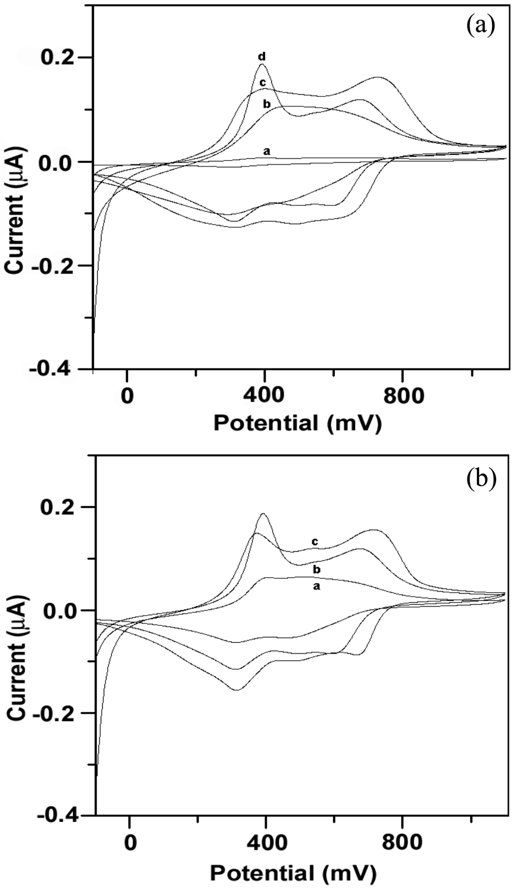

Fig. 3. CVs of NiO(x)/POT(y) nanocomposite (A) NiO(20)/POT(10) (a), NiO(20)/POT(20) (b), NiO(20)/POT(30) (c), NiO(20)/POT(40) (d); (B) NiO(20)/POT(40) (a), NiO(40)/POT(40) (b), NiO(60)/POT(40) (c) in 0.1 M H_2SO_4.

peaks at 0.39 V and 0.77 V showed increase in peak current for the NiO(x)/POT(y) nanocomposite film prepared with increasing concentration of OT. The increased peak current indicated the increased amount of POT in the NiO(x)/POT(y) nanocomposite. The shoulder around 0.52 V may be due to benzoquinone/hydroquinone formed as bye-products.

CVs were also recorded for the NiO(20)/POT(40) (a), NiO(40)/POT(40) (b), NiO(60)/POT(40) (c) nanocomposite film (Fig. 3(b)). Here, one could clearly notice a steady increase in peak current at ~0.52 V for the prepared with increasing content of NiO-NPs. This indicates that more quantity of benzoquinone/hydroquinone may be formed as a result of increasing content of NiO in the nanocomposite.

The electrochemical properties of NiO(20)/POT(40) nanocomposite film were examined at different scan rates (Fig. 4(a)). The peak potential corresponding to the first redox transition in POT showed a positive shift with increase in sweep rates. The cathodic counterpart showed a negative shift. The shift in anodic and cathodic peak potentials may arise from the increased polarization overpotentials that resulted from diffusion of electrolyte ions (SO_4^{2-}) and electron transfer from electrode to electrolyte. The peak currents of anodic/cathodic peak were found

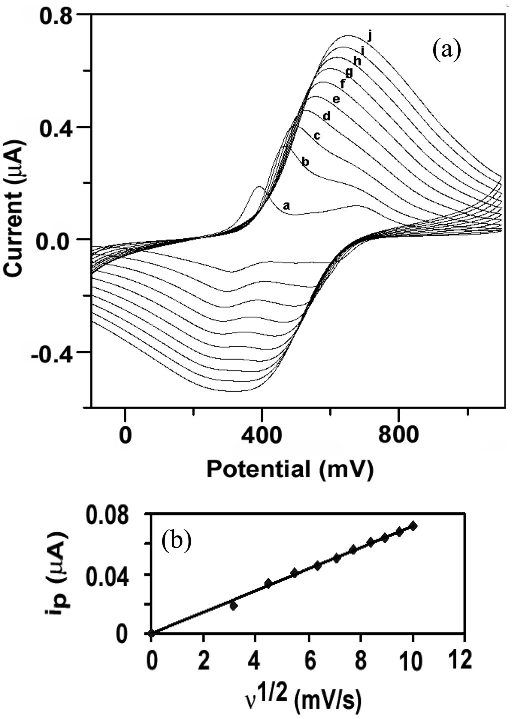

Fig. 4. (A) Cyclic voltammogram of NiO(20)/POT(40) nanocomposite at different scan rates from 10 to 100 mV/s (a-j) in 0.1M H_2SO_4; (B) Plot of $n^{1/2}$ vs anodic peak current.

to increase with scan rates. Typically, the peak current showed square root dependence on scan rates (Fig. 4(b)). This informed that electron transfer at the drop casted NiO(x)/POT(y) nanocomposite film (20 μL nanocomposite solution/cm^{-2}) modified electrode is a diffusion controlled process.

4. Conclusions

New NiO(x)/POT(y) nancomposites were prepared using different conditions. The electrochemical behavior of the NiO(x)/POT(y) nanocomposite electrode was sensitive to the amount of NiO (x) in the nanocomposite. The conductivity values of the composite were found to increase with increase in NiO-NPs (x) and POT (y) content in NiO(x)/POT(y) nancomposites. The present methodology for the preparation of nanocomposites can be extended for preparing other metal oxide nanoparticles incorporated conducting polymer composites.

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