

Electrophoretic deposition behavior of ZnO nanoparticles and their properties on conductive fabrics

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Uniform coating of ZnO nanoparticles on copper coated-polyester fabric was obtained by electrophoretic deposition (EPD). Deposition rate on the fabrics and plates were examined using a kinetic equation. Fabric gives more deposit weight than flat substrate due to rough surface or high surface area. The morphologies and structure of the deposited ZnO layers showed uniform deposition without preferred orientation on both substrates, but a higher deposition rate results in cracks on the surface after drying. The results by PL, UV transmission, and Raman presents slight decrease of bandgap and the shift of Raman peak due to smaller particle size in the as-deposit ZnO films.

Key words: EPD, Conductive fabric, ZnO nanoparticle

Introduction

Much efforts to control the structure and function of materials at the nanoscale have made due to their great potential for a wide range of applications, such as energy conversion devices, electronic components, data storage devices, biosensors and biomedical applications [1, 2]. As methods to build nanostructures on the surface of materials, coating from solution precursors such as electrolytic deposition (ELD) and electrophoretic deposition (EPD) has been applied [3]. In particular, the electrophoretic deposition (EPD), one of colloid techniques provides various advantages in the processing of ceramic materials because of its high versatility for coating a wide variety of compounds with different structures as well as low cost equipment [4-7]. Uniform coating of electrophoretically deposited materials has been demonstrated on three-dimensional, porous, and even flexible substrates [6]. In case of flexible fibers or wire substrates for EPD, there are reports on bohemite coating on stainless steel fiber mats [8] and alumina on stainless steel wires [9]. The applicability of EPD by coating metal oxides on solid substrates has been well studied, but few studies have been performed on fabrics. The use of fabrics for embedding or coating nanostructured functional materials could leverage wearable multi-functional devices [10-12].

In this study, ZnO nanoparticles were coated by EPD on flexible fabric and solid plate substrates. The effects of applied voltage and substrate type on the EPD

kinetics and morphological properties were investigated. The structural and optical properties of deposit ZnO layers by EPD were also examined by X-ray diffraction (XRD), Micro-Raman spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS), and Photoluminescence (PL) spectroscopy.

Experimental

Commercially available ZnO powder (Sigma-Aldrich with average particle size of 80 nm) and anhydrous ethanol (Fisher Scientific) were used for preparing suspensions for the EPD. Polyethyleneimine (PEI, molecular weight = 25,000, Alfa Aesar) with 0.1 wt% was added as a dispersant. The pH levels of the suspensions were adjusted with ammonium hydroxide (Sigma-Aldrich). The suspensions were ultrasonicated for 1 hour to improve dispersion, and then were immediately used for EPD. Zeta potentials of the suspensions was measured via zeta potential analyzer (Malvern Zetasizer 2000) with 0.1 wt% suspensions of ZnO prepared in ethanol. Copper coated fabric (PCPTF, LessEMF) and a copper plate (Sigma-Aldrich) were used as deposition substrates. A stainless steel substrate with the same dimension was used as the counter electrode. All substrates were cleaned with ethanol prior to deposition. The deposition cell is comprised of a glass beaker containing the counter electrode and the working electrode. The dimensions of cathode and anode was 1 cm² each and the distance between working and counter electrode was kept constant at 1 cm during the deposition. During EPD process, various voltages were applied across the electrodes and the cell current was recorded. After

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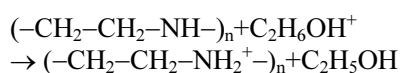
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deposition, the substrates were dried in air for 24 hour at room temperature, and the deposition yields were determined by weighing the dried deposits.

The morphology of the coated ZnO layer was examined by a field emission scanning electron microscope (FESEM, JEOL JSM-7000F). The crystalline phase of the ZnO was analyzed by X-ray diffraction (XRD, Bruker D8 Discover) using CuK α radiation in the 2 θ ranging from 20 to 80° range at a step size of 0.02°. Room temperature micro-Raman spectroscopy was employed using the 441.6 nm line (80 mW) from He-Cd laser (Kimmon Electric). The UV-vis DRS measurements were performed with the commercial AvaSpec-2048-USB fiberoptic UV-vis spectrometer. The spectra were measured from 245 to 800 nm. Barium sulphate was used as a white reference material. Room temperature PL spectrum was measured with 325 nm line (20 mW) from a continuous-wave He-Cd laser (Kimmon Electric).

Results and Discussion

Zeta potential of ZnO nanoparticles in ethanol and PEI suspensions prepared at different pH levels were characterized. Since ZnO is easily soluble in acid [13], suspensions were measured at basic pHs. Figure 1 shows that PEI charges ZnO surface positively. ZnO has a relatively high positive zeta potential at pH 9, and then it decreases with increasing pH levels. It is reported that PEI in ZnO aqueous suspension modifies the surface of ZnO particles by increasing the isoelectric point (IEP) [13, 14]. PEI can adsorb protons in the suspension due to the imido functional group (–NH) so that PEI becomes positively charged [13, 14]. Since the protonated structure of PEI can be maintained at basic pH levels, PEI is regarded as an effective dispersant [14]. The reactions of PEI in ethanol suspensions had not been reported. But the following reaction on the positive charge of PEI in ethanol can be expected from PEI and water system:



It is likely that ZnO surface may lose protons and zeta potential become lower at high pH. This can explain the decrease of zeta potential with pH as shown in Fig. 1. Once stable suspensions are obtained, one of the important parameter to influence EPD kinetics can be the electrophoretic mobility since the mobility of particles is directly proportional to zeta potential. Therefore, pH 9 representing the highest positive charge, was kept and other parameters relating to EPD such as voltage and time were investigated.

Suspensions of ZnO nanoparticles with a concentration of 2.5 wt% in ethanol were used in this EPD. ZnO nanoparticles were deposited on flexible fabrics and

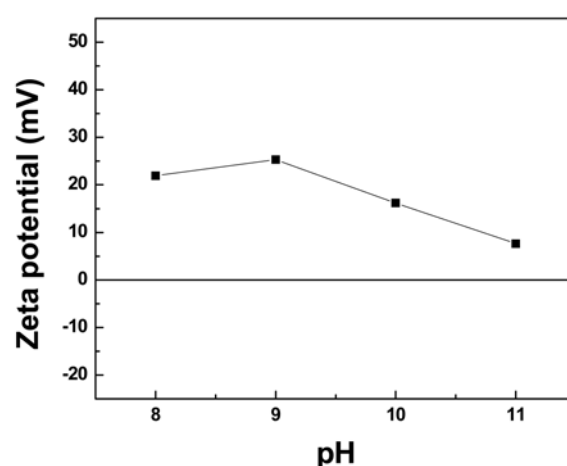


Fig. 1. Zeta potential of ZnO nanoparticles dispersed in ethanol with PEI.

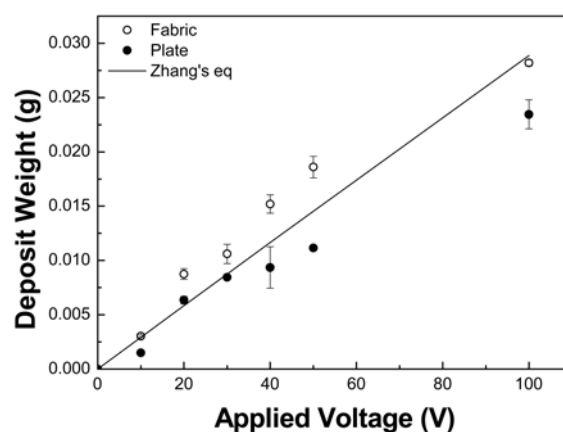


Fig. 2. Deposit weight of ZnO nanoparticles by EPD on Cu coated fabric and Cu plate as a function of applied voltage.

solid plates for comparative study. The weight gain of the deposit on both substrates was measured as a function of applied voltage as shown in Fig. 2. The weight gain of ZnO deposits on both Cu coated fabric and Cu plate increased linearly with the applied voltage. The kinetic equation proposed by Zhang *et al.* [15] was used to observe the deposition behavior. The equation shows that the weight of the deposit (W) can be expressed as an exponential function of time of the reaction:

$$W = W_0(1 - e^{-kt}) \text{ with } k = \frac{A\epsilon\zeta}{4\pi V\eta}(E - \Delta E)$$

where the kinetic constant is k , the deposition time is t , the deposition area is A , the volume of suspension is V , the starting weight of the particle in the suspension is W_0 , the dielectric constant of the liquid is ϵ , the zeta potential of the particle in the solvent is ζ , the viscosity of the suspension is η , the applied voltage is E , and the voltage drop across the deposited layer is ΔE . The experimental and the calculated data indicate good agreement. But larger deposition weight of ZnO nanoparticles on Cu coated fabric was observed than

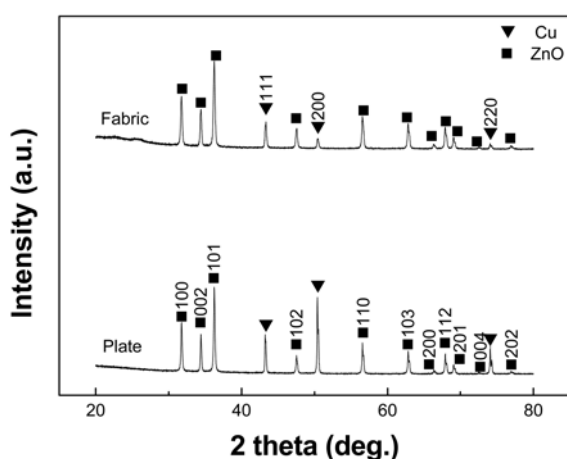


Fig. 3. XRD patterns of ZnO nanoparticle layer by EPD on a Cu coated fabric and a plate.

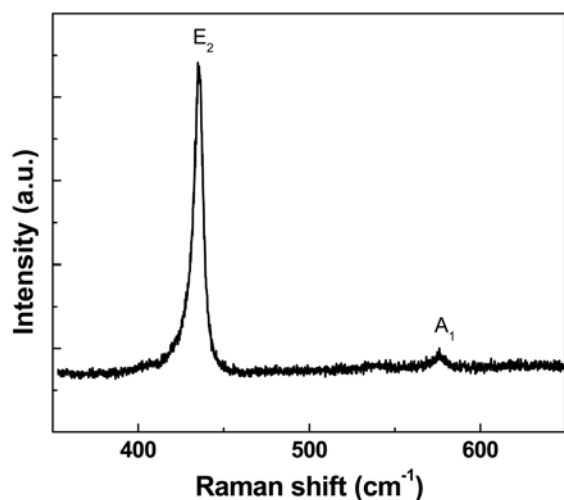


Fig. 4. Micro-Raman spectrum of ZnO nanoparticle layers by EPD on a Cu plate.

the predicted values by the Zhang's equation. Larger surface area of woven fabric due to non-flat surface can be attributed to more deposition of ZnO nanoparticles. At higher applied voltage of 100 V, ZnO deposition showed smaller weight than the predicted values by the equation. The reduced potential by shielding effect [6] of pre-deposited particles can lower the deposition rate.

The deposited ZnO particles on Cu plate and fabric were examined by XRD as shown in Fig. 3. The deposition was performed at 10 V and 1 min. XRD patterns show only peaks of ZnO and Cu for both samples. No preferred orientation of ZnO layers was observed. Micro-Raman spectroscopy was employed to characterize ZnO nanostructure deposited by EPD on Cu plate. Lorentzian functions were used to fit Raman spectra. Fig. 4 shows a very strong band at 435 cm^{-1} corresponding to E_2 vibration and a weak band at 576 cm^{-1} presenting A_1 vibration, which are typical ZnO peaks in Raman spectrum. The E_2 phonon frequency of the as-deposited ZnO layer is comparable

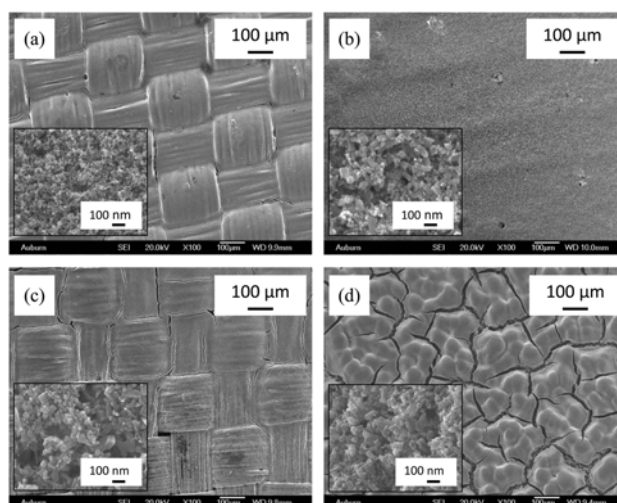


Fig. 5. SEM images of ZnO layers by EPD at 10 V on (a) Cu coated fabric and (b) Cu plate and at 50 V on (c) a Cu coated fabric and (d) a Cu plate.

to the report [16]. The observed E_2 vibration frequency of the ZnO layer was decreased compared to that of bulk ZnO (438.5 cm^{-1}) due to the phonon confinement or the presence of intrinsic defect on nanostructures [16].

The morphologies of EPD ZnO on Cu substrates are shown in Fig. 5. ZnO coverage on both Cu plate and fabrics appears to be uniform. But ZnO layer deposited at 10 V shows slightly dense and less porous microstructure compared with ZnO deposited at 50 V. Higher electric field in EPD process promotes particles to be coated more quickly, but uniform and dense coating may be limited. In addition, faster EPD deposition showed cracks on the surface for both substrates as a consequence of the drying gradient. Therefore, an adequate control of the suspensions and deposition rate is necessary to obtain crack-free deposits.

The optical properties of dried ZnO layer on Cu coated fabrics deposited at 10 V was studied by UV-Vis DRS as shown in Fig. 6. The absorption spectra of ZnO was expressed as the Kubelka-Munk function $[F(R_\infty)]$ obtained from diffuse reflectance measurements as shown in Fig. 6(a), and the diffuse reflectance spectrum of the ZnO layer is given in Fig. 6(b). In the UV-Vis absorption spectrum, a sharp decrease in intensity is observed around 390 nm, and the reflectance spectrum shows broad absorption below 400 nm. Such change is caused by band edge absorption as reported [17–19]. In Fig. 6(c), $[F(R) \cdot E]^2$ versus photon energy (E) is plotted, where $F(R)$ is the Kubelka-Munk function with $F(R) = (1-R)^{1/2}/2R$ and R that is the observed diffuse reflectance [18, 20]. The intersection between the linear line and the axis of photon energy represents the value to E_g [18, 20]. The band gap energy is determined to 3.23 eV, which is comparable to nanostructured ZnO [17, 18, 20]. Compared with reported bulk-shaped ZnO (3.37 eV), the smaller value could be

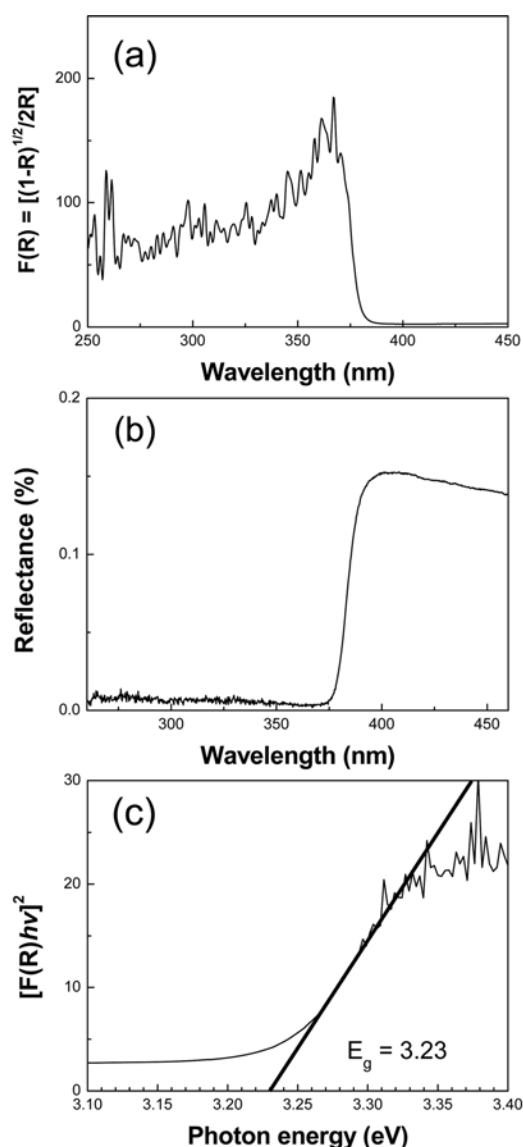


Fig. 6. (a) UV-Vis absorption spectrum, (b) diffuse reflectance spectrum, and (c) Kubelka-Munk transformed reflectance spectrum of ZnO layer deposited at 10 V on Cu coated fabric.

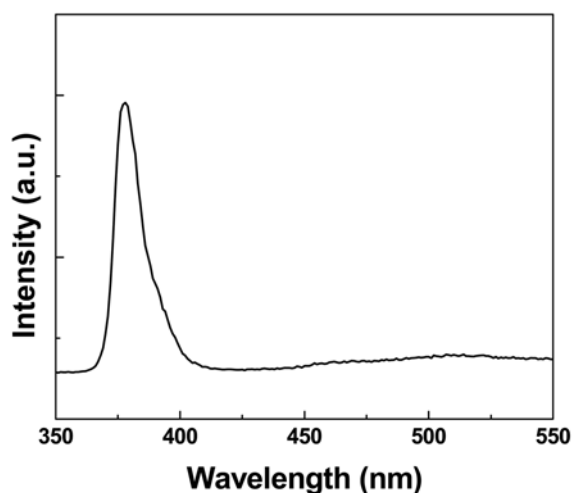


Fig. 7. Photoluminescence spectrum of ZnO nanoparticle layers by EPD on a Cu plate.

attributed to the presence of surface defects driven by low drying temperature and/or smaller nanoparticle size [17, 18, 20]. Photoluminescence spectrum of the ZnO layer on Cu plate by EPD is shown in Fig. 7. A very strong emission peak was detected at 379 nm (3.27 eV) which is very similar to the reported values [16, 21], but the peak was slightly shifted to lower value. The peak shift in the as-deposited ZnO layer could result from higher defect density on the surface of the ZnO layer [16, 21].

Conclusions

The EPD was performed to deposit ZnO nanoparticles on conductive fabrics and plates from ZnO-ethanol suspension system. Deposition behavior of ZnO nanoparticles was examined by varying applied voltage and compared using a kinetic equation. Although the deposition weight shows linear relationship with applied voltage, rough surface or larger surface area of woven fabric yields higher weight gain than flat plate substrate. The dried morphology of ZnO nanoparticle layers shows uniform at lower applied voltage, but higher voltage corresponding to faster deposition rate gives crack on the surface during drying. ZnO layers without preferred orientation was confirmed by XRD. An ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) shows good UV blocking properties and energy bandgap comparable to reported values. PL and Raman spectra also show similar results with bulk ZnO. Slightly shifted values compared with bulk ZnO in PL, UV, and Raman spectra can be attributed to smaller particle size and defects in the as-deposited ZnO layer. EPD can be an effective method for uniform deposition of ZnO nanoparticles onto fabrics at lower temperature. The EPD method will be useful for developing multifunctional devices on flexible substrates.

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