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Humidity Influence on Optical Properties of Nanowire Colloids with Modulated Visual Response to Electrostatic Charge

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ABSTRACT

Electric field created by the nearby electrostatic charge orients the colloidal nanowires in the medium of low dielectric constant, causing a visible color change. We show that the kinetics of subsequent color restoration correlates well to ambient relative humidity. Presented principle could be used for detecting humidity, which affects net surface electrostatic charge possibly via chemical reactions.

Electrostatic surface charge (also called triboelectric charge) has applications in electrostatic separation [1], laser printing [2], mechanical energy harvesting [3], self-powered pressure sensors [4] and gas sensors [5]. Electrostatic surface charges may also cause serious technological problems, such as shocks and explosions or damage electronic equipment, resulting in sizeable loss on a global scale [6].

The magnitude of generated electrostatic surface charge is influenced by several factors including material composition, surface roughness and surrounding environment [5]. We demonstrate here that the latter feature can be employed for detecting changes in ambient humidity using optically responsive polarizable nanowire colloids. In presented case, electrostatic charge is created on the surface of a glass container filled with transition metal (TM) doped ZnO nanowire colloid by peeling off an acrylate-based adhesive tape. Humidity significantly influences the generation of electrostatic charge on the surface and its longevity. The dynamics of resulting change in optical properties of the colloid correlates to ambient humidity in a manner that can be useful in a humidity detector concept. The color change can be monitored either by CCD camera, or even by naked eye for relative humidity estimation at different precisions.

The $Zn_{0.95}Ni_{0.05}O$ nanowires used in the colloids were synthesized solvothermally in ethanol solution. Zinc acetate dihydrate ($(CH_3CO_2)_2{\cdot}2H_2O$) and nickel (II) acetate tetrahydrate ($(OCOCH_3)_2{\cdot}4H_2O$) were dissolved in 15 ml absolute ethanol in desired stoichiometric ratio to obtain 0.1 M solution. Simultaneously, 30 ml of 0.5 M NaOH solution in ethanol was obtained. Both solutions were heated to 80 °C and stirred in a closed glass vial until clear solutions were obtained. The two solutions were mixed and left under stirring at 80 °C for the next 5 h. The mixture was transferred into a 50 ml Teflon-lined stainless steel autoclave and heated at 150 °C for 24 h. After solvothermal synthesis, obtained precipitates were centrifuged and washed with methanol for five times. After washing and centrifuging, methanol (supernatant liquid) was exchanged with medium consisting of hexane and amino terminated polydimethylsiloxane (amino-PDMS, Gelest, AMS-162, USA) mixed at 1:1 volume ratio so that 0.05 vol% nanowire concentration was achieved.

Nanowires were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), diffuse reflectance and X-ray photoelectron spectroscopy (XPS) measurements. The XRD measurements were performed on Ultima + X-ray diffractometer (Rigaku, Japan) using Cu-Kα radiation. The SEM micrographs were taken by Helios Nanolab, FEI. ATR-FTIR spectra were obtained using a Bruker Vertex 70 FTIR spectrometer equipped with a Platinum ATR accessory. The XPS were performed using a Scienta SES100 hemispherical analyzer and a VG Scientific XPS/1 X-ray gun, which provided Al-Kα excitation ($h\nu$ = 1486.6 eV) for recording the spectra shown in Fig. 1 and Mg-Kα excitation ($h\nu$ = 1253.6 eV) for the spectra displayed in Fig. 2. Two different excitation sources were used to achieve better ionization cross-sections for different peaks with different binding energies. Mg-kα also offers slightly better energy resolution, due to the narrower FWHM of the Mg-kα. But it cannot be used to measure Zn 2p lines due to the high binding energy of those peaks. Absorption spectra in the UV-NIR range were obtained using UV-NIR spectrophotometer (Agilent, Cary

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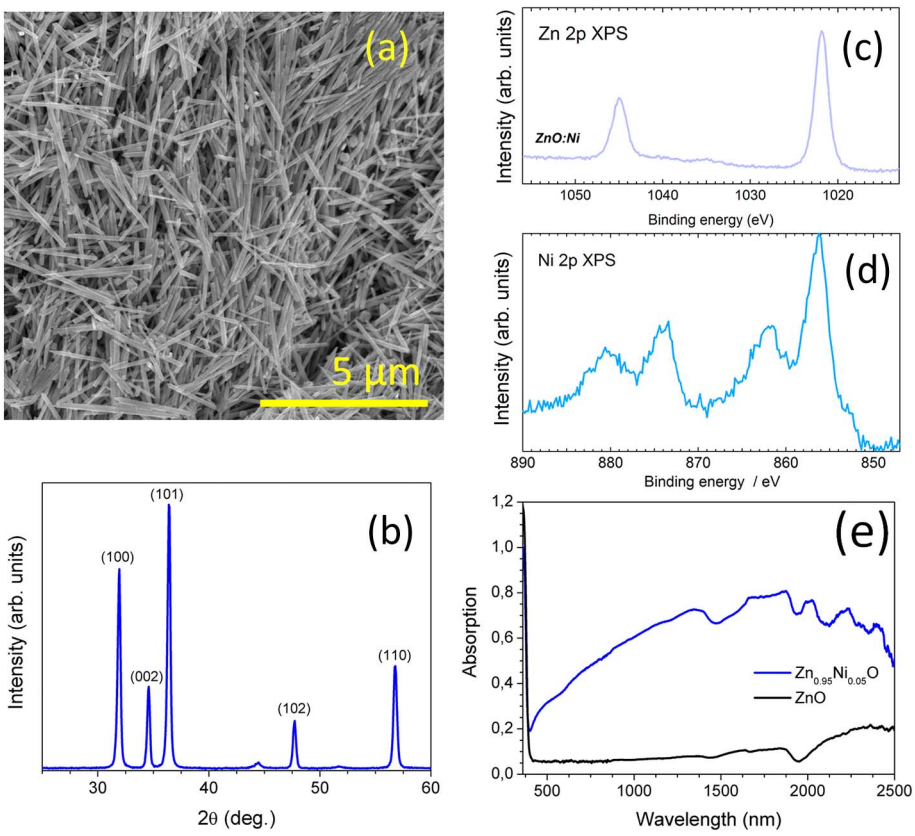

Fig. 1. Morphological, structural and optical features of the $Zn_{0.95}Ni_{0.05}O$ nanowires used in electrostatic charge responsive colloids: (a) SEM image, (b) XRD graph, (c) Zn 2p photoelectron spectrum, (d) Ni dopant 2p photoelectron spectrum, (e) the optical absorption spectra of the synthesized $Zn_{0.95}Ni_{0.05}O$ and pristine ZnO nanowires.

4000 UV-Vis, Germany).

For transmittance measurements in the 400–900 nm wavelength range, colloids were sandwiched between two indium tin oxide-coated glass plates (sheet resistance of 15 Ω/sq., Kintec) using 150 µm thick fluoropolymer spacer. The nanowires in colloids were aligned in the direction of the light propagation by an AC electric field (1 V/µm, 100 Hz). AC field has been used to avoid any electrochemical reactions and to prevent migration of nanowires towards electrodes. In transmittance measurements, light was collected in up to a 2.5° deviation angle.

The color restoring kinetics of nanowire colloids was monitored by Nikon D750 camera equipped with Nikkor 105 mm f/2.8 G VR AF-S lens after peeling off acrylate based adhesive tape from the glass surface. Measurements were performed in climate chamber Memmert CTC 256.

Nanoparticle colloids that are responsive to electrostatic surface charge were prepared by dispersing solvothermally synthesized Ni doped ZnO ($Zn_{0.95}Ni_{0.05}O$) nanowires into low dielectric constant medium, as described in experimental section. Dielectrophoretic or electrophoretic alignment of one-dimensional nano-objects is initiated by inducing a dipole moment along the oblong nanoparticle [7]. The induced dipole then proceeds to align along the direction of the applied field. Low dielectric constant medium is required, because the low polarizability of the medium prevents the screening of the electric field and enables the polarization of the nanowires [7]. Similar rearrangement in electric field has been used before to modulate the optical properties of electro-optical devices based on suspensions of one-dimensional nanostructures (carbon nanotubes, metal, semiconductor or oxide nanowires) by means of electrophoresis [8].

Solvothermally synthesized Ni-doped ZnO ($Zn_{0.95}Ni_{0.05}O$) nanowires used for electrostatic responsive colloids were 50 to 200 nm in diameter and up to 5 µm long (Fig. 1(a)). As expected, solvothermally synthesized $Zn_{0.95}Ni_{0.05}O$ nanowires exhibit phase pure zincite structure (ICDD: 04-001-7297) indicated by XRD analysis (Fig. 1(b)). The Zn 2p XPS of synthesized nanowires (Fig. 1(c)) agrees with earlier reported data for compounds containing Zn2 + in Td ligand configuration [9], the 2p line has two distinct maxima due to spin-orbit splitting, while the Ni 2p3/2 XPS (Fig. 1(d)) peak (more commonly analyzed in literature) with binding energy of 856 eV indicates substitutional Ni at Zn (Td) sites. A minor presence of metallic Ni^0 is proven by the presence of a small shoulder just below 853 eV.

Ni was added to ZnO for visible light absorbance, the inherent color of the nanowires also defines the appearance of corresponding colloid in case of random particle orientation. Virtually black appearance is expected to be achieved by nanowire alignment where nanowires absorb visible light on the same principle as black body absorbers from vertically aligned nanowires [10]. Common optical absorption spectrum of synthesized nanowires is shown in Fig. 1(e). Ni doping causes strong absorption from visible to mid infrared range. For comparison, the absorption spectrum of un-doped ZnO nanowires is demonstrated, which are completely transparent in visible wavelength range. The Ni-doped nanowires appear in blue-gray color.

After synthesis nanowires were dispersed in low dielectric constant solution of amino-terminated PDMS in hexane. It is known that amino-PDMS adsorbs strongly to ZnO surface [11]. This prevents nanowire agglomeration and ensures relatively good colloidal stability. Agglomerates must be avoided to observe change of optical properties in electric field because, due to undefined shape, agglomerates behave like isotropic, non-oblong particles. Consequently, the optical properties of agglomerated nanowire colloids can't be altered in electric fields.

To monitor adsorption of amino-PDMS, ZnO nanowires dispersed in amino-PDMS/hexane solution were consequently washed and centrifuged 10 times in pure hexane and studied by XPS and ATR-FTIR. Both XPS and ATR-FTIR show that the washed nanowires have amino-PDMS on the surface. ATR-FTIR spectrum (Fig. 2(a)) exhibits absorption bands at 1000–1100 cm^{-1} related to Si-O-Si stretching vibrations in amino-PDMS. XPS (Fig. 2(b)) show Si 2p signal for nanowires with amino-PDMS adsorbed on the surface.