Rapid Communication

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

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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 \cite{1}, laser printing \cite{2}, mechanical energy harvesting \cite{3}, self-powered pressure sensors \cite{4} and gas sensors \cite{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 \cite{6}.

The magnitude of generated electrostatic surface charge is influenced by several factors including material composition, surface roughness and surrounding environment \cite{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\textsubscript{0.95}Ni\textsubscript{0.05}O nanowires used in the colloids were synthesized solvothermally in ethanol solution. Zinc acetate dihydrate (Zn\textsubscript{4}(CH\textsubscript{3}COO)\textsubscript{4}·2H\textsubscript{2}O) and nickel (II) acetate tetrahydrate (Ni\textsubscript{2}(OCOCH\textsubscript{3})\textsubscript{4}·4H\textsubscript{2}O) were dissolved in 15 ml absolute ethanol in desired stoichiometric ratio to obtain 0.1 M solution. Simultaneously, 30 ml of the Mg-k\textsubscript{2}O nanowire concentration was achieved. 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-K\alpha 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-K\alpha excitation (h\nu = 1486.6 eV) for recording the spectra shown in Fig. 1 and Mg-K\alpha 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-K\alpha also offers slightly better energy resolution, due to the narrower FWHM of the Mg-K\alpha. 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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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 (Zn0.95Ni0.05O) 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 (Zn0.95Ni0.05O) nanowires used for electrostatic charge responsive colloids were 50 to 200 nm in diameter and up to 5 μm long (Fig. 1(a)). As expected, solvothermally synthesized Zn0.95Ni0.05O 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 Ni0 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 adsorbed 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.

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by a 150 µm Teflon spacer. Nanowire colloids were responsive to external electric field and, upon nanowire alignment towards light propagation direction, exhibited decrease in transmittance in broad spectral range as demonstrated in Fig. 2(c). Decrease in transmittance shows that nanowire colloids exhibit stronger light absorption when nanowires are aligned to direction of electric field and light propagation. The mechanism could be the same as it is in black body absorbers from vertically aligned nanowires [10]. Light is scattered/reflected in between aligned nanowires and at every interaction, some portion of light is absorbed. Multiple reflections of scattered light ensure complete light absorption [10].

Nanowire colloids filled in glass vials are also optically responsive to electric field from electrostatic charges. As demonstrated in Fig. 3(a), when the acrylate based adhesive tape is peeled from the glass vial filled with nanowire colloid, its initial blue-gray color becomes significantly darker or black. This can be attributed to nanowire alignment in electric fields arising from electrostatic charge on glass surface. Created net surface charge values are typically in nC/cm² range [12–14] and electric field strength can be up to 2·10⁵ V/m, as we simulated in our previous work [8]. Different mechanisms exist for electrostatic charging – electron transfer [2], ion transfer [12], material transfer [13] or heterolytic cleavage of covalent bonds [14,15]. Electron transfer mechanism occurs when two metals with different work functions are contacted and separated [2], while ion transfer occurs on polymer electrolytes [16], surfaces with movable ions [12] and/or water adsorbates [17]. In case of acrylate adhesive tape and glass, heterolytic bond breaking and material transfer, as well as ion transfer may take a place. Glass, for example, has mobile protons and alkali metal cations on its surface [16].

We monitored the kinetics of color restoring (resulting from nanowire reorientation) in colloids at different relative humidity (RH) at constant temperature (25 °C). A strip of adhesive tape was peeled off from the surface of the glass vial in a climate chamber held at constant relative humidity. Reorientation kinetics was monitored by recording the RGB color components as a function of time by using CCD video camera. Fig. 3(b) shows the time dependence of intensity (I = (R + G + B) / 3) at different RH, where R, G and B are red green and blue color components, respectively. The color intensity of the colloid in its resting state, i.e. at random nanoparticle orientation was estimated at 60 and color change was monitored at 10 s intervals until a value close to that was reached. At starting point (0 s) the intensity corresponds to the state of aligned nanowires immediately after peeling off the adhesive tape. The kinetics of the restoration of color intensity strongly depends on the humidity level. The time length necessary for complete restoration decreases from approximately 120 s at RH = 30% to 30 s at RH = 60%, while color intensity restoring rate constants (Fig. 3(c)) increases 2.5 times from 0.0125 min⁻¹ to 0.0317 min⁻¹, respectively. Ambient humidity annihilates surface electrostatic charge [18]. Additionally, electric field screening occurs due to high dielectric constant of water and the presence of mobile ionic species (H⁺, OH⁻ and H₂O⁺) in surface adsorbed water [19]. At humidity levels close to 70% and higher, no color change of colloid was observed after peeling off adhesive tape from glass vial, which can be attributed to the formation of a layer of liquid water on the glass surface [20]. Electrolytic conductivity in liquid water layers on glass surface becomes a dominant factor, which is provided by Grotthuss chain reaction of H⁺ and H₂O⁺ movement [21].

At lower RH the change of color intensity (ΔI, Fig. 3(d)) is larger than at higher RH, demonstrating clearly that the initial electrostatic charge density on the vial is higher at lower humidity. These results show that electrostatic charge-responsive nanowire colloids can be used also to monitor the magnitude of accumulated electrostatic charges on surfaces.

In conclusion, we have presented a humidity influence on optical properties of electrostatic charge responsive nanowire colloids. The formation and change of the surface charge induces visible changes in

Fig. 2. Properties of electrostatic charge responsive nanowire colloids: (a) ATR-FTIR spectra of amino-PDMS, Zn₉₅Ni₅O nanowires and the same nanowires with adsorbed amino-PDMS; (b) Si 2p and Zn 3p XPS (Mg-Kα) of Zn₉₅Ni₅O nanowires (from the top) and with adsorbed layer of amino-terminated PDMS; (c) decrease of transmittance of 150 µm thick sample cell with the 0.05 vol% Zn₀·₉₅Ni₀·₀₅O nanowire colloid in an applied electric field (1 V/µm).

Response of nanowire colloids to electric fields was studied by performing electrophoretic manipulation in a cell where nanowire colloid was sandwiched between two ITO-coated glass slides separated
the optical properties in the colloid and the color change kinetics provides information about the relative humidity level in the surrounding environment. The accumulation of electrostatic charges and their stability is strongly affected by the ambient humidity. Presented principle could be used for optical humidity detecting. In addition, nanowire colloids could be used for quantitative determination of surface electrostatic charges.

Conflicts of Interest

There are no conflicts of interests to declare.

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