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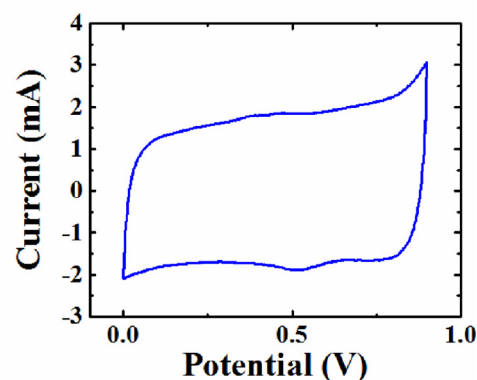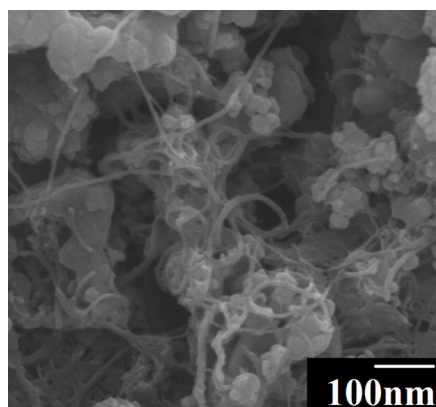# Electrophoretic deposition of materials using humic acid as a dispersant and film forming agent

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HIGHLIGHTS

- Humic acid (HA) films were deposited by electrophoretic deposition (EPD).
- HA was used as a dispersant for oxides, minerals, metals, SiC and carbon nanotubes.
- EPD of materials and composites was performed using HA.
- Composite materials prepared by EPD were used for electrochemical supercapacitors.
- The electrodes showed good capacitive behavior.

GRAPHICAL ABSTRACT

ABSTRACT

Electrophoretic deposition (EPD) method has been developed for the deposition of humic acid (HA) from solutions in water or mixed water–ethanol solvent. The deposition mechanism was based on the electrophoresis of anionic HA species, local pH decrease at the anode, charge neutralization and HA precipitation. The deposition yield can be varied by the variation of HA concentration and deposition voltage. HA showed remarkable adsorption on various materials, which involved different adsorption mechanisms. HA was used as a dispersing, charging and film forming agent for the EPD of materials of different types, such as oxide nanoparticles of TiO_2 and MnO_2, mineral particles of halloysite nanotubes and huntite platelets, metal nanoparticles of Ni and Pd, and other materials, such as SiC and multi-walled carbon nanotubes (MWCNT). The use of HA as a co-dispersant allowed for the fabrication of MnO_2–MWCNT composites with various MWCNT content. The obtained films can be used for different applications based on the functional properties of the deposited materials, such as catalytic, flame retardant, molecular storage and electronic properties. Testing results showed promising performance of MnO_2–MWCNT composites for applications in the electrodes of electrochemical supercapacitors.
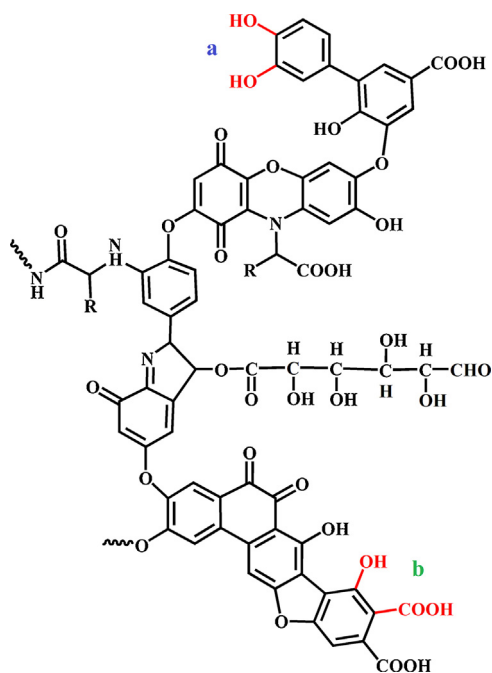
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1. Introduction

Humic acid (HA) is one of the most abundant organic macro-molecules on the Earth [1]. It exhibits a unique set of properties, such as strong adsorption on various organic and inorganic

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Fig. 1. Schematic of chemical structure of HA (a—catechol ligand, b—salicylate ligand).

materials, chelating and redox active properties [1]. Of particular interest is the ability of HA to bind virtually all transition metals and a high binding capacity [1]. Metal chelation is a salient feature of HA, which allows for HA adsorption on surfaces of various inorganic materials. HA showed strong adsorption on different minerals, such as palygorskite [2], kaolinite and hematite [3,4], smectite [5] and different oxides such as Al_2O_3 [6], SiO_2 [7], magnetite [8] and ZnO [9]. HA, adsorbed on mineral particles, promoted the sorption of organic molecules as well as cations of metals [10,11]. Hybrid double hydroxides-HA materials have been developed, which allowed good adsorption of heavy metals [12]. The adsorption of metal ions on alumina nanoparticles was enhanced in the presence of HA due to the formation of ternary complexes [13]. Moreover, HA efficiently adsorbed on hydroxides [14], polymers [15,16], multiwalled carbon nanotubes (MWCNT) [17] and other carbon materials [18,19]. HA showed strong interactions with various polyaromatic molecules. The interactions involved different chemical mechanisms, such as ion exchange reactions, ion bridging, hydrogen bonds, charge transfer, covalent bond formation and hydrophobic interactions [20]. Of particular importance are investigations [1] of HA interactions with herbicides and pesticides used in agriculture.

Fig. 1 shows a schematic of the chemical structure of HA, which includes aromatic rings, hydrocarbon chains and anionic functional groups, such as carboxyl and phenol groups. The structural properties of HA facilitate chemical interactions with a variety of organic and inorganic materials via multiple reaction pathways. A discrete fragment model has been developed for the analysis of contributions of different ligands to the chelating properties of HA [21]. Of particular interest are catechol and salicylate ligands (Fig. 1), which showed strong complexation with metal atoms [22]. Many investigations were focused on the analysis of adsorption mechanisms [14,23] and kinetics [24]. It was found [23] that HA adsorption on oxides exhibited a complex behavior. It was initiated by electrostatic interactions and followed by the ligand exchange and surface complexation, involving carboxylic groups of HA [23]. The adsorption was governed by different factors [6,17], including solution pH and ionic strength. The adsorption mechanism was based on

the complexation of metal atoms on the material surface with HA ligands [8] and electrostatic attraction [13]. It was found that adsorption of HA on reduced graphene oxide involved π-π interactions [25].

The strong adsorption properties of HA are of particular interest for surface modification of materials and colloidal technologies. The adsorbed HA promoted the dispersion of carbon nanotubes in water [17,26]. HA improved colloidal stability of nano zero-valent iron [27], magnetite [8], hematite [28] and montmorillonite [29]. HA was used as a reducing agent for the synthesis of Ag nanoparticles and dispersing agent for the fabrication of stable suspensions [30]. The literature data on the adsorption of HA on inorganic and organic materials and dispersion of different materials indicate that HA is a promising dispersant for application in electrophoretic deposition (EPD) technology.

The goal of this investigation was the application of HA as a charging and dispersing agent for EPD. An important finding was the possibility of the deposition of HA films by anodic EPD. The film forming properties of HA offered additional benefits for the EPD of various materials. HA was used as an anionic dispersant and film forming agent for the EPD of materials of different types, including oxide nanoparticles, such as TiO_2 and MnO_2, minerals, such as halloysite and huntite, nanoparticles of metals, such as Ni and Pd, MWCNT and SiC. The films, prepared by EPD are promising for various applications, based on the catalytic, flame retardant and other properties of the deposited materials. Moreover, HA was used as a co-dispersant for the fabrication of MnO_2-MWCNT composites, which showed promising performance for applications in electrodes of electrochemical supercapacitors.

2. Experimental procedures

Commercial Pd and Ni nanoparticles (<100 nm), TiO_2 nanoparticles (<50 nm, anatase), halloysite nanotubes (outer diameter 60 nm, length 2 μm) (Aldrich, USA), humic acid (HA, Alfa Aesar), SiC (<200 nm, Ibiden Co., Japan), multiwalled carbon nanotubes (MWCNT, ID 4 nm, OD 13 nm, length 1–2 μm, Bayer, Germany), huntite (average particle size 0.56 μm, Sibelco, Netherlands) were used. MnO_2 nanoparticles with average particle size of 30 nm and Mn oxidation state of 3.6 were prepared by the reduction of aqueous $KMnO_4$ solutions with ethanol using a method described in a previous investigation [31].

EPD of pure HA films was performed from HA solutions in water or water-ethanol solvent (50% water). The HA concentration in the solutions was in the range of 0.1–1.0 g L^{-1}. The use of water–ethanol solvent offered the advantages of reduced gas evolution at the electrodes. TiO_2, MnO_2, huntite, halloysite, Pd, Ni, SiC and MWCNT were dispersed in the HA solutions in a mixed ethanol-water solvent using ultrasonication during 30 min. The obtained suspensions were used for EPD. The electrochemical cell for EPD contained a stainless steel substrate and two Pt counterelectrodes (50 × 30 × 0.1 mm). The distance between the electrodes was 15 mm, the deposition DC voltage was 100 V.

Quartz crystal microbalance (QCM922, Princeton Applied Research, USA) method was used for the in-situ investigation of the deposition yield of HA. The mass Δm of deposited material was calculated using Sauerbrey's equation [32]:

$$-\Delta F = \frac{2F_0^2}{A\sqrt{\rho_q \mu_q}} \times \Delta m \qquad (1)$$

where ΔF is frequency decrease of the QCM, F_0 is the parent frequency of QCM (9 MHz), A is the area of gold electrode (0.2 cm^2), ρ_q is the density of the quartz and μ_q is the shear modulus of quartz. The EPD cell contained a gold coated quartz substrate and Pt conterelectrode. The distance between the electrodes was 15 mm, the