



## Bio-inspired catechol chemistry for electrophoretic nanotechnology of oxide films

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### ARTICLE INFO

#### Article history:

Received 19 February 2012

Accepted 19 April 2012

Available online 11 May 2012

#### Keywords:

Caffeic acid

L-3,4-dihydroxyphenylalanine

Manganese dioxide

Zirconium dioxide

Adsorption

Electrophoretic deposition

### ABSTRACT

Bio-inspired chemical approach has been developed for the surface modification and electrophoretic deposition of manganese dioxide and zirconia nanoparticles, prepared by chemical precipitation methods. Caffeic acid, trans-cinnamic acid, p-coumaric acid, and 2,4-dihydroxycinnamic acid were investigated for the surface modification of the nanoparticles. The influence of the structure of the organic molecules on their adsorption on the oxide nanoparticles has been investigated. The mechanism of caffeic acid adsorption was similar to that of natural catecholic amino acid, L-3,4-dihydroxyphenylalanine. The use of caffeic acid allowed for agglomerate-free synthesis, efficient dispersion, charging, electrophoretic deposition and co-deposition of manganese dioxide and zirconia nanoparticles. The deposition yield data, coupled with the results of thermogravimetric analysis, X-ray diffraction analysis, and Fourier transform infrared spectroscopy, showed that surface chemistry, rather than the crystal structure, determined the adsorption behavior. Electron microscopy and energy dispersive spectroscopy investigations showed the formation of nanostructured oxide films and composites. The deposit composition can be varied.

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### 1. Introduction

Electrophoretic deposition (EPD) is an important colloidal technique for the fabrication of inorganic, polymer, and composite films [1–5]. EPD is achieved via the electrophoretic motion of charged particles in a suspension and film formation at the electrode under the influence of an applied electric field [6–8]. EPD technology has faced a new challenge with increasing interest in nanostructured materials [9,10]. The dispersion of nanoparticles in suspensions presents difficulties, attributed to their high surface area and strong tendency for agglomeration [11]. It was found that particle size reduction introduced problems related to electric field induced agglomeration during EPD [11]. Moreover, stirring of suspensions containing very fine particles promoted their agglomeration and sedimentation, which reduced the EPD yield [11].

It is well known that surface chemistry controls the electrophoretic behavior of inorganic nanoparticles [12]. For example, zirconia powders prepared at various experimental conditions showed different electrokinetic behavior [12]. The particles were positively or negatively charged, depending on the method of their preparation. Moreover, the dependencies of particle mobilities on suspension pH showed significant differences [12].

The charging of inorganic particles in suspensions could be achieved by the adsorption of metal ions from added metal salts [13]. However, according to the Derjaguin–Landau–Verwey–Over-

beek (DLVO) theory [7], the addition of metal salts can result in lower suspension stability due to increased ionic strength of the suspension. Iodine was used as a charging additive for EPD of inorganic particles from suspensions in various solvents [9,14]. Many investigations were focused on the use of phosphate ester dispersant for EPD of various oxide materials [7,15–17]. However, the use of metal salts, iodine, phosphate ester, and other organic additives containing phosphorus [17] or sulfur [18] introduces inherent problems related to deposit contamination. It was found that polyelectrolytes provided efficient charging of nanoparticles in suspensions and allowed for the formation of anodic or cathodic deposits by EPD [19,20]. This approach has some limitations related to the bridging flocculation of nanoparticles by polyelectrolytes [21]. Recently, carboxylic acids were investigated for anodic aqueous EPD of oxide materials [22,23]. Despite the impressive progress achieved in the EPD of various materials, there is a need for simple and versatile methods for efficient chemical modification, dispersion, charging, and deposition of colloidal particles. The chemical interactions of inorganic nanoparticles with charging or dispersing agents are especially important and must be well understood to predict the adsorption mechanism and dispersion efficiency.

Recent studies highlighted the importance of efficient organic dispersants with strong adhesion to the particles [24–26]. An adsorbed ionic dispersant imparts a charge to the particles and allows for their EPD. However, a non-adsorbed ionic dispersant acts as an electrolyte. According to the DLVO theory, it decreases the electrostatic repulsion of particles in the suspension and facilitates agglomeration. Moreover, the non-adsorbed ionic dispersant increases the suspension conductivity and electric current at the

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constant voltage EPD. The increase in electric current results in increased gas evolution at the electrodes, which leads to porous deposits with low adhesion. The electromigration of non-adsorbed ionic dispersant toward the electrode and its accumulation at the electrode surface can affect the deposition of particles at the electrode.

The fabrication of stable suspensions of charged colloidal particles is extremely important for EPD. However, the particles must coagulate at the electrode surface to form adherent deposits. Previous investigation showed that high zeta potential and dispersion stability of particles does not necessarily allow for their deposition [7]. It was found that mutual repulsion of charged particles at the electrode surface prevented their coagulation and deposit formation. Another difficulty is related to pH changes at the electrode surface [7]. The redox reactions involving water or alcohols resulted in significant pH increase at the cathode and pH decrease at the anode. It is important to note that oxide nanoparticles exhibit pH dependent charge with charge reversal at the isoelectric point. Therefore, pH changes at the electrode surface can result in charge reversal of the oxide particles. In this case, the particle–electrode repulsions reduced the deposition efficiency [7]. It is also known that pH changes at the electrode surface can prevent the deposition of zwitterionic organic molecules, which exhibit charge reversal at the isoelectric point [27]. Previous investigations indicated that organic materials containing carboxylic groups offered important advantages for application in EPD. The materials containing dissociated carboxylic groups acquired a negative charge in solutions for anodic EPD [28]. The pH decrease at the anode surface resulted in protonation of the carboxylic groups and charge neutralization, which promoted deposit formation at the electrode surface.

The goal of this investigation was the use of caffeic acid as a charging and dispersing agent for EPD of inorganic nanoparticles. This research is motivated by recent advances in the investigation of the mechanism of mussel adhesion to metal and mineral surfaces in water, which showed that strong adhesion is attributed to the chelation of natural catecholic amino acid, L-3,4-dihydroxyphenylalanine (DOPA) [29–31]. The chemical structure of caffeic acid is similar to that of DOPA. Therefore, the bio-inspired chemistry of caffeic acid adhesion to inorganic nanoparticles was in the focus of this investigation. The results presented below indicated that caffeic acid is a promising charging and dispersing agent for EPD of inorganic materials and composites. It was found that the adsorption of caffeic acid on inorganic particles and deposition efficiency are influenced by the surface chemistry of the inorganic particles. The experimental data obtained for caffeic acid and other molecules with similar structures were compared. These results provide an insight into the chemical mechanism of caffeic acid adsorption.

## 2. Experimental procedures

KMnO<sub>4</sub>, ZrOCl<sub>2</sub>·8H<sub>2</sub>O, caffeic acid (CA), trans-cinnamic acid (TCA), p-coumaric acid (PCA), and 2,4-dihydroxycinnamic acid (DCA) were purchased from Aldrich. Manganese dioxide nanoparticles with an average particle size of 30 nm were prepared by the reduction in aqueous KMnO<sub>4</sub> solutions using ethanol as a reducing agent by the method described in a previous investigation [32]. Zirconia particles were prepared by chemical precipitation from 0.1 M ZrOCl<sub>2</sub> solutions in deionized water without CA (zirconia I) or containing 4 g L<sup>-1</sup> CA (zirconia II). The pH of the solutions was adjusted to pH = 8 using NaOH. The precipitated zirconia was filtered, washed with water and ethanol, and then dried in air for 48 h.

EPD was performed on stainless steel and Pt foil substrates (60 × 30 × 0.12 mm) using 9 g L<sup>-1</sup> suspensions of manganese dioxide or zirconia in ethanol. The substrates were cleaned using

ultrasonic cleaner (Branson Ultrasonics, Model 3510) in water, acetone, and then in ethanol for 5 min. The suspensions were ultrasonically agitated for 30 min before the deposition experiments. The EPD cell included a substrate and two Pt counter electrodes. The distance between the substrate and counter electrodes was 15 mm. The deposition voltage was varied in the range of 20–150 V using EPS 2A200 power supply (Amersham Biosciences Corp.). Deposition yield was studied for the films deposited on stainless steel substrates. A minimum of three samples were prepared in each deposition experiment. All the deposits were obtained using fresh solutions. The deposition yield measurements were repeatable, and the error was less than 5%.

Fourier transform infrared spectroscopy (FTIR) studies, thermogravimetric analysis (TGA), and X-ray diffraction studies (XRD) were performed for the deposits formed on Pt substrates and removed from the substrates after drying in air for 72 h. FTIR studies were performed using Bio-Rad FTS-40 instrument. TGA investigations were carried out in air at a heating rate of 5 °C min<sup>-1</sup> using thermoanalyzer (Netzsch STA-409). XRD studies were performed with a diffractometer (Nicolet I2) using a monochromatic CuKα radiation at a scanning speed of 0.5 deg min<sup>-1</sup>. The microstructures of the films were investigated using a JEOL JSM-7000F scanning electron microscope (SEM), equipped with energy dispersive spectroscopy (EDS).

## 3. Results and discussion

Fig. 1 compares chemical structures of DOPA, CA, TCA, PCA, and DCA. The chemical structure of DOPA (Fig. 1a) includes two OH groups bonded to adjacent carbon atoms of the aromatic ring, carboxylic, and amino groups. The total charge of zwitterionic DOPA molecules is governed by ionization of the different functional groups [33]. The functional groups of DOPA are protonated at low pH. Therefore, the positive charge of DOPA at low pH is attributed to the protonated amino group (NH<sub>3</sub><sup>+</sup>) [33]. The pH increase leads to deprotonation of carboxylic, phenolic, and amino groups. As a result, DOPA possesses a negative charge at high pH. It was found [33] that the amino group was protonated below pH = 10, reducing the total negative charge of the molecule at relatively high pH. As pointed out above, the EPD of zwitterionic molecules and their application as charging agents presents difficulties due to charge reversal. Therefore, CA molecule (Fig. 1b), containing only anionic groups, offers advantages for application in EPD. The

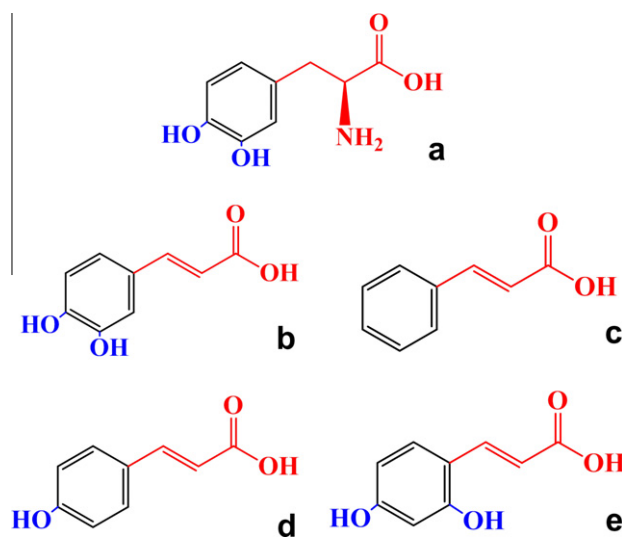


Fig. 1. Chemical structures of (a) DOPA, (b) CA, (c) TCA, (d) PCA, and (e) DCA.

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