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Surface modification and electrophoretic deposition of materials using carboxyalkylphosphonic acids



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ABSTRACT

Bipolar carboxyalkylphosphonic acid molecules were investigated for dispersion and charging of inorganic particles in ethanol and film formation by electrophoretic deposition (EPD). The analysis of deposition yield for different molecules and FTIR data provided an insight into the influence of interactions of the molecules with different surface metal atoms on adsorption of the molecules, particle dispersion and charge. The dispersant molecules showed strong adsorption on MnO_2 and allowed for anodic EPD of MnO_2 for electrodes of electrochemical supercapacitors. In contrast, huntite particles showed preferred adsorption of protons and cathodic huntite films were obtained by EPD for applications based on flame retardant properties of this material.

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1. Introduction

Electrophoretic deposition (EPD) is widely recognized as an essential tool for the fabrication of films and coatings of different materials [1]. The major challenge in EPD is the development of efficient dispersing agents. The key to achieving good particle dispersion is the strong adsorption of a charged dispersant on a particle surface. Recent studies [2] analyzed molecules, containing catecholate, salicylate and gallate ligands, which provided strong bonding to the particle surface and allowed efficient particle dispersion and EPD. These studies highlighted the importance of further development of dispersants with special ligands for efficient adsorption and analysis of their interactions with metal atoms on a particle surface.

It is known that monodentate ligands allow relatively weak bonding [3]. More stable bonding can be achieved using polydentate ligands [3]. Therefore, organic molecules from the phosphonate family have a potential for surface functionalization and dispersion of inorganic particles. The three oxygen atoms of the phosphonate ligands allow for bi- or tri-dentate (Fig. 1A(a)–(d)) bonding [3]. Three oxygen atoms can bind to the same metal site by chelation mechanism (Fig. 1A(a) and (d)) or bind to different metal atoms on the particle surface (Fig. 1A(b) and (c)). The adsorption of phosphonates from aqueous solutions was studied on different

materials, such as Al_2O_3 , TiO_2 , SiO_2 , ZnO , indium tin oxide, ilmenite, Fe_3O_4 , hydroxyapatite, clay, and calcium carbonate [3–6].

The goal of this investigation was the application of bipolar carboxyalkylphosphonic acids for dispersion, charging and EPD of MnO_2 and huntite. We analyzed the adsorption of the molecules on inorganic particles, particle charging mechanisms and kinetics of EPD.

2. Experimental procedures

3-Phosphonopropionic acid (CA3PA), 16-phosphonohexadecanoic acid (CA16PA), octadecylphosphonic acid (18PA) (Aldrich), huntite (average particle size $0.56\ \mu\text{m}$, Sibelco, Netherlands) were used. MnO_2 with average particle size of 30 nm and Mn oxidation state of 3.6 was prepared by the reduction of aqueous KMnO_4 solutions with ethanol using a method described in a previous investigation [7]. In this investigation we used relatively small particles with particles size below $1\ \mu\text{m}$. Such particles can be efficiently dispersed and charged in the suspension for application in EPD. In contrast, the use of particles with particle size above 5–10 μm presents difficulties due to poor suspension stability.

The deposition cell contained a stainless steel substrate and Pt counter electrode. The distance between the electrodes was 15 mm. EPD was performed at a deposition voltage of 20 V using $4\ \text{g L}^{-1}$ suspensions of MnO_2 or huntite in ethanol, containing

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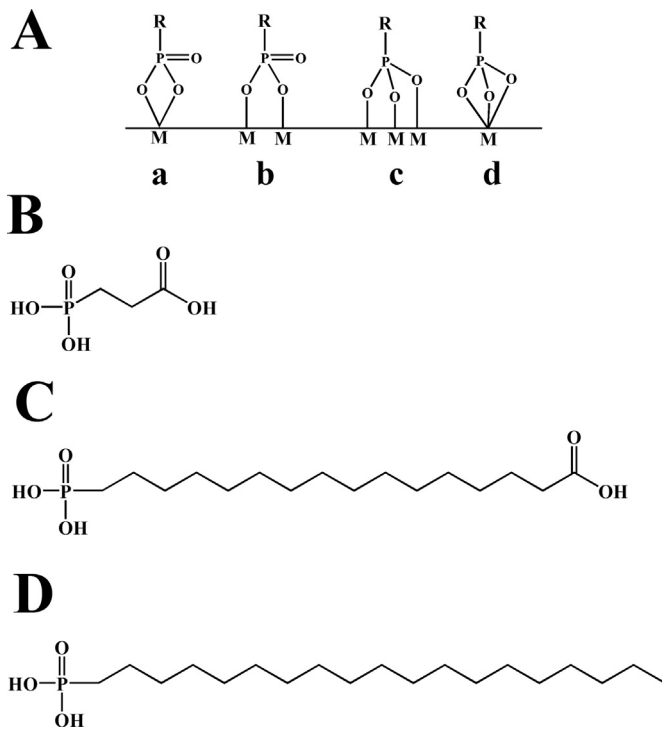


Fig. 1. Bonding modes (A) of phosphonic acids to metal atoms (M) on inorganic surfaces: (a) chelating bidentate, (b) bridging bidentate, (c) bridging tridentate and (d) chelating tridentate; chemical structures of (B) CA3PA, (C) CA16PA and (D) 18PA.

dissolved CA3PA, CA16PA and 18PA dispersants. The use of ethanol solvent for EPD offered the advantage of low conductivity. The suspensions were stirred and then ultrasonically agitated during 30 min before the EPD. The application of the concept of zeta potential to the nanoparticles, containing adsorbed large organic molecules presents difficulties due to the liquid flow inside the adsorbed organic layer. Therefore, we performed measurements of the deposition yield versus time for the analysis of electrokinetic behavior of the particles.

Scanning electron microscopy (SEM) (JEOL, JSM-7000F) and FTIR spectroscopy (Bio-Rad, FTS-40) were used for the characterization of the deposited materials.

3. Results and discussion

Bipolar carboxyalkylphosphonic acids, such as CA3PA and CA16PA molecules (Fig. 1(B) and (C)), containing COOH and PO₃H₂ polar groups were used as dispersants for EPD. For comparison, 18PA molecules without COOH groups (Fig. 1D) were used. Both COOH and PO₃H₂ polar groups can provide adsorption of the molecules on the particle surface. However, numerous investigations showed that alkyl phosphonates and phosphonic acid bond much more strongly than carboxylic acids to a wide range of inorganic materials [3,4,8,9]. Therefore, it was hypothesized that bonding of PO₃H₂ polar groups to metal atoms on the particle surface can provide adsorption of the bipolar molecules on the particles, whereas the dissociated of COOH groups can impart a negative charge.

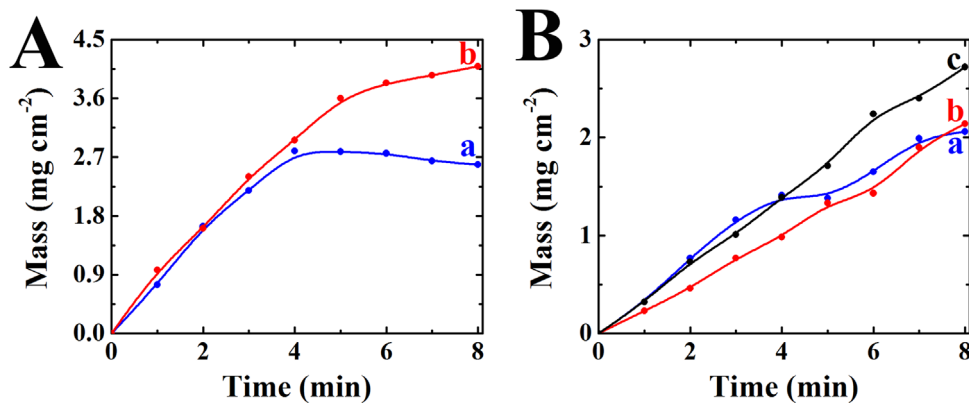


Fig. 2. Deposit mass versus deposition time at a deposition voltage of 20 V for (A) 4 g L⁻¹ MnO₂ suspensions, containing 0.3 g L⁻¹ of (a) CA3PA and (b) CA16PA and (B) 4 g L⁻¹ huntite suspensions, containing 0.5 g L⁻¹ of (a) CA3PA, (b) CA16PA and (c) 18PA.

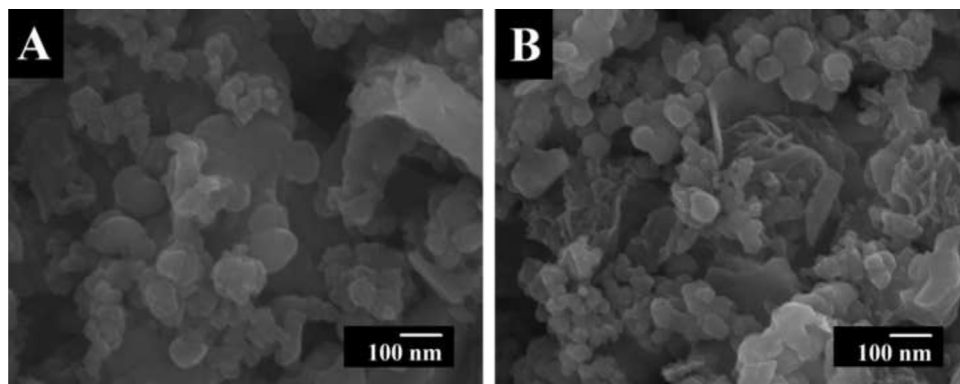


Fig. 3. SEM images of MnO₂ films, deposited from 4 g L⁻¹ MnO₂ suspensions, containing 0.3 g L⁻¹ of (A) CA3PA and (B) CA16PA at a deposition voltage of 20 V.

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