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Electrophoretic Deposition of MnO_2 using Folic Acid as Advanced Dispersing Agent

[*1]Mustafa Sami ATA

Amasya University, Technology Faculty, Mechanical Engineering Dept. Amasya TURKEY

ORCID: 0000-0003-0944-4276

Reseach Article

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*Corresponding author: mustafa.ata@amasya.edu.tr

Abstract

The deposition mechanism of MnO_2 has been investigated by using electrophoretic deposition (EPD) method. Folic acid, a biocompatible dispersing agent, was analyzed for the dispersion of MnO_2 and MWCNT and anodic deposition of MnO_2 in ethanol. Fourier transform infrared spectroscopy and scanning electron microscopy were used for morphology analysis. The amount of the deposited material can be controlled by the variation of dispersing agent concentration in the solution based on the deposition yield measurements and deposition time. The deposition mechanism is discussed. The films prepared by EPD method are promising materials for application in electrochemical supercapacitors.

Key Words: EPD, Colloidal, Advanced Dispersing Agent

Özet

MnO_2'nin biriktirme mekanizması elektroforetik biriktirme (EPD) yöntemi kullanılarak araştırılmıştır. Biyouyumlu bir dispersiyon ajanı olan folik asit, MnO_2 ve MWCNT'nin dispersiyonu ve MnO_2'nin etanol içinde anodik birikimi için analiz edildi. Morfoloji analizleri için Fourier dönüşümü kızılötesi spektroskopisi ve tarayıcı elektron mikroskopundan yararlanıldı. Biriken malzemenin miktarı, biriktirme verimi ölçümlerine ve biriktirme süresine bağlı olarak çözelti içindeki dispersiyon maddesi konsantrasyonunun değişimi ile kontrol edilebilir. Biriktirme mekanizması tartışılmıştır. EPD yöntemiyle hazırlanan filmler elektrokimyasal süper kapasitörler de uygulama için ümit vaat eden malzemelerdir.

Anahtar Kelimeler: EPD, kolloidal, İleri Etken Çözücü Madde

1. Introduction

Electrophoretic deposition (EPD) is an important technique for the fabrication of MnO2 and composites films for electronic, catalytic and energy storage applications due to high deposition rate and possibility of deposition of thick films of controlled thickness(Sarkar & Nicholson, 1996; Chicatún et al., 2007; Limmer, Chou, & Cao, 2005; Van der Biest & Vandeperre, 1999). The mechanism of EPD is based on the motion of charged particles in a stable suspension, containing well dispersed charged colloidal particles, toward an electrode and deposit formation under an applied electric field (Sarkar & Nicholson, 1996; Van der Biest & Vandeperre, 1999). There are many studies explaining the EPD deposition mechanisms and related applications (Sarkar & Nicholson, 1996; Van der Biest & Vandeperre, 1999; Limmer et al., 2005; Besra & Liu, 2007; Olevsky, Wang, Maximenko, & Meyers, 2007).

Due to the increasing demand in carbon-based materials and their composites with metal oxides for supercapacitor, solar panels and battery applications (Im et al., 2010; Sahoo et al., 2010), EPD has faced new challenges. Based on the mechanism of EPD, it requires stable suspensions and homogenously dispersed carbon nanotubes, metal oxides and their composites. In the literature, there are different attempt for dispersion (Casagrande et al., 2008; Esumi et al., 1996; Sahoo et al., 2010; Thomas et al., 2005; Vaisman et al., 2006). There is another approach for film-forming by using dispersing agents, which increase the adhesion

of the film and solubility of the carbon and metal oxides and composites(Ata et al., 2014).

Folic acid is an essential for immune system since the absence of FA increases the chance of the some diseases such as heart attack, stroke, leucopoenia etc. (Prasad et al., 2010). FA is a vitamin for strengthening the human body which makes it a natural biocompatible material. Especially, during the women's pregnancy period, FA intake is encouraged(Honein et al., 2001). MWCNTs are very popular due to their unique advantages such as high surface area, high conductivity and good chemical stability (Zhang et al., 2009) and therefore, FA/MWCNT composites become attractive. In 1996 Britto et.al successfully investigated electrochemical oxidation of dopamine of MWCNT electrode prepared by EPD(P J Britto et al., 1996). Also, protein and some other biocompatible materials investigated by other researchers (Davis et al., 1997; Pichumani J Britto et al., 1999). Due to FA is a biocompatible material, it has been very widely used for drug delivery(Sudimack & Lee, 2000; Gabizon et al., 2004; Bae et al., 2005), biosensing(Boström Caselunghe & Lindeberg, 2000; Castillo et al., 2013; Mirmoghtadaie et al., 2013), pregnancy(Hibbard, 1964; Milunsky et al., 1989; Scholl & Johnson, 2000) and biochemical reactions(Farber et al., 1948; Boushey et al., 1995).

FA is known as anionic molecule and promising dispersing agent for anodic EPD. The aromatic structure of the dispersant important for adsorption on MWCNT by π-π interactions(Ata et al., 2014). This kind of molecules also can be used for MnO2-MWCNT composites as co-dispersants. In this work, EPD of MnO2 investigated in the presence of FA.

2. Materials and Methods

Folic acid and $KMnO_4$ were purchased from Aldrich Co., and Multiwalled carbon nanotubes (MWCNTs) were supplied by Arkema Inc., USA. Average particle size of MnO_2 nanoparticles was 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(Cheong & Zhitomirsky, 2009). The MWCNT had average inner and outer diameters of about 4 and 13 nm, respectively, length of 1-2 μm and C-purity above 99%.

EPD was performed from suspensions of MWCNTs and MnO_2 in ethanol using FA as a dispersing and charging agent. Before EPD, the suspensions were ultrasonicated during 30 min. The obtained suspensions were used for EPD. The electrochemical cell for EPD contained a stainless steel substrate and two Pt counter electrodes (50 × 30 × 0.1 mm). The distance between the electrodes was 15 mm, the deposition DC voltage was 20 V.

Fourier transform infrared spectroscopy (FTIR) study was performed for the deposits formed on Pt substrates in order to avoid any risk of contamination. The deposits were removed from the substrates after drying in air for 72 h for the FTIR. FTIR studies were performed using Bio-Rad FTS40 instrument.

3. Results and Discussion

The main issue in EPD technique is the fabrication of stable suspension of charged nanoparticles especially in ceramic particles. Therefore, the selection of suitable dispersing agents plays very important role. The mechanism of mussel adhesion to organic and inorganic surface was explained in the literature(Lee et al., 2007; Waite, 2008). However, the adsorption mechanism of mussel is not understood very well.

The chemical structure of FA (Fig. 1A) includes aromatic rings and a catechol group bonded to the aromatic rings. The catechol group enable to adsorption on metal oxides nanoparticles. For dispersion of carbon nanotubes, conjugated bonds formed by carbon atoms give high solubility. Aromatic compounds with conjugated bonds increase the adsorption with sidewalls of carbon nanotubes by π-π stacking method(Woods et al., 2007; Lin & Xing, 2008;Björk et al., 2010).

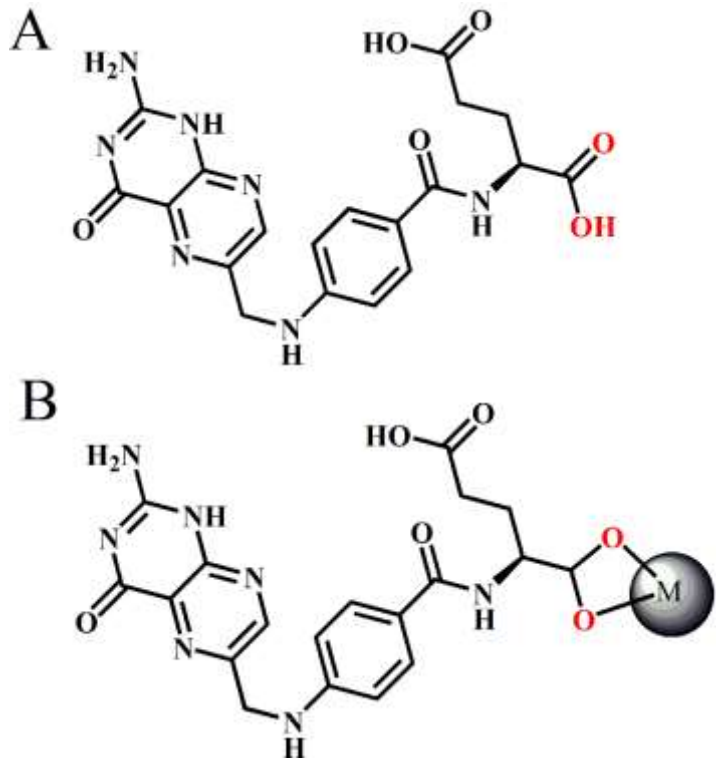

Figure 1.(a) Structure and **(b)** adsorption mechanism of FA

The aromatic ring of FA increases the stability with MWCNT, yet, EPD wasn't achieved by suspension of MWCNT. On the other hand, the adsorption mechanism of FA on MnO_2 was referred to carboxylic group (Mohapatra et al., 2007; Ata et al., 2014) which allows the electrosteric stabilization on adsorb particle.

The carboxylic group adsorption mechanism (Mohapatra et al., 2007; Hamed et al., 2009) shown in Fig. 1B. The anodic EPD was achieved from MnO_2 suspension containing FA (Fig. 2). Anodic deposits were immediately obtained with an increase in the concentration amount of FA. Especially from 0.025 to 0.2 g L^{-1}, deposition yield increased significantly and slightly decreased after 0.4 g L^{-1}. Fig. 3 shows the deposit mass as a function of time from 4 g L^{-1} MnO_2 suspension containing 0.5 g L^{-1} of FA. The amount of the deposited material can be varied by increasing time.

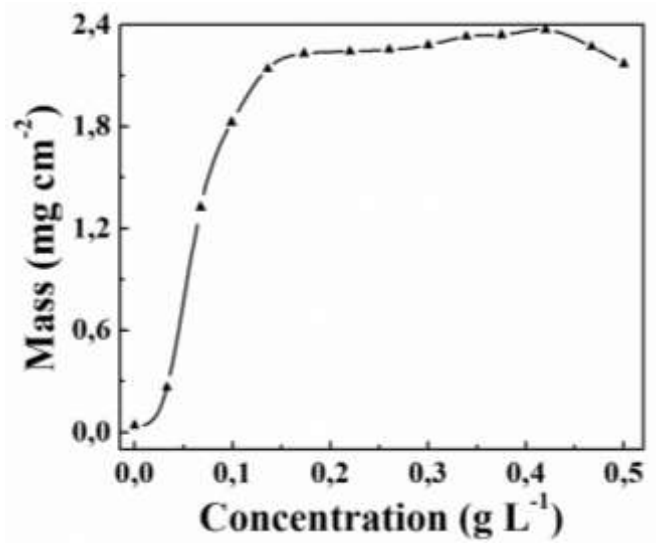

Figure 2. Deposit mass versus FA concentration in 4 g L^{-1} MnO_2 suspension at a deposition voltage 20 V and a deposition time 5 min

With increasement of the deposition time, the decrease in deposition rate observed. In the literature similar slope decreases were also observed and explained very well. (Zhitomirsky, 2000; Ata & Zhitomirsky, 2012).

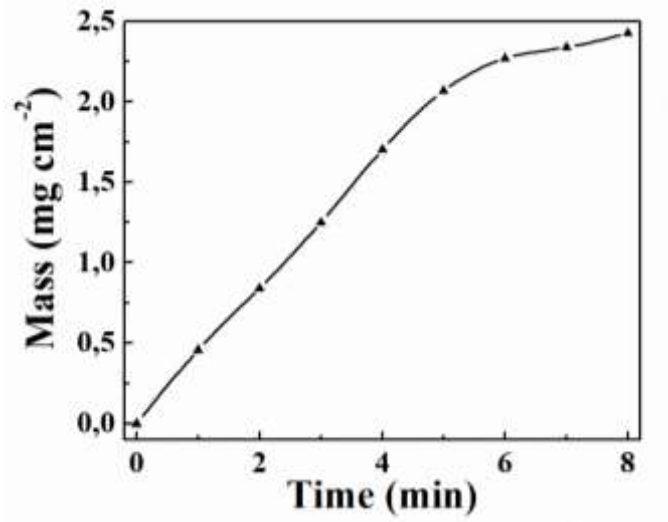

Figure 3. Deposit mass versus deposition time for 4 g L^{-1} MnO_2 suspension, containing 0.5 g L^{-1} FA at a deposition voltage 20V.

Figure 4 shows the FTIR spectrum of deposits prepared from suspensions containing pure FA powder (Fig. 4a) and MnO_2 suspension containing FA (Fig. 4b).

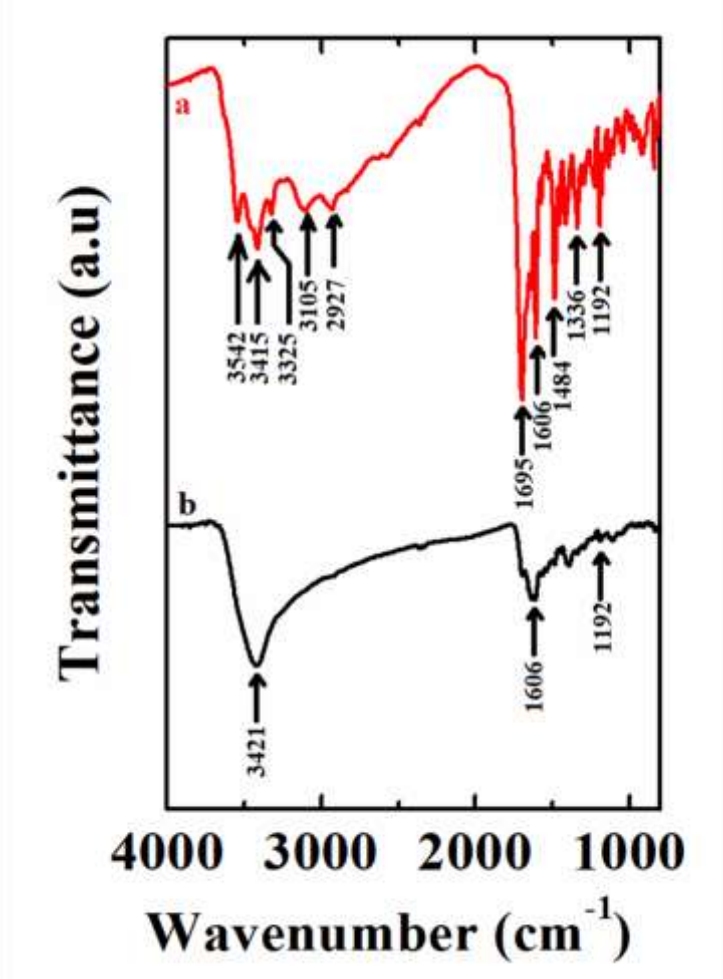

Figure 4. FTIR spectra of (a) pure FA powder and (b) 4 g L^{-1} MnO_2 suspensions containing 0.5 g L^{-1} FA.

The adsorption of FA on MnO_2 was confirmed by FTIR. The essential band assignments are represented in Table 1. The band assignments were based on literature data(Rajh et al., 2002; Hamed et al., 2009; He et al., 2009; Wu & Zhitomirsky, 2011). The spectrum of the FA exhibits a very strong absorption band at 1695 cm^{-1} due to C=O stretching vibrations of free ketonic of the carboxylic group(Hamed et al., 2009), while the band at 1606 cm^{-1} exhibits bending mode of

NH-. The bands between 3542 and 3325 cm^{-1} are the stretching bands of hydroxyl (OH) of FA and adsorb on MnO_2(He et al., 2009). Some peaks of pure FA were disappeared compared with the adsorb on MnO_2 nanoparticles due to the deprotonation of COOH groups and bonding metal atoms (Hamed et al., 2009). Therefore, FTIR data confirmed that the deposition process resulted in the formation of folic acid and MnO_2 suspension containing FA.

Table 1. Band assignments for pure FA and MnO2 deposits obtained using FA

FA	MnO_2	Band Assignment
3542, 3415, 3325	**3421**	**υ(O-H)**(Rajh et al., 2002; Hamed et al., 2009; He et al., 2009)
3105, 2927	**----**	**υ(C-H)** (Rajh et al., 2002; Hamed et al., 2009)
1695	**1606**	**$\upsilon_{as}(COO^-)$**(Hamed et al., 2009)
1606	**----**	**δ(N-H)** (He et al., 2009)
1484	**----**	**$\upsilon_s(COO^-)$** (Hamed et al., 2009; Wu & Zhitomirsky, 2011)
1336, 1192	**1192**	**υ(C-N)** (Hamed et al., 2009)

The wavenumbers were given in cm^{-1}. υ-stretching mode, δ-bending mode

4. Conclusions

This study shows that a typical folic acid can interact with MnO_2 and MWCNT. Both suspensions were stable for couple days. The presence of the FA as a dispersing agent showed promising results for deposition of MnO_2. The anodic EPD method has been developed for the fabrication of MnO_2 films containing FA. FTIR spectrum data showed the adsorption mechanism of the FA organic molecules on the MnO_2 nanoparticles which involves COOH and OH groups complexations with Mn atoms on the particle surface.

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