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Electrostatic layer-by-layer and electrophoretic depositions as methods for electrochromic nanoparticle immobilization

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ABSTRACT

The present paper describes the immobilization of nanoparticles onto conducting substrates by using both electrostatic layer-by-layer and electrophoretic deposition (EPD) methods. These two techniques were compared in high-performance electrochromic electrodes based on mixed nickel hydroxide nanoparticles. In addition to easy handling, EPD seems to be the most suitable method for the immobilization of nanoparticles, leading to higher electrochromic efficiencies, lower response times and higher stability upon coloration and bleaching cycling.

1. Introduction

Nanotechnology has promoted research into new morphologies, which has lead to performance increases (as softer and high durable materials) or changes in the chemical properties of materials [1,2]. In the field of electrochromism [3,4], nanomaterials have been widely studied, with the huge electroactive surface being the main point of interest for fast intercalation processes. In this sense, the development of nanostructured electrochromic materials such as SnO_2 [5], nickel hydroxide [6,7], WO_3 [8,9], TiO_2 modified with dyes [10,11], Prussian blue [12] and its analogues (i.e., copper hexacyanoferrate) [13], can be found in the literature, with the goal of using nanostructures to achieve highly efficient electrodes with high and tunable chromatic contrasts, high electrochromic efficiencies and low switching times.

Different syntheses of nanomaterials have been reported, such as sol–gel [14], solvothermal [15] and sonochemical [16]. Many techniques for immobilizing the nanostructures onto electrode surfaces have been developed; the simplest one can be described as spreading a colloidal nanoparticle solution onto the surface followed by solvent evaporation. Another possibility is the spin-coating method, providing homogeneous films, but this technique requires high cost equipment and has restrictions regarding electrode geometry and the viscosity of colloidal solutions [17,18]. Other techniques such as physical vapor deposition (PVD) and chemical vapor deposition (CVD) are thoroughly described in the literature, providing homogenous nanostructured thin films with controlled thickness [19,20], but specific high cost equipment is required.

The development of reliable, easy-to-handle and low cost methodologies for the immobilization of nanomaterials is required. The electrostatic layer-by-layer deposition technique (LbL), reported by Decher [21] is a well-known method that comprises the sequential dipping of the electrode in dilute solutions containing charged species such as polyanions and polycations. Assemblies involving nanoparticles and charged polymers are also reported in the literature, i.e., SiO_2 nanoparticles and polydiallyldimethylammonium PDDA [22], Prussian blue nanoparticles and PAH [23], or electrochromic polymers [24,25]. Superficially charged nanostructures can also be employed for electrophoretic deposition (EPD), which is a traditional processing method in the ceramic industry [26,27]. EPD is achieved by the motion of charged particles towards an opposite charged surface due an external applied electric field, where parameters such as deposition time, distance between electrodes and applied potential can be easily controlled in order to obtain different morphologies and thicknesses.

This work describes the deposition of electrochromic doped nickel hydroxide nanoparticles onto transparent electrodes using both, LbL and EPD techniques; the electrochromic performances of electrodes prepared by the two different methods will be compared and discussed.

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2. Experimental

$Ni(NO_3)_2{\cdot}6H_2O$ (CPQ), $Co(NO_3)_2{\cdot}6H_2O$ (CPQ), $Cd(NO_3)_2$ (Aldrich), KOH (Shynth), NH_4OH, HCl (Shynth), polydiallyldimethylammonium (PDDA) (Aldrich) were used as received, without further purification. All solutions were prepared using purified water from a UHQ Elga System. For nanoparticle synthesis, 10 mL of an aqueous solution containing 7.7 mmol L^{-1} of $Ni(NO_3)_2$, 2.0 mmol L^{-1} of $Co(NO_3)_2$ and 0.3 mmol L^{-1} of $Cd(NO_3)_2$, was mixed in a sonication flask with 200 μL of a 1 mol L^{-1} NH_4OH solution. This mixture was irradiated with high intensity ultrasonic radiation for 5 min using a direct immersion titanium horn (20 kHz, 10 W cm^{-1}) that was dipped to a depth of 1 cm into the solution. This procedure resulted in 5 nm particles [28]. In this way, colloidal suspensions of nanoparticles were obtained and used for the immersion of conducting substrates during the layer-by-layer (LbL) deposition technique and direct EPD. According to ICP-OES determinations, the proportion found for mixed nanoparticles was slightly different from those of aqueous feed solutions; from now on, mixed nanoparticles will be referred to considering the real proportions of nickel, cobalt and cadmium: $Ni_{0.74}Co_{0.22}Cd_{0.04}(OH)_2$ [28].

Nanoparticles were immobilized onto indium-doped tin oxide substrates (ITO, Delta Technologies, sheet resistance < 20 Ω/□, surface area 0.5 cm^2) using the layer-by-layer (LBL) self-assembly method [6]. Thin films prepared by EPD were obtained by applying a potential difference of 1.0 V during different times between two parallel ITO electrodes placed 1 cm apart in an electrochemical cell containing the colloidal nanoparticle suspension.

Atomic force microscopy (AFM) topographic images were obtained by using a Pico SPM-LE Molecular Imaging system with cantilevers operating in the intermittent contact mode (AAC mode), slightly below their resonance frequency of approximately 305 kHz

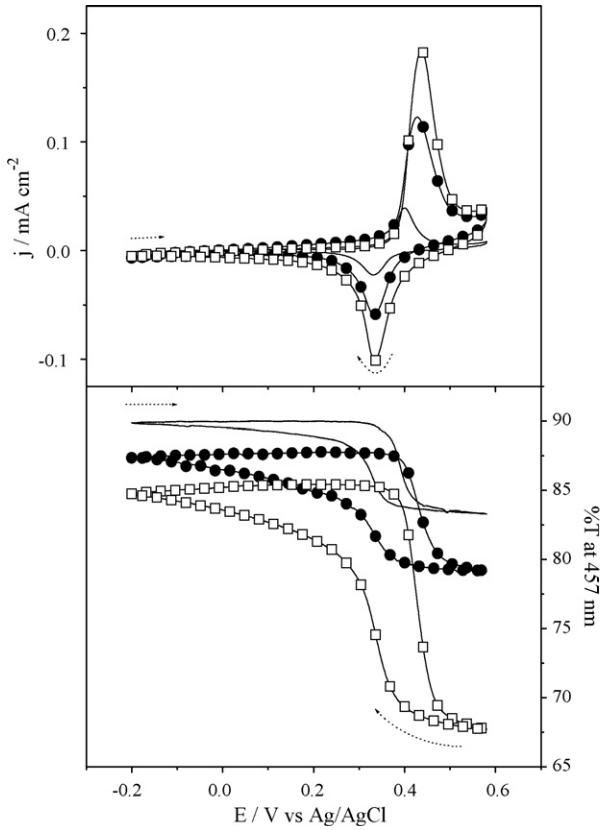

Fig. 1. j/E and $\%T/E$ potentiodynamic profiles recorded with electrodes modified with different number of PDDA/$Ni_{0.74}Co_{0.22}Cd_{0.04}(OH)_2$ nanoparticle bilayers: (—) 1 bilayer, (-●-) 2 bilayers and (-□-) 3 bilayers. Electrolytic solution 0.1 mol L^{-1} KOH, $v = 5$ mV s^{-1}.

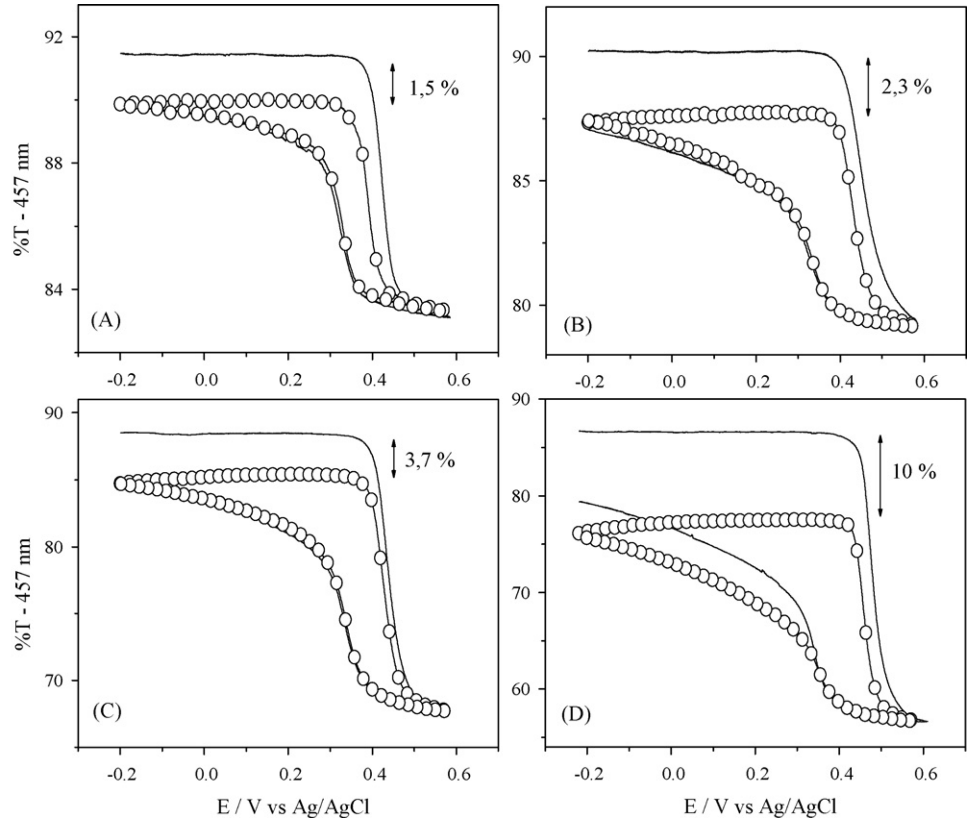

Fig. 2. $\%T/E$ potentiodynamic profiles for LbL $Ni_{0.74}Co_{0.22}Cd_{0.04}(OH)_2$ nanoparticle-modified electrodes: (A) 1 bilayer, (B) 2 bilayers, (C) 3 bilayers and (D) 6 bilayers. (—) 1st cycle and (-○-) 10th cycle. Electrolytic solution 0.1 mol L^{-1} KOH, $v = 5$ mV s^{-1}.