



# Electrochemical synthesis of Cd–Ag bimetallic particles and the involved alloy formation



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## ABSTRACT

The formation of bimetallic Cd–Ag nanoparticles on vitreous carbon (VC) and the involved alloy formation have been studied by conventional electrochemical techniques and ex-situ atomic force microscopy (AFM). Both metals were deposited by sequential electrodeposition using single potentiostatic pulses. The AFM images of Ag deposits showed small differently sized Ag nanocrystallites uniformly distributed over the VC-substrate. This modified substrate was immersed in an electrolyte solution containing Cd<sup>2+</sup> ions and bimetallic Cd–Ag particles were prepared by underpotential deposition (UPD) of Cd. The alloy formation phenomena observed previously during Cd UPD on massive Ag electrodes were found also in the case of Cd UPD on Ag nanoparticles. The desorption spectra in the system Cd/Ag (nanoparticles)/VC employing different polarization times, showed three desorption peaks associated with the dissolution of the Cd OPD and UPD deposits and an Ag–Cd alloy formed at low underpotentials, respectively. The electrochemical behavior of the bimetallic system was also studied applying other polarization routine designed for this purpose.

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## 1. Introduction

The development of metal nanoparticles has attracted much attention in recent years due to their interesting chemical, physical and mechanical properties as well as for their potential applications in nanotechnology, specially in electrocatalysis [1] and sensing [2]. Different methods have been employed to obtain these structures [3], being one of them the electrochemical deposition. Bimetallic particles composed by different metals were obtained by this method, for example Ag/Au nanoparticles fabricated by UPD-redox replacement on VC substrates [1], Cu/Pd crystals electrodeposited on VC [4], and Cu/Ag particles formed on graphite [5], between others.

In particular, it is interesting to generate bimetallic particles with metals that present the phenomenon of the so-called underpotential deposition (UPD) on massive electrodes.

The UPD process is referred as the electrodeposition of 1–2 monolayers or sub-monolayers of a metal (Me) on a foreign substrate (S) at potentials more positive than the Nernst equilibrium potential of the three-dimensional (3D) metal bulk phase ( $E_{3DMe}$ ). By this method, substrates modified by ultrathin and uniform

metallic layers can be generated onto nano or microparticles potentiostatically formed, which provide a higher active surface area for electrocatalysis. Most relevant in this study is the UPD of Cd on Ag single crystals electrodes. Underpotential deposition of Cd on Ag single crystals was extensively studied by STM and electrochemical techniques [6–10]. Also the formation of Ag/Cd films onto Au (1 1 1) substrates [11] has been reported in the literature due to their valuable catalytic properties for the electroreduction of nitrate and nitrite ions, being both contaminants of effluents. In particular, focus on the knowledge of the strong interaction between the Cd and Ag metals, it is interesting to generate bimetallic particles of these metals on an economical support like a VC substrate. Furthermore, as an Ag–Cd surface alloy formation involving a place exchange between adsorbed Cd atoms and the Ag atoms of the underlying massive electrode was found at lower underpotentials [6,9,12], it is expected that a similar alloy formation will take place also in the case of Cd UPD on Ag nanoparticles.

The aim of this work is to study the electrochemical synthesis of bimetallic Ag/Cd nanoparticles supported on VC and the involved surface alloy formation, by conventional electrochemical techniques. This phenomenon has not been yet previously reported for the use of these nanoparticles. The modified substrate Ag/VC used for the Cd electrodeposition was characterized by AFM ex-situ. Desorption spectra using different polarization routines were employed in order to study the alloy formation phenomena.

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## 2. Experimental

A vitreous carbon rod sealed into a Teflon holder (exposed area  $A = 0.071 \text{ cm}^2$ ) was used as working electrode. Prior to each experiment, the surface was first mechanically polished with progressively finer emery paper and then with  $0.3 \mu\text{m}$  particle size alumina powder, until a mirror-like finished surface was obtained. Finally, the electrode was rinsed with tri-distilled water.

The solutions used for metal deposition were:  $1 \text{ mM Ag}_2\text{SO}_4 + 0.02 \text{ M H}_2\text{SO}_4 + 0.1 \text{ M Na}_2\text{SO}_4$  and  $2 \text{ mM CdSO}_4 + 0.1 \text{ M Na}_2\text{SO}_4$  ( $\text{pH} = 2.28$ ), whereas a  $0.1 \text{ M Na}_2\text{SO}_4$  ( $\text{pH} = 2.28$ ) solution was employed as blank electrolyte. All of them were prepared with suprapure chemicals and tri-distilled water. Prior to each experiment the solutions were deaerated by nitrogen bubbling.

Electrochemical measurements were performed in a standard three-electrode electrochemical cell using a Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> saturated electrode (SSE) and a platinum sheet as reference and counter-electrodes respectively. All potentials in this study are referred to the SSE. The experiments were performed with an EG&G Princeton Applied Research Model 273A potentiostat/galvanostat controlled by a microcomputer. The characterization of Ag deposits were carried out with a standard Nanoscope III AFM microscope (Digital Instruments, Santa Barbara, CA, USA) operated ex-situ in contact mode using oxide-sharpened silicon nitride probes (Veeco Probes).

## 3. Results and discussion

Prior to the formation of Ag–Cd bimetallic particles on VC, the electrodeposition process of Ag on VC as well as Cd on VC from solutions containing the corresponding cations, was initially evaluated qualitatively by cyclic voltammetry. The results showed the response of a 3D nucleation and growth process controlled by diffusion (Fig. 1a), which are in agreement with those reported by other authors for the case of Ag/VC [13], but analysis of Cd electrodeposition on this type of substrate was not found in the

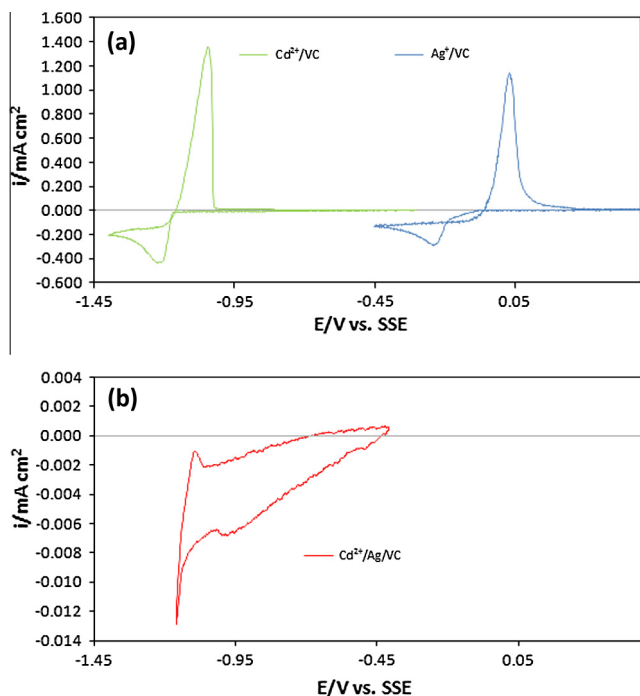
literature. These voltammetric measurements also indicated that the potential values at which the electrodeposition of Ag and Cd on VC take place are sufficiently separated, being feasible the initial deposition of Ag and subsequently the deposition of Cd on the previously deposited Ag crystals. The deposition of Cd on the Ag modified VC substrate, occurs at more positive potentials than on VC substrates indicating the preference of the Cd to nucleate on Ag nanoparticles, as it is expected because Cd presents UPD on Ag substrates [9].

The voltammogram of the system VC/Ag (nanoparticles)/Cd<sup>2+</sup>, shows two cathodic peaks (Fig. 1b). The first one at  $E \sim -0.98 \text{ V}$ , and the second cathodic peak corresponding to the beginning of the bulk deposition of Cd at approximately  $E = -1.13 \text{ V}$ . The dissolution peak of these massive Cd deposits during the reverse sweep was also observed. The first adsorption peak could be attributed to Cd UPD on Ag because it is located in the potential range where Cd UPD on Ag(111) and Ag(100) macroelectrodes takes place, i.e.  $-1.15 \leq E/\text{V} \leq -0.75$  [9,10]. In these systems, four and three adsorption/desorption peak pairs are evidenced respectively, indicating that Ag nanoparticles show qualitatively different adsorption behaviour in relation with Ag single crystals but more similar features were observed when using a Ag polycrystalline electrode. Mech et al. [14] investigated the Cd UPD on polycrystalline silver obtained evaporating Ag on glass substrates, and their cyclic voltammetric results performed in the same solution as in this work revealed that the Cd UPD process is evidenced by a small shoulder which starts at  $E = -0.859 \text{ V}$  and a very small peak around  $-1.109 \text{ V}$ . In the potential range analyzed, the current densities remain below the x axis revealing a net cathodic process, indicating that the deposition of Cd occurs together with hydrogen evolution reaction.

Ag deposits on the VC substrate were obtained applying a single potentiostatic pulse ( $E = -0.23 \text{ V}$ ,  $t = 1 \text{ s}$ ) and characterized by ex situ AFM. Fig. 2a shows an AFM image of the Ag deposit consisting of many small Ag nanoparticles uniformly distributed on the VC surface. The corresponding size distribution of Ag nanoparticles is shown in Fig. 2b. An arithmetic mean particle size of  $57 \text{ nm}$  was obtained with a relative standard deviation of  $0.787$ , which can be related to the presence of some particles with a larger size. The observed morphology of the Ag deposit in Fig. 2a corresponds to an electrodeposition mechanism involving 3D-nucleation and growth of hemispherical islands as reported previously for Ag deposition on carbon substrates by other authors [13,15].

In order to analyze the electrodeposition of Cd on Ag nanoparticles supported on VC, the modified substrate was immersed in the solution containing Cd<sup>2+</sup> ions, and a potentiostatic pulse was applied ( $E = -1.14 \text{ V}$ ) for different polarization times,  $t_p$ . After each pulse, the potential was swept back recording the corresponding  $i$ – $E$  desorption spectra (Fig. 3). The Ag deposit on VC was kept constant during all Cd desorption experiments in order to assure the same amount of Ag nanoparticles.

The desorption spectra of the system VC/Ag (nanoparticles)/Cd<sup>2+</sup>, exhibit three anodic peaks and a net dissolution current density, for polarization times ( $t_p$ )  $\geq 300 \text{ s}$ . This later result is expected because Cd is not a good electrocatalyst for the hydrogen reaction, and the deposition of a large amount of Cd occurs during these experiments. The first peak, considerably higher and sharper than the others (located between  $E = -1.14 \text{ V}$  and  $E = -1.00 \text{ V}$ ), and the second broad one (between  $E = -1.00 \text{ V}$  and  $E = -0.81 \text{ V}$ ), were both mainly related to the dissolution of Cd deposit on the Ag nanoparticles. These peaks did not appear when this experiment was performed on a VC substrate without the presence of Ag deposits using a  $t_p = 500 \text{ s}$ . Since the Nernst equilibrium potential for a concentration of  $2 \text{ mM Cd}^{2+}$  is  $-1.122 \text{ V vs. SSE}$ , it is expected that there is some bulk deposition of Cd on the Ag nanoparticles because Cd electrodeposition was performed at  $E = -1.14 \text{ V}$ ,



**Fig. 1.** Voltammetry of the systems: (a) VC/1 mM Ag<sub>2</sub>SO<sub>4</sub> + 0.02 M H<sub>2</sub>SO<sub>4</sub> + 0.1 M Na<sub>2</sub>SO<sub>4</sub> and VC/2 mM CdSO<sub>4</sub> + 0.1 M Na<sub>2</sub>SO<sub>4</sub> ( $\text{pH} = 2.28$ ) and (b) VC/Ag (nanoparticles)/2 mM CdSO<sub>4</sub> + 0.1 M Na<sub>2</sub>SO<sub>4</sub> ( $\text{pH} = 2.28$ ) in UPD range.

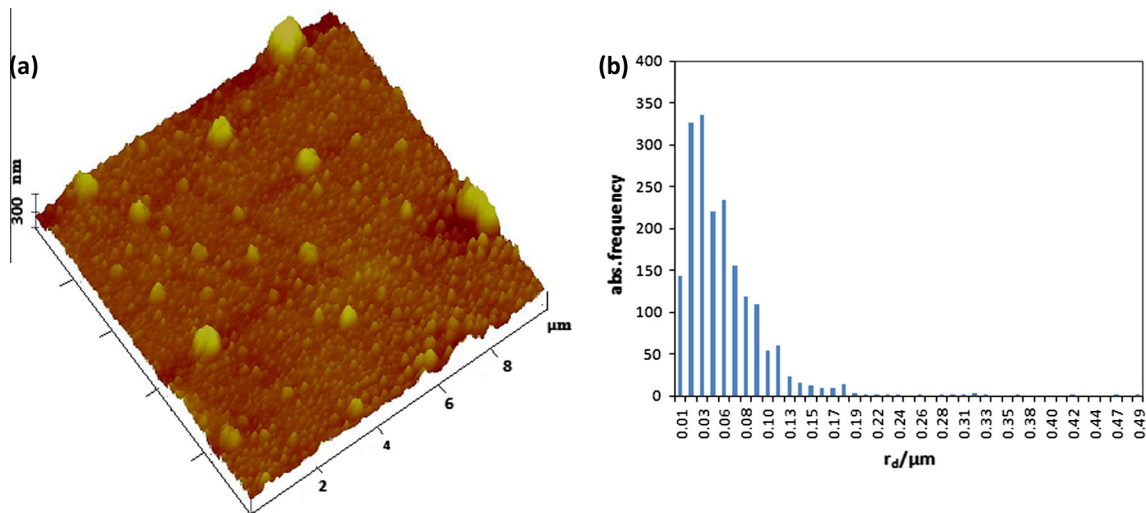


Fig. 2. (a) AFM image of the Ag deposit on VC obtained by a simple potentiostatic pulse and (b) size distribution.

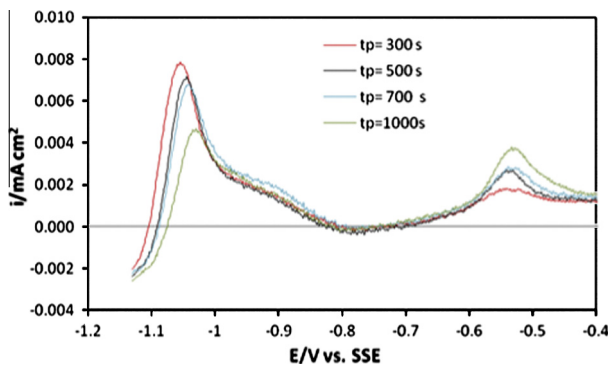


Fig. 3. Desorption spectra of the system VC/Ag (nanoparticles)/Cd<sup>2+</sup> obtained at different polarization times,  $t_p$ . Solution: 2 mM CdSO<sub>4</sub> + 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH = 2.28),  $dE/dt = 10$  mV/s.

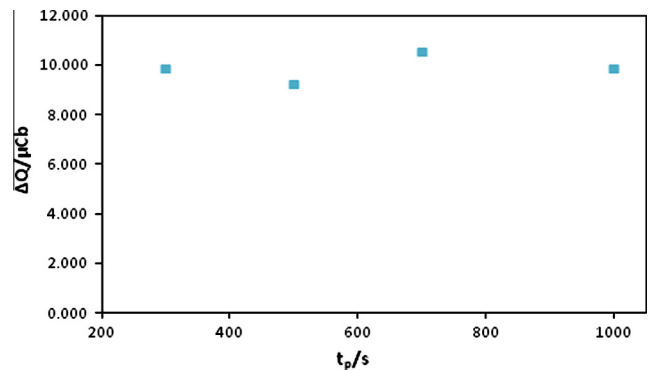


Fig. 4. Dependence of the stripping charge  $\Delta Q$  on polarization time,  $t_p$ .

therefore the first and second peak would be related to the dissolution of the OPD and UPD deposit respectively and probably alloying between metals. The second dissolution peak, for different polarization times, seems to be superimposed in some degree and this behavior was observed by other authors in the study of Cd UPD on polycrystalline silver [14]. The fact that this second peak for all polarization times used, have approximately the same shape allows to infer that it may be due to the dissolution of 1–2 monolayers, stabilized by sulfate ions [9,16,17], formed in the UPD process, being them independent of polarization time. On the contrary, the first peak varies with increasing  $t_p$  because at the potential used, the deposition of several monolayers by an OPD process is feasible. Finally, the stripping curves show an additional peak ( $E = -0.53$  V) located at more positive potentials and long polarization times, which becomes higher as  $t_p$  is increased. Considering this observation which is consistent with the changes noted in the first peak, the formation of an alloy between Cd and Ag can be inferred. The observed change of stripping peaks with increasing polarization time,  $t_p$ , and in particular the shift of the first stripping peak to more positive potentials, indicate the occurrence of surface transformations.

The corresponding stripping charge  $\Delta Q$  calculated at long polarization times from the desorption spectra shown in Fig. 3, is plotted as a function of  $t_p$  in Fig. 4. This stripping charge does not change significantly with  $t_p$ . This behavior was interpreted by other authors [10] as a thin Ag–Cd alloy formation, confined to a layer in the surface, in the system Ag(111)/Cd<sup>2+</sup>. Nevertheless,

the shift of the first desorption peak to more positive potential values as  $t_p$  is increased and the occurrence of an additional peak in the desorption curves showing some irreversibility of the process suggest the occurrence of the alloy formation phenomenon in the case of Ag–Cd nanoparticles.

The application of another polarization routine was performed in order to obtain more information related to the Ag–Cd alloy formation process. The procedure consisted on a simple pulse of  $E = -1.15$  V,  $t_p = 500$  s, applied to the Ag (nanoparticles)/VC modified substrate, and after a delay time ( $t_d$ ) at open circuit, the potential was swept back recording the corresponding anodic stripping spectra, in a potential range where the Ag deposits were stable and only Cd deposits or an alloy between both metals can be dissolved. Fig. 5 shows the desorption spectra for different  $t_d$ . The anodic peaks are higher than those shown for different polarization times (c.f. Fig. 3) due to the use of a higher overpotential for the deposition of Cd. In this figure, a pronounced first peak associated to the bulk dissolution of Cd deposits onto Ag crystals and an Ag–Cd alloying followed by another peak less sharp were observed for all  $t_d$  employed up to 10 min. The first peak reduces its magnitude as  $t_d$  is increased, this fact can be related to the Cd dissolution due to a spontaneous reaction in acid sulphate solutions [18] and also to a possible atomic exchange of Cd adatoms with surface Ag atoms and diffusion of Cd inside the Ag nanoparticles, reducing both effects the coverage of Cd over the Ag nanoparticles. Also the second peak exhibits changes associated with the  $t_d$  shifting to more positive potentials, which probably corresponds to the formation of an alloy between the two metals. In addition, as it is

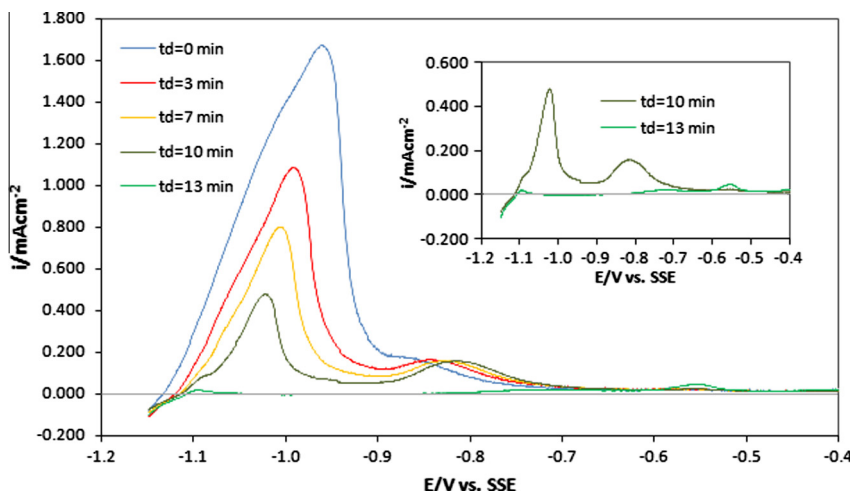


Fig. 5. Desorption spectra of the system VC/Ag (nanoparticles)/Cd obtained after different delay times,  $t_d$ . Solution: 2 mM CdSO<sub>4</sub> + 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH = 2.28),  $dE/dt = 10$  mV/s.

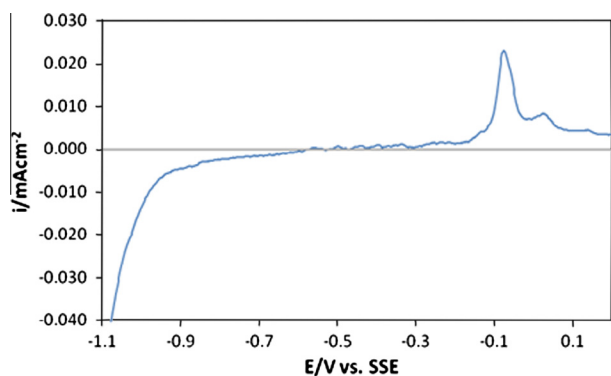


Fig. 6. Stripping curve of the system VC/Ag (nanoparticles)/Cd in 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH = 2.28) blank solution,  $dE/dt = 10$  mV/s.

shown in the inserted figure, the changes in the peaks are significant when the anodic stripping curves for  $t_d = 10$  min and 13 min are compared. The stripping curve for  $t_d = 13$  min leads to a complete disappearance of the first and second peaks and a new peak at a potential of approximately  $-0.56$  V appears. This behavior and the observed in the previous experiment can be directly related to changes at the surface and inside the bimetallic nanoparticles, offering strong evidence of alloy formation between Ag and Cd metals.

On the other hand, Fig. 6 shows the stripping curve in the 0.1 M Na<sub>2</sub>SO<sub>4</sub> (pH = 2.28) blank solution of the Cd/Ag deposit obtained after applying the polarization routines above indicated. The peak observed at  $E = -0.08$  V, corresponds to the dissolution of Ag which occurs at very positive potential values, indicating that the Ag nanoparticles are very stable. Also evaluating the desorption charge, it was verified that it is higher than the charge associated to the Ag deposit. This fact also confirms the dissolution of Cd, whose atoms rearrange with the Ag nanoparticles forming stable alloy structures which need positive potentials above the equilibrium potential of Ag to be dissolved.

#### 4. Conclusions

Bimetallic Cd/Ag particles were synthesized on VC substrates by sequential electrodeposition of both metals using potentiostatic pulses. The cyclic voltammetric experiments showed that it is possible to deposit initially Ag and then the Cd without dissolving the first metal, indicating also qualitatively that the process for both

single systems follows a 3D nucleation and growth controlled by diffusion. Cd UPD on Ag nanoparticles was verified through voltammetric experiments and desorption spectra, showing different adsorption behaviour in relation with single- and poly-crystalline Ag substrates. The presence of hydrogen evolution process in the analyzed potential range was confirmed. The desorption spectra reveal the dissolution of Cd OPD and UPD on the pre-deposited Ag nanoparticles supported on VC. The formation of an alloy between the involved metals could also be inferred. This phenomenon was confirmed also applying an anodic stripping of Ag/Cd deposits to more positive electrode potentials in a blank electrolyte solution.

#### Conflict of interest

There is no conflict of interest among authors.

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