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Cyclic voltammetry study of electrochemically synthesized Ag/PVP nanocomposite

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Introduction

Metal nanoparticles, such as silver particles, attract a considerable interest due to their distinctive optical, thermal, chemical and physical properties, which make them applicable in various fields, including biomedicine. However, high reactivity and fast aggregation, originated from the high level of superficial energy of nanoparticles, induce the particle growth leading to the loss of the desired nanoparticle properties. One of the proposed options for the control of interparticle interactions is the use of the water-soluble polymers as particle matrices, such as poly(*N*-vinyl-2-pyrrolidone) (PVP), which are susceptible to the sol-gel transition when γ-irradiated in the aqueous solutions.[1,2] PVP hinders silver particle aggregation by a steric effect.[3] Biocompatibility and the ability to prevent the microbial penetration make PVP useful in biomedical applications, also.[1] In combination with silver nanoparticles having the significant antimicrobial activity,[4] PVP can be potentially used for soft tissue implants, catheter coatings, wound dressings, *etc*.

There are reports on the electrochemical synthesis of silver nanoparticles (AgNPs) in the aqueous solutions.[5,6] In order to produce the Ag/PVP nanocomposite biomaterial in this work AgNPs were inserted into the PVP hydrogel matrix by electrochemical reduction of Ag^+ ions. To check the electrochemical properties, Ag/PVP nanocomposite was characterized by cyclic voltammetry.

Experimental

Ag/PVP nanocomposite was obtained by electrochemical synthesis of AgNPs within PVP hydrogel. PVP hydrogel was previously prepared by γ-irradiation of the 10 wt. % PVP (M_w 360 000) solution in demineralized water (4D, *Millipore, Billerica, MA*), using ^{60}Co radiation facility at room temperature. Integral radiation dose used was 25 kGy, at approximate dose rate of 0.6 kGy h^{-1}.[7] PVP hydrogel has been swollen in the aqueous solution containing 3.9×10^{-3} mol dm^{-3} $AgNO_3$ and 0.10 mol dm^{-3} KNO_3 for 24 h. The electrochemical synthesis of AgNPs was performed by imposed voltage between the two platinum electrodes (9 x 10 mm^2) with 5 mm thick swollen hydrogel in between. The synthesis was performed at constant voltage of 200 V during 4 min at room temperature. Cyclic voltammetry experiments, using the same working and counter electrode assembly, were performed with Ag/PVP nanocomposite, Ag/PVP nanocomposite after air drying for 24 h and reswelling in 0.10 M KNO_3 solution, and Ag/PVP nanocomposite without Ag surface layer (mechanically removed by cutting) formed during the synthesis.

Cyclic voltammetry experiments were carried out using the Gamry Reference 600 potentiostat/galvanostat/ZRA. A reswollen nanocomposite was placed in between the two Pt plates and a saturated calomel electrode (SCE) was a reference electrode. The salt bridge with 0.20 M KNO_3 was used to prevent the contact of Cl^- ions in SCE and Ag^+ ions in the hydrogel. The measurements were recorded in the potential region between -1 and 1 V *vs.* SCE, at a scan rate of 50 mV s^{-1}, starting from the open circuit potential, E_{ocp}. The values of E_{ocp} for each investigated system are presented in Table 1. In order to get straightforward insight into the insertion process, cyclic voltammograms of: Pt electrode in 0.10 M KNO_3; the system Pt/pure PVP hydrogel in 0.10 M KNO_3; Pt electrode in 0.10 M KNO_3 solution containing 3.9 mM $AgNO_3$, with and without solution deoxigenation by N_2; Ag coated Pt electrode in 0.10 M KNO_3 solution containing 3.9 mM $AgNO_3$ obtained by potentiostatic deposition of silver on Pt electrode at 0 V *vs*. SCE during 30 s, were also recorded. All figures represent the stationary cyclic voltammograms (the n^{th} sweep).

Table 1. The values of E_{ocp} used as an initial value for cyclic voltammetry measurements

Investigated system	E_{ocp} / mV *vs.* SCE
Pt / 0.10 M KNO_3	750
Pt / 0.10 M KNO_3 + 3.9 mM $AgNO_3$	730
Pt / N_2–bubbled 0.10 M KNO_3 + 3.9 mM $AgNO_3$	750
Ag coated Pt electrode / 0.10 M KNO_3 + 3.9 mM $AgNO_3$	660
Pt/PVP / 0.10 M KNO_3	540
Pt/Ag/PVP nanocomposite immediately after the synthesis, rinsed with 0.10 M KNO_3	610
Pt/Ag/PVP nanocomposite reswollen in 0.10 M KNO_3	590
Pt/Ag/PVP nanocomposite after the removal of Ag surface layer	360

Results and Discussion

Fig. 1 shows the cyclic voltammograms of a Pt electrode in 0.10 M KNO_3 solution (curve a), a Pt electrode in 0.10 M KNO_3 solution containing 3.9 mM $AgNO_3$ (curve b), Pt electrode in 0.10 M KNO_3 solution containing 3.9 mM $AgNO_3$ deoxygenated by N_2 (curve c) and an Ag coated Pt electrode in 0.10 M KNO_3 solution containing 3.9 mM $AgNO_3$ (curve d). Despite the differences in the experimental systems (curves b and c were obtained by running CV in 0.10 M KNO_3 solution containing 3.9 mM $AgNO_3$, and curve d was obtained after the Ag deposition on Pt electrode from the same solution prior to CV measurements), two anodic and two cathodic peaks can be observed on the curves related to the presence of silver (curves b, c and d).

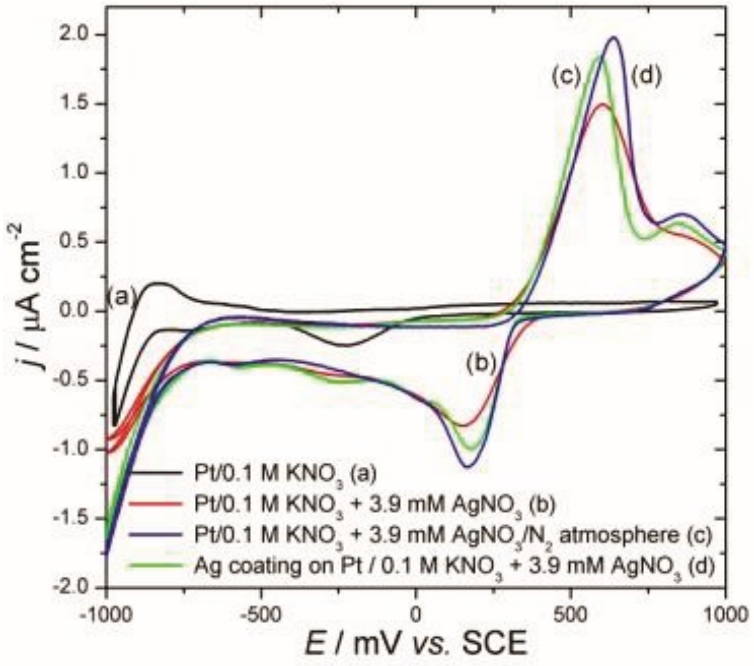

Fig. 1. Cyclic voltammograms of a Pt electrode in: 0.10 M KNO_3 (a), 0.10 M KNO_3 + 3.9 mM $AgNO_3$ (b), 0.10 M KNO_3 + 3.9 mM $AgNO_3$ solution deoxygenated by N_2 (c), and Ag coated Pt electrode in 0.10 M KNO_3 + 3.9 mM $AgNO_3$ (d).

The anodic peaks, appearing around 600 and 850 mV, respectively, could be related to the Ag/Ag^+ reaction and possible silver oxides formation. For all curves, only one cathodic peak appears at about 160 mV, which could correspond to the silver deposition on the Pt electrode and reduction of silver oxides. The curve (c), obtained by performing the CV measurements in 0.10 M KNO_3 solution containing 3.9 mM $AgNO_3$ and deoxygenated by bubbling the N_2, exhibited no significant difference comparing to the curves b and d.

Fig. 2 represents cyclic voltammograms of the systems Pt/pure PVP hydrogel (curve a) and Pt/Ag/PVP nanocomposites immediately after the synthesis, rinsed with 0.10 M KNO_3 solution (curve b) and after drying and reswelling in 0.10 M KNO_3 solution for 24 h (curve c).

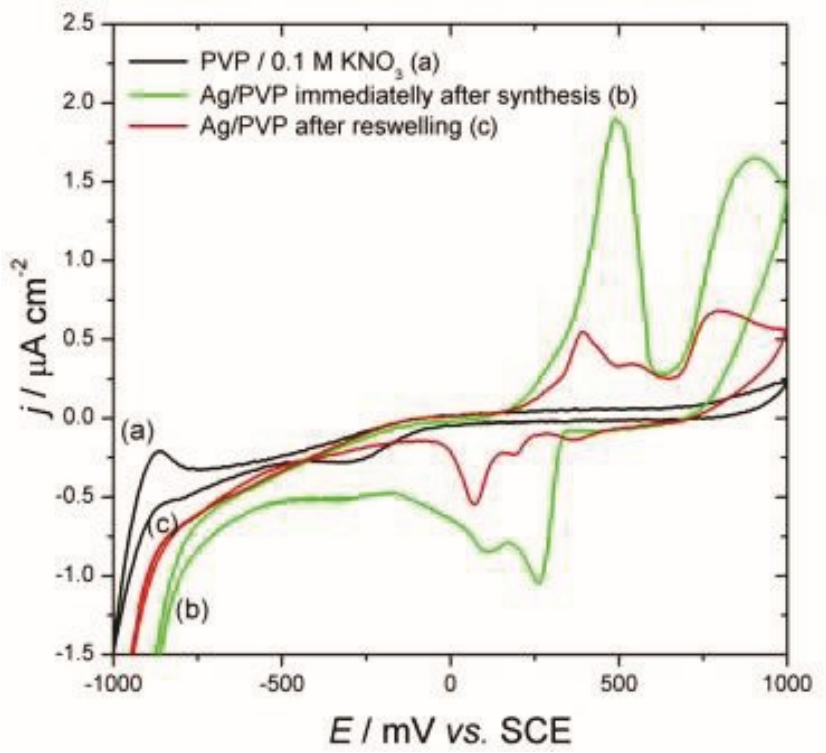

Fig. 2. Cyclic voltammograms of PVP hydrogel (a), Ag/PVP nanocomposite immediately after synthesis (b), and Ag/PVP nanocomposite after reswelling (c) in 0.10 M KNO_3 solution.

It can be observed that Ag/PVP nanocomposite immediately after the synthesis (curve b) causes one anodic peak around 490 mV that is significantly higher than those of reswollen Ag/PVP nanocomposite in the same potential range. There are three anodic peaks with reswollen Ag/PVP nanocomposite (curve c), at around 400 mV, 450 mV and 550 mV, which relate to the oxidation of the silver species as nanoparticles (even slightly agglomerated) or in the nanocomposite. Much higher current seen in curve b, corresponding to the greater mobility of system components, indicates that the majority of the silver present in this Ag/PVP nanocomposite is still in the form of residual Ag^+ ions, and that the reduction of which is not completed. This consideration is in accordance with visual observation that the freshly prepared Ag/PVP nanocomposite is not colored, while the reswollen one is dark yellow. Actually, the freshly obtained, colorless Ag/PVP nanocomposite becomes dark yellow in time and during drying and reswelling procedure. The cyclic voltammograms of reswollen Ag/PVP nanocomposite (curve c) exhibited peaks with significantly lower intensity of current, confirming the entrapment of AgNPs inside the PVP network. This could indicate that the electric current initiates the reduction of silver ions inside the PVP network, and that the reduction takes place even after the electrochemical experiment is finished. The cathodic peak at about 360 mV, that appears only in cyclic voltammogram of reswollen Ag/PVP nanocomposite (curve c), probably relates to the further reduction of AgNPs (*i.e.* nanoparticle growth). Very low intensity of this cathodic peak suggests that the AgNPs growth is very limited by the presence of the PVP network, preventing the further nanoparticle growth and/or agglomeration.

Fig. 3 presents cyclic voltammograms of Ag/PVP nanocomposite after drying and reswelling in 0.10 M KNO_3 solution for 24 h as well as of the same Ag/PVP nanocomposite after the removal of the silver surface layer by cutting. The main difference between two curves in Fig. 3 is as follows: anodic peak at 550 mV seen in CV of the Ag/PVP nanocomposite, and the related cathodic counterpart at 190 mV, disappeared when the silver surface layer of the Ag/PVP hydrogel nanocomposite was removed from the Ag/PVP surface. This means that those peaks correspond to the presence of Ag surface layer at the Ag/PVP hydrogel surface, formed during the synthesis of Ag/PVP nanocomposite. After the elimination of Ag surface layer and its effects, two anodic and two cathodic peaks present in cyclic

voltammograms of both Ag/PVP nanocomposites are seen. Anodic peak at about 800 mV is similar to the peak present in cyclic voltammograms in 0.10 M KNO_3 solution containing 3.9 mM $AgNO_3$ (Fig. 1), related to the oxidation of silver species.

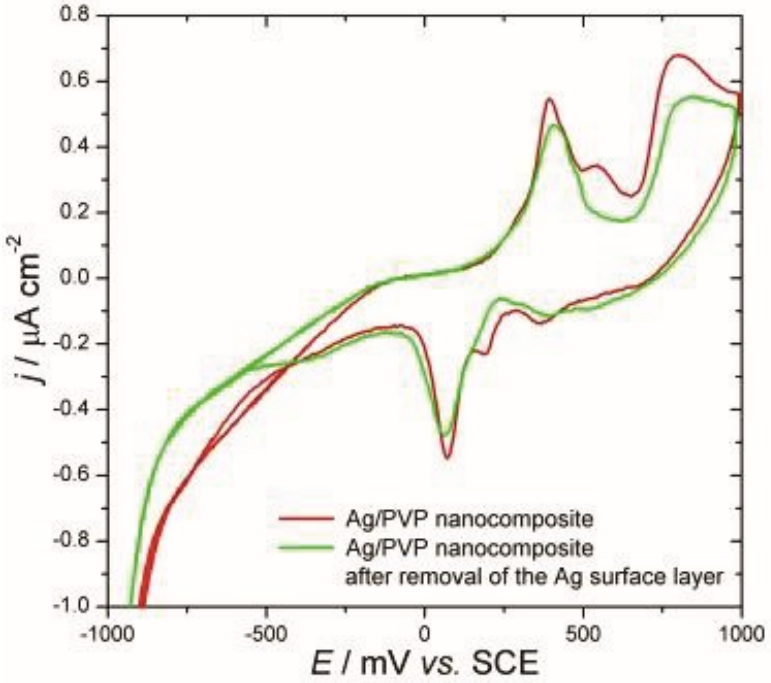

Fig. 3. Cyclic voltammograms of Ag/PVP nanocomposite and Ag/PVP nanocomposite after removal of the Ag surface layer of Ag/PVP nanocomposite in 0.10 M KNO_3 solution.

The obvious difference between Figs. 1 and 3 is the intensity of registered current. The lower current values, observed in Fig. 3, are the consequence of the lower mobility of silver species embedded in PVP hydrogel network, in comparison to the solution, which hinders the rate of electrochemical process. It appears to be that silver nanoparticles in hydrogel exhibit anodic and cathodic peak potentials more negative than those of Ag/Ag^+ in the solution, suggesting that AgNPs could be oxidized more easily.[8] In any case, this indicates an important role of PVP network and requires further detailed investigations.

Conclusion

The Ag/PVP nanocomposite was synthesized by electrochemical insertion of Ag into the PVP hydrogel network. The nanocomposite was characterized by the cyclic voltammetry. The comparison of the cyclic voltammograms of the system Pt/Ag/PVP nanocomposite and Pt electrode in the solution containing Ag^+ as well as Ag coated Pt suggests the differences for redox processes and the activity of the silver in different forms. It can be concluded that hydrogel network enables the preservation of the form, size and activity of synthesized AgNPs.

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