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Electrochemical fabrication of Cu/Pd multilayer nanowires in polycarbonate template

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Abstract

In this work,copper/palladium (Cu/Pd) multilayer nanowires were successfully prepared by electrodeposition method using polycarbonate template. The fabrication of Pd/Cu multilayer nanowires was controlled by analyzing the current–time transient during electrodeposition using potentiostat.The morphological properties of the nanowires were studied by scanning electron microscopy (SEM) and result showed that almost each nanowire had the same length of ≈ 4 μm and the diameter of 90 nm .X-ray diffraction pattern showed that Pd and Cu grow in their face-centered-cubic (fcc) lattice structures.The chemical composition was determined by examination of the energy dispersive X-ray (EDX) spectra.

Keywords: Cu/Pd multilayer nanowires, electrodeposition, polycarbonate template

1. Introduction

There is a great deal of interest in nanostructures for potential applications in such areas as electronics, biochemistry, materials, and medicine. One-dimensional structured materials, such as nanowires are candidate materials for these applications of nanotechnology. Recent advances from the convergence of nanotechnology and biotechnology are accelerating the development of sensor research. Nanostructured materials, for example metal nanowires, have the properties of novel optical, electrical, catalytic, and magnetic properties, which make the nanowires the promising sensing materials for ultrasensitive, trace-level biological and chemical nanosensors [1, 2].

Metal nanowires are promising nanomaterials for chemical and biological sensors and optical and electronic devices because of their unique electrical, magnetic, optical, as well as mechanical properties. Increasing attentions have been given to the fabrication of multilayer nanowires [3-5] in comparison with the extensive studies of monometallic metals.It has been demonstrated in many reports that bimetallic catalysts are more efficient at the catalytic reduction as compared to monometallic ones. The bimetallic catalysts consist of a noble metal (Pd, Pt and Rh) and a promoting transition metal (Cu, Ni, Fe, Sn and In) [6, 7]. The role of the transition metal is to reduce toxic ions according to a redox process leading to its oxidation; the role of the noble metal is to stabilize the transition metal in its lower oxidation states. Bimetallic catalysts, preferablyPd-Cu, exhibit a high activity for nitrates reduction [8]. Pd-Cu nanowires can be used for hydrogenolysis of glycerol [9], hydrogen feed gas purification [10] and selective sensing of hydrogen gas [11].

One-dimensional nanostructures can be produced by a variety of techniques such as molecular beam epitaxy, nanolithography, vapour–liquid–solid growth and electrodeposition. Electrodeposition of metals into the pores of nanoscale templates (such as alumina membranes, nuclear track-etched polymer membranes, mesoporous silica or porous silicon) has been particularly attractive [12, 13] because (a) it is a simple, low-cost, high-throughput technique for fabricating large arrays of nanowires with monodispersive diameter and length, (b) it provides the ability to tailor size, length, shape and morphology of the material deposited by controlling the template morphology and the synthesis parameters and (c) it provides the ability to introduce composition modulation along the wire length, which in turn enables precise control on architecture and magnetic properties [14].

Typically, the templates are polymer nanoporous membranes, with parallel cylindrical pores obtained by swift heavy ions bombardment and subsequent etching.

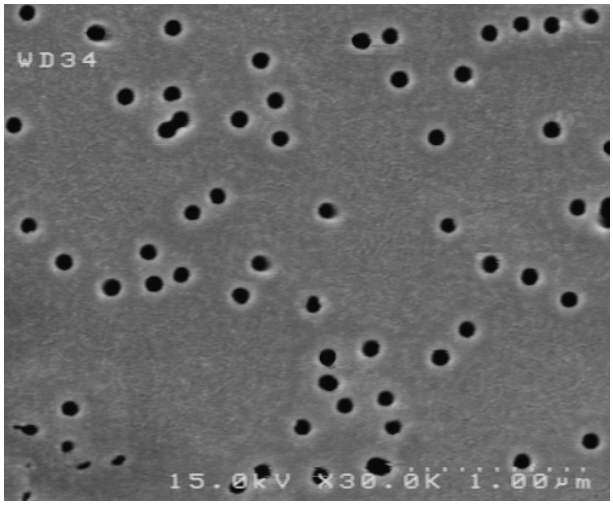

Figure 1. The porous polycarbonate template.

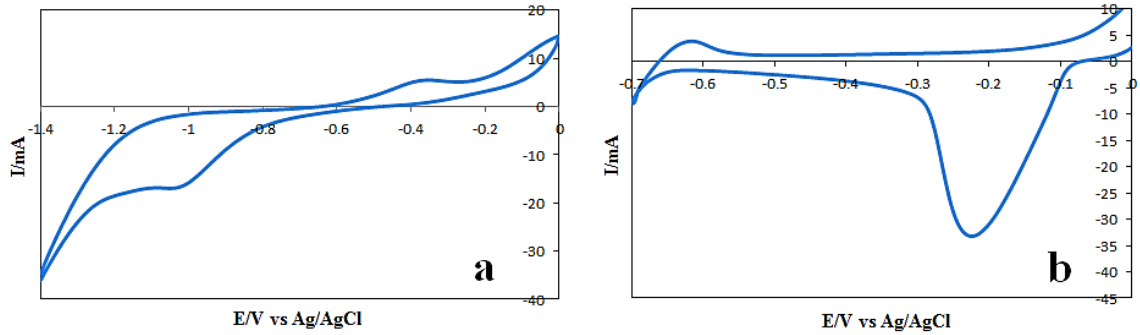

Figure 2. Cyclic voltammograms of a) Pd^{2+} and b) Cu^{2+} ions on polycarbonate template.

The polymer ion track membranes are ideal from several points of view for being used as templates for magnetic nanowires growth [15].

In this work, the electrodeposition technique has been used to fill the polycarbonate template pores with Pd/Cu multilayer nanowires since the method is more reliable for deposition into high aspect ratio materials and also can compensate for the slow diffusion-driven transport in the narrow pores. SEM and XRD were employed to nanostructure morphology characterization. The chemical composition of the prepared nanostructures was measured by EDX performed in SEM.

2. Experimental procedure

Commercially available ion track-etched polycarbonate templates with pore-diameter of 100 nm, pore length of 4µm were used as a template material for growing multilayer nanowires. It is manufactured by Millipore USA and used for fabricated nanowires (Figure 1). A gold layer of approximately 100 nm thick was sputtered at the backside of this membrane.The gold-sputtered membrane was used as the working electrode of the electrodeposition process. A small platinum mesh was used as the counter electrode and Ag/AgCl in 3 M KCl was used as the reference electrode.

The nanowires were grown inside the polycarbonate membrane using a potentiostatic electrodeposition procedure. Using the dual-bath technique, Cu and Pd segments were alternately electrodeposited into the pores by moving the substrate between two different electrolyte baths. One bath consisted of $CuCl_2.2H_2O$ (0.2 M) and KCl (0.1M). The pH value was maintained at 3. The other consisted of KCl (0.1M) and K_2PdCl_4(0.03M). The electrolysis was carried out at 25 °C. The electrochemical behavior of Cu^{2+} and Pd^{2+} on polycarbonate template was investigated using cyclic voltammetry (Figure 2). Figure 2 shows that the deposition potential of Cu^{2+} and Pd^{2+} on polycarbonate template is -0.22 and -1.00 V, respectively. In the case of Cu, in order to accelerate precipitation rate of Cu^{2+} ions, we applied an overvoltage and worked at -1.1 volt.

The deposition process was accomplished while monitoring the current–time profiles to derive information related to the growth mechanism.

Structure of sample was studied using X-ray diffraction (Philips powder diffractometer type PW 1373 gonimeter). The XRD was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405Å and diffraction patterns were recorded in a 2θ range ($10\text{-}80^0$), with a scanning speed of 2°/min. To obtain the SEM images of electrodeposited nanowires, polycarbonate templates were dissolved in dichloromethane and the remains consisted of nanowires

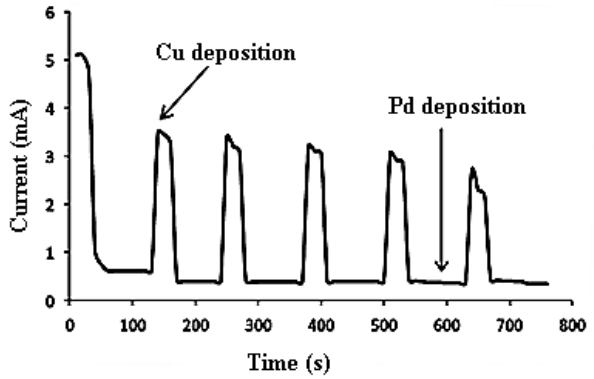

Figure 3. The current transient during the electrodeposition of the Cu/Pd multilayer nanowires in the polycarbonate template.

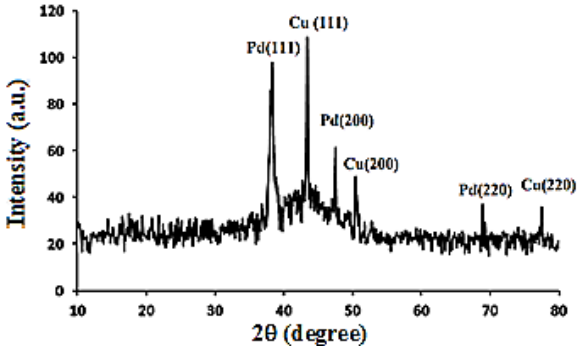

Figure 4. XRD patterns of the segmented Cu/Pd multilayer nanowires.

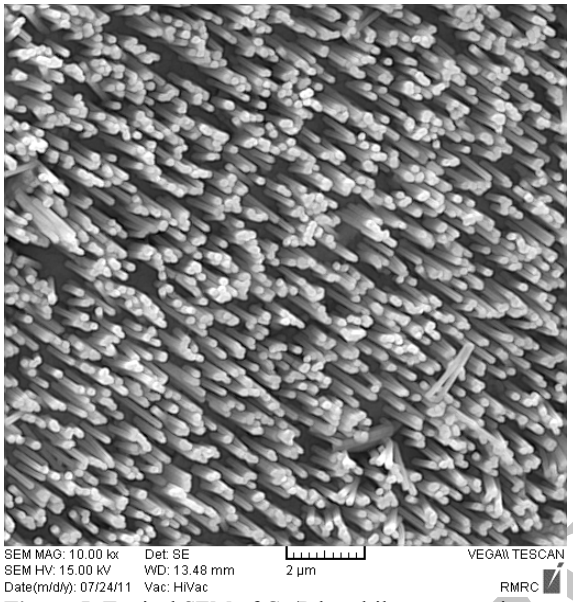

Figure 5. Typical SEM of Cu/Pd multilayer nanowires.

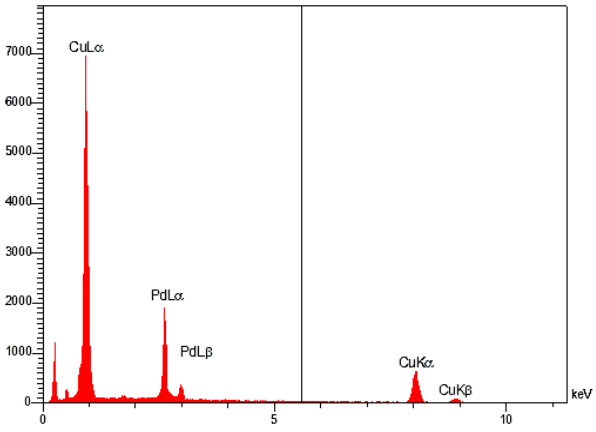

Figure 6. EDX of the Cu/Pd multilayer nanowires deposited in polycarbonate template.

and a gold layer was served as a sample for SEM observation. The sample morphology and images of nanowires have been studied by VEGA TEScan SEM. The chemical composition of the prepared nanostructures was measured by EDX performed in the SEM.

3. Results and discussion

Deposited amount of Cu and Pd at the cathode was determined by the product of the current at the deposition time. Figure 3 shows current-time diagram during electrodeposition of Cu/Pd multilayer nanowires in polycarbonate template after six steps (each step includes first 30 s electrodeposition of Cu ions at -1.1 V and then 100 s for Pd ions at -1V). Figure 3 shows that cathodic current produced during electrodeposition of Cu layer is more than Pd layer. This maybe due to higher concentration and higher applied overvoltage of Cu ions compared with Pd ions.

Structure of samples was studied using XRD technique. Figure 4 shows XRD patterns of the segmented Cu/pdmultilayer nanowires. The sharp peaks of the (111), (200), (220) diffractions indicate that the Pd segment has fcc structure [16], and sharp peaks of the (111), (200), (220) diffractions peaks show that the Cu segment has fcc structure[17].The diffraction peaks of Pd are rather broad, suggesting that grain size is smaller than Cu. To confirm this assumption, we evaluated the grain size using Scherrer'sequation [18], and we found an average size of 4.97± 0.15 nm and 2.95 ± 0.09 nm for Cu and Pd, respectively.

Figure 5 shows the typical SEM image of the Cu/Pd multilayer nanowires electrodeposited in the porous polycarbonate templates. Clearly, the nanowires are cylindrical shape and almost each nanowire had the same length of ≈ 4 µm and the diameter of 90 nm.

A quantitative EDX spectrum was taken to determine the elemental composition of the Cu/Pd multilayer nanowires deposited in the polycarbonate templates. The results are presented in figure 6. From this figure, it is confirmed that there is no other elemental impurities present in the nanowires composition. The analysis gives the percent by weight (Wt %) and percent number of atom (At %) of each element identified, which is given in Table 1.

4. Conclusion

The present work describes the successful fabrication of Cu/Pd multilayer nanowiresin PC template by electrodeposition method. The Cu/Pd multilayer

Table 1. EDX elemental composition of the Cu/Pd multilayer nanowires.

Element	Wt%	At%
Cu	93.82	96.49
Pd	6.18	3.51
Total	100.00	100.00

nanowires have the diameters of about 90nm. The growth mechanism and the behaviors in current–time curves are investigated in depth. The proposed explanation of the mechanism gives us the in-situ control of the growth of a multilayer nanowire by controlling current–time transients. The fabricated Cu/Pd multilayers are well arranged (Figure 5). The XRD pattern shows that multilayer nanowires consist of a pure phase of copper and palladium with fcc structure without a preferred orientation. We believe that such structures can be used as an active element for sensor and catalyst applications.

References

1. R Tarushee Ahuja, and D Kumar, *Sensors and Actuators B: Chemical,***136**(2009)275.
2. C Kong, Zh A Hu, H X Zhao, Y Y Yang, X L Shang, LJ Ren, and Y P Wang, *Int. J. Electrochem. Sci.*, **2** (2007) 133.
3. Q F Liu, CX Gao, J JXiao, and D S Xue, *J. Magn. Magn. Mater.*, **260**(2003)151.
4. B Jaleh, AOmidvar Dezfuli, V Jaberian Hamedan, M Najafi, and E Tamari, IJPS, **6**(2011) 4775.
5. Y A Fedutik, G P Shevchenko, V S.Kurilo, and A Y Valendo, *Surf. Sci.*, **297**(2004) 566.
6. KDVorlop, UPrusse, in: F.J. Jansen, R.A. vanSanten (Eds.), Catalytic Science Series, **1** (1999) 195.
7. U Prusse, and KD Vorlop, *J. Mol. Catal. A: Chem*., **173** (2001) 313.
8. J Trawczynski, P Gheek, J Okal, M Zawadzki, and M JIlan Gomez, *Appl. Catal., A: General,***409– 410** (2011) 39.
9. S Xia, Z Yuan, L Wang, P Chen, and Z Hou, *Appl. Catal. A: General*, **403** (2011) 173.
10. F Wang, and G Lu, *Int. J. Hydrogen Energy*, **35** (2010) 7253.
11. F Favier, E C Walter, M P Zach, T Benter, and R M Penner, *Science,* **293**(2001) 2227.
12. C Frantz, N Stein, Y Zhang, E Bouzy, O Picht, M E Toimil-Molares, and C Boulanger, *Electrochim. Acta*, **69** (2012) 30.
13. M Gupta, D Pinisetty, J CFlake, and J JSpivey, *J. Electrochem. Soc.*, **157** (2010) 473.
14. S Aravamudhan, J Singleton, P A Goddard, and S Bhansali, *J. Phys. D: Appl. Phys.*,**42**(2009)115008.
15. E Matei, I Enculescu, M Enculescu, and R Neumann, *JOAM*, **10** (2008) 508.
16. H Wang, C Xu, F Cheng and S Jiang, *Electrochem. Commun.*, **9** (2007)1212.
17. J U Cho, Q X Liu, J H Min, S P Ko, and Y K Kim, *J. Magn. Magn. Mater*., **304** (2006) 213.
18. R Inguanta, S Piazza, and C Sunseri, *Electrochem. Commun.*, **11** (2009) 1385.