VNU Journal of Science: Mathematics – Physics, Vol. 33, No. 2 (2017) 16-23

CoNiP/Au Multisegment Magnetic Nanowires: Synthesis and Aminothiophenol (4-ATP) Functionalization

Do Quang Ngoc[1], Hoang Thi Nu[1], Luu Van Thiem[2], Luu Manh Quynh[1], Le Tuan Tu[1,*]

[1]*Faculty of Physics, VNU University of Science, 334 Nguyen Trai, Hanoi, Vietnam*
[2]*Faculty of Basic Science, Hanoi Industrial College for Textile, Garment and Fashion, Gia Lam, Hanoi*

Received 17 March 2017
Revised 20 April 2017; Accepted 25 May 2017

Abstract: The magnetic properties in CoNiP/Au multisegments nanowire were investigated. All the samples were prepared by electrodeposition method with pH of 5.5 and room temperature. The electrochemical potential of CoNiP was determined by cycle voltammetary. The crystalline structure and morphology of the samples were characterized by X-ray diffraction (XRD), Scanning Electron Miroscopy (SEM) and High-resolution transmission electron microscopy (HRTEM), respectively. The hysteresis loops were measured at room temperature using vibrating sample magnetometry (VSM). The SEM and TEM image showed that the CoNiP/Au nanowires with diameters about 50 nm. The lattice spacing of the CoNiP samples were 0.205 nm. The obtained results of VSM show that, the coercivity is 1006 Oe. The 4-Aminothiophenol (4-ATP) functionalized CoNiP/Au were combined by inverse emulsion method in order to apply to biomedicine. The characteristic Surface Enhanced Raman peak positions of 4-ATP absorbed on the Au segments were occurred without any alterations, which significantly predicted attractive applicability of the colloids for biomedical labeling.

Keywords: Nanowires, multisegment, electrodeposition, magnetic properties, functionalized.

1. Introduction

Among these types of nanowires, multisegment nanowires play the most important role in the significant application in multiplexed bioanalysis, biosensors, magnetic cell separation and gene delivery with multiple functionalities [1]. The strength of multisegment nanowires is a wonderful combination of magnetic and nonmagnetic segments in only wire. In most of multisegment nanowires, gold (Au) is used popularly as the nonmagnetic segment because of its particular properties. Gold nanowires are high conductive, more transparent, non-corrosive and are resistant to corrosion or oxidation. The individual gold nanowires are widely used for electrodes and interconnections in the semiconductor industry and nanoelectronics research [2-4]. In biomedicine field, gold nanowires are

*Corresponding author. Tel.: 84- 1269114333.
Email: letuantu@hus.edu.vn
https//doi.org/ 10.25073/2588-1124/vnumap.4198

also for living cell study, gene delivery [5-7] and in biosensor. In previous reports, the syntheses, characterization and growth of multisegment soft magnetic nanowires like NiFe/Cu, Au/Fe, Co/Pt and Au/Co have been described [8]. The multisegment nanowires including Au segment have been applied successfully in many areas especially nanomedicine. For example, Au/Ni/Au multisegment nanowires are used to separating of His-tagged proteins; the gene delivery using Ni/Au multisegment magnetic nanowires exhibits obvious advantages [9]

The properties including length, diameter, and surface of nanowires depend mainly on the synthesis technique [10]. The templating method is the most attractive, as it can be used for synthesizing nanowire with desired composition, size and aspect ratio. Using this technique, different segments can be introduced along the axis of a nanowire, and it is particularly attractive for the realization of multi-functionality. Therefore, the template assisted electrochemical deposition method has been used extensively for synthesizing multisegment nanowires.

Hence, our work focused on manufacture and studied properties of multisegment nanowires, particularly CoNiP/Au multisegment nanowires and then based on the success of the fabricated magnetic nanowire we can also give application oriented that is 4-aminothiophenol (4-ATP) attached to the surface of CoNiP/Au magnetic nanowire .

2. Experimental

The multi-segment nanowires were prepared via sequential electrodeposition (Potentiostatic mode) of CoNiP/Au segments within a polycarbonate membrane (50 nm diameter) by changing the corresponding electrolytes in an electrodeposition cell. The room temperature electrolyte for the CoNiP contains 47.5 g/l $NiCl_2.6H_2O$ + 26.7 g/l $CoCl_2.6H_2O$ + 27 g/l NaH_2PO_2 + 24.7 g/l H_3BO_3 + 1.3 g/l Saccharin with pH around 5.5 and the electrolyte for the Au contains 6.8 g/l $HAuCl_4$.

We optimized different parameter such as electrode potential, growth rate, temperature and pH for single segment of CoNiP and Au nanowires in prior to the deposition of multi-segmented nanowires. The electrochemical deposition for CoNiP and Au were performed at constant potential of -0.9 V and -0.81 V respectively.

Figure 1 depicts a schematic of the template-based synthesis process. Conducting polymers show preferential deposition along the walls of the poly-carbonate membrane resulting in nanotubule structures due to solvophobic interactions. These tubules close up as the deposition time is increased and eventually results in nanowires. Following nanowires electrodeposition, the conducting film used for electrochemical polymerization and the template are then subsequently dissolved using appropriate acids or bases. Organic solvents may be used to dissolve polymer templates.

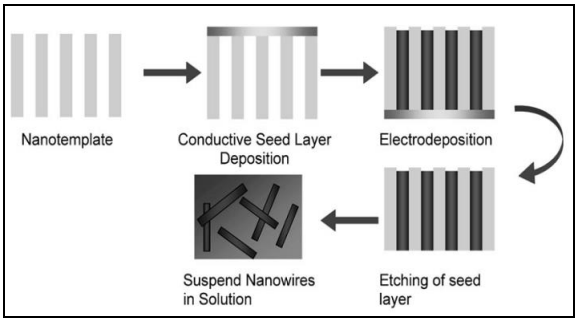

Fig. 1. Schematic of template-based synthesis of nanowires.

Particularly, two segments CoNiP and Au were deposited into a nanoporous polycarbonate membrane (50 nm in diameter) in order by changing the corresponding electrolytes in an electrodeposition cell [11,12]. The multisegment CoNiP/Au nanowires were separated from the polycarbonate membrane by dissolving the template in dichloromethane. After few minutes, the polycarbonate membrane dissolved in this solution and we obtained the CoNiP/Au multisegment nanowires [13].

The electrodeposition process was performed at room temperature. Subsequent to the deposition, the magnetic properties of the sample films were measured by a vibrating sample magnetometer (VSM) with the magnetic field applied parallel to the plane of the film. The elemental compositions were carried out by energy dispersive X-ray spectroscopy (EDX).

4-Aminothiophenol (4-ATP, sometime called *p*-aminothiophenol) has benzene ring with amino group (-NH_2). 4-ATP was used widely to link to the surface biological elements easily [14].

Figure 2 shows the schematic procedure of 4-aminothiophenol (4-ATP) on the nanowire surface. One hundred microgram of CoNiP/Au nanowires were mixed with 1 mL of 4 ATP dissolved in Chloroform solution. The resultant solution was kept in an ultrasonic bath for a few minutes to avoid the aggregation of nanowires and expose all surface areas of individual nanowires to the 4-ATP solution. After that, the dispersed nanowire solution was kept at room temperature for 24 hours, followed by washing with Chloroform solution several times by centrifugation and purification by repeated magnetic purification method using a hard magnet.

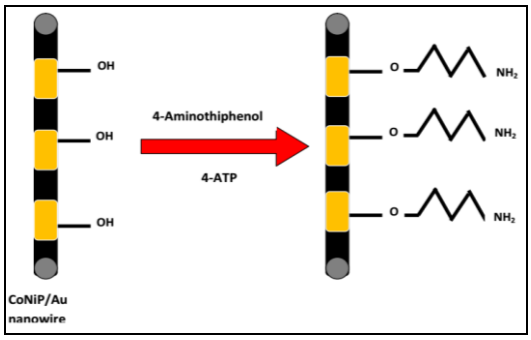

Fig. 2. Schematic graph attached 4-ATP on to CoNiP/Au magnetic nanowire.

The characteristic of CoNiP/Au nanowire functionlized was analysed by Raman spectroscopic and UV-vis method.

3. Results and discussion

Figure 3 shows CV characteristic curve of solution containing 0.7 M NaCl, 0.4 M H_3BO_3, 0.2 M $NaCl_2$.6 H_2O, 0.206 M $CoCl_2$.6 H_2O and 0.146 M NaH_2PO_2. The cyclic voltammetry were recorded at scan potential limits between -1.5 V and 1 V. In this figure, the deposition process (reduction process) stared from -0.5 V and to be expanded to -1.02 V. Having addition composition NaH_2PO_2 in solution makes the ions that are polarized easily

This curve shows that, Ion Co^{2+} and Ni^{2+} do not appear reduction peaks in the electrolytic solution maybe their standard electrode potential is distributed very closely in the electrochemical array. Specifically, the standard electrode potentials of Co^{2+} / Co and Ni^{2+} / Ni are -0.283 V and -0.236 V respectively. Moreover, the addition NaH_2PO_2 in solution makes the ions that are easily polarized, it

also can change kinetic of deposition components of Co and Ni. Therefore, the reduction process occurs in the solution that will be combination of two half reactions.

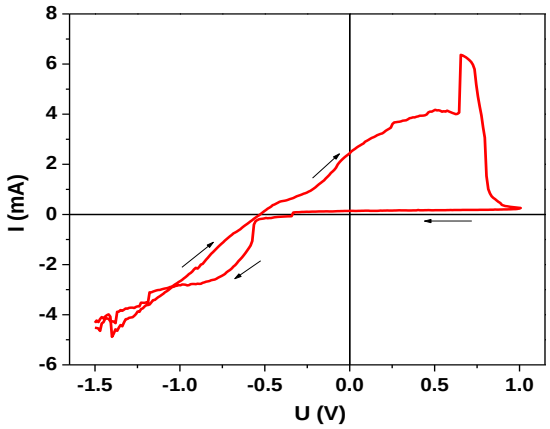

Fig. 3. CV characteristic curve of electrolytic solution containing Co-Ni-P.

The reduction hypophosphite ion can be described by:

$$H_2PO_2^- + 2H^+ + e \rightarrow P + 2H_2O \quad (E_0 = -0.25\ V) \qquad (1)$$

The sample was fabricated and separated from the polycarbonate membrane by dissolving the template in dichloromethane. The morphology of CoNiP/Au multisegment nanowires was observed by SEM micrographs. SEM images of the nanowires are shows in figure 4.

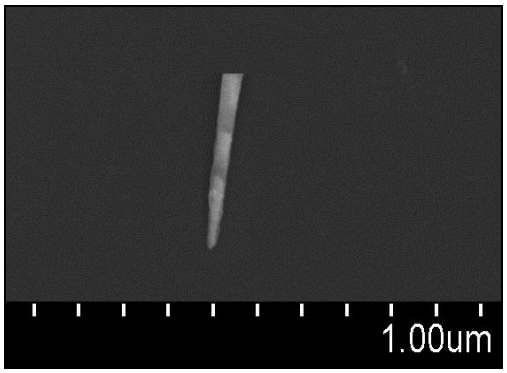

Fig. 4. Dispersed CoNiP/Au nanowire after the removal of the membrane.

Figure 4 shows SEM images of multisegment nanowires composed of alternative segment of CoNiP/Au. CoNiP segments are alternate Au segments. The electron contrast in back scattered SEM images is the difference in atomic weights. The black and white contrast represents the CoNiP (darker) and Au (lighter) segment.

CoNiP/Au multisegment nanowires have very uniform length 350 nm. The average diameter of CoNiP/Au multisegment nanowires is almost equivalent with the diameter of nanopore in polycarbonate membrane with 50 nm. The deposition rate of Au and CoNiP are 1.3 Å/s and 2.9 nm/s, respectively.

Figure 5 shows HRTEM, micrograph that gave more detail about these nanowires to measure lattice space of CoNiP segment nanowire. The lattice space was determined to be about 0.205 nm as shows in figure 5.

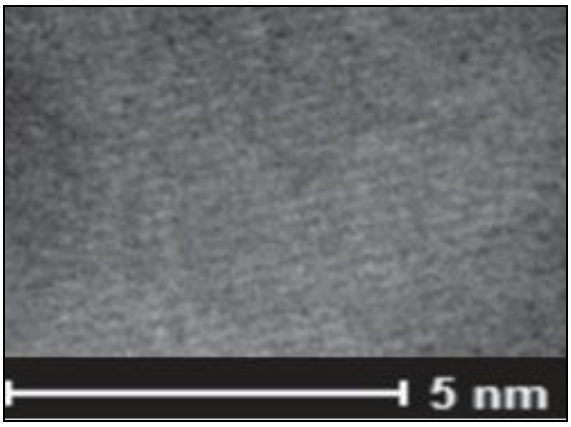

Fig. 5. HRTEM micrograph of a CoNiP segment nanowire.

Figure 6 shows the EDS spectrum analysis. The EDS results showed that atom composition of CoNiP nanowires including Co, Ni, P with ratio 73.12: 20.34:6.54. For CoNiP/Au multisegment nanowires, it indicates the presence of cobalt (Co), nickel (Ni), phosphorus (P) and gold (Au) elements. There are no other impurity elements present in the nanowires composition, where the physical or chemical properties shows by the nanowires are completely an outcome from Co, Ni, P and Au elements. The individual CoNiP and Au segments was also measured by EDS for the confirmation of purity of Au and CoNiP elements (data not show here).

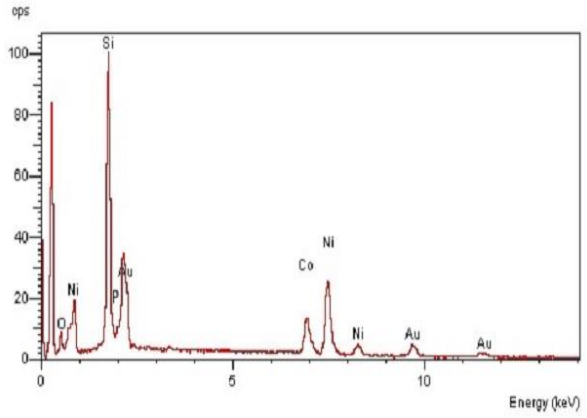

Fig. 6. EDS spectrum analysis of CoNiP/Au nanowires

Figure 7 shows hysteresis loops for CoNiP/Au multisegment nanowires embedded in polycarbonate membrane at room temperature when the magnetic field was applied parallel the axis of the wires.

To specify, the value of coercivity H_c was 1006 Oe for CoNiP/Au with the magnetic field was applied along the wire axis [15].

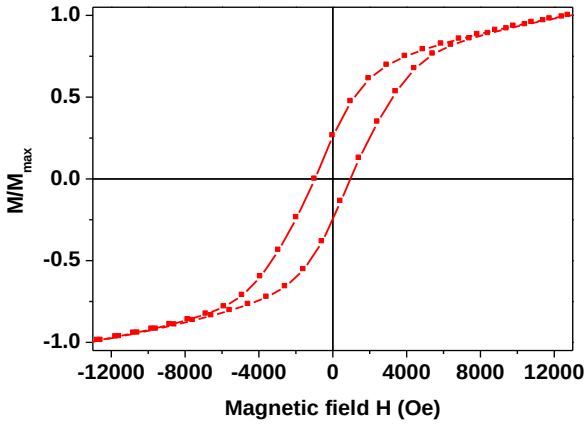

Fig. 7. Hysteresis curve of array of CoNiP/Au nanowire.

Figure 8 presents absorption spectra of CoNiP/Au nanowire and CoNiP/Au attached 4-ATP. Figure 8 shows that analytical results UV-Vis of CoNiP/Au multisegments magnetic nanowire materials in Chloroform solution has appeared two maximum absorption peak at 236,5 nm and 273,50 nm, respectively. The two maximum absorption peaks may be absorption spectrum peak of CoNiP multisegment magnetic nanowire.

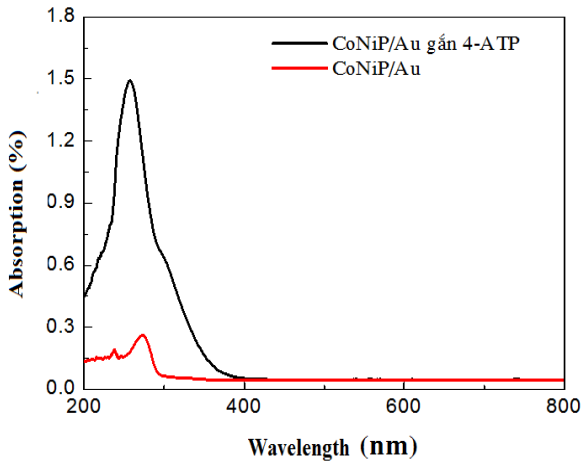

Fig. 8. Absorption spectra of CoNiP/Au nanowire and CoNiP/Au attached 4-ATP.

Figure 9 is results of Raman spectroscopic measurement of CoNiP/Au and CoNiP/Au attached 4-ATP. Figure 7 shows that the characteristic spectral peak of CoNiP multi-segments magnetic nanowire material is located at 462, 83; 554,87 and 667,25 cm^{-1} respectively. However, 4-ATP functionalied on the surface CoNiP/Au multisegments magnetic nanowire material, it shows that one peak is located at 743 cm^{-1}. This spectral peak is very large and covers on the peaks of CoNiP/Au sample. Therefore, the absorption spectrum peak at 743 cm^{-1} can exit of benzene ring with amino group (-NH_2). It shows that we have been functionalized successfully CoNiP/Au magnetic nanowire materials with 4-ATP attached on the nanowire surface.

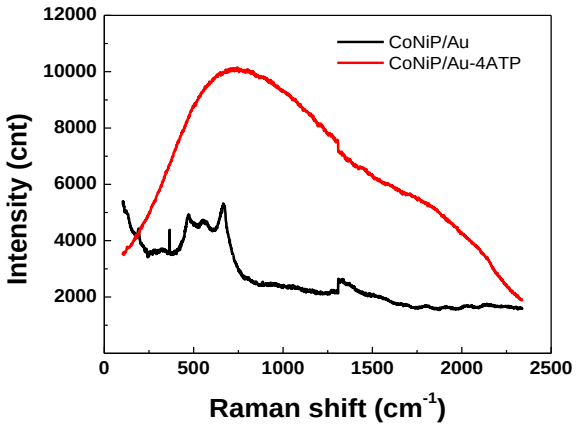

Fig. 9. Raman spectroscopic of CoNiP/Au nanowire and CoNiP/Au attached 4-ATP

4. Conclusions

In summary, we have prepared CoNiP thin films by the electrodition method. By CV characteristic curve analysis method of CoNiP, we found reduction potential range to put deposition potential. CoNiP/Au multi-segment nanowires were fabricated to have diameter of 50 nm and length of 350 nm. Morphological structure and hysteresis loop of the sample were defined with the lattice space is determined about 0,205 nm. The maximum coercivity value is 1006 Oe. CoNiP/Au magnetic nanowire materials were functionalized successfully with 4-ATP attached on the nanowire surface.

Acknowledgements

The current work was financially supported by project VNU QG.14.14.

References

[1] T. S. Ramulu, R. Venu, B. Sinha, S. S.Yoon and C. G. Kim, Electrodeposition of CoPtP/Au Multisegment Nanowires: Synthesis and DNA Functionalization, Int. J. Electrochem. Sci, 7 (2012), 7762 – 7769.

[2] T.Tahmasebi, S.N.Pira'manayagam, Nanoscience and nanotechnology for memory and data storage, Cosmos, 7 (2011), 25- 30.

[3] William D. Callister, Materials Science and Engineering, An Introduction Edition, 7 (2007), 66- 70.

[4] Yong Peng, Tony Cullis, and Beverley Inkson, Applied Physics letters, 9(3) (2008), 183-200.

[5] Cristian Zet, Cristian Fosalau, Magnetic nanowire based sensors, Digest Journal of Nanomaterials and Biostructures; 7(1), (2012) 299 – 306.

[6] Chiung-Wen Kuo, Peilin Chen, The Applications of Metallic Nanowires for Live Cell Studies, Electrodeposited Nanowires and their Applications, Nicoleta Lupu (Ed.), 9, (2010) 953-978.

[7] K.B.Lee, Park, S., Markin and C.A, Multicomponet magnetic nanorods for biomolecular separation, Angew. Chem. Int. Ed, 43 (2004) 3038.

[8] K.B.Lee, Park, S., Markin and C.A, Multicomponet magnetic nanorods for biomolecular separation, Angew. Chem. Int. Ed, 43 (2004) pp.3038.

[9] V. Varadan, L.F. Chen and J. Xie, Nanomedicine: Design and Applications of Magnetic Nanomaterials, Nanosensors and Nanosystems, Wiley (2008) 240-250.

[10] Luu Van Thiem, Le Tuan Tu, Dependence of magnetic properties on diameter of CoNiP nanowires", Proceedings of the International Conference on Advanced Materials and Nanotechnology, (2014) 289-293.

[11] H.J.Yang, F.W.Yuan and H.Y.Tuan, Vapor-Liquid-Solid growth of silicon nanowires using organosilane as precursor, Chem. Commum, 4(6) (2010) 6105.

[12] Jaya Sarkar, Gobinda Gopal Khan and A Basumallick, Nanowires: properties, application and synthesis via porous anodic aluminium oxide template, Bull. Mater. Sci, 30(3) (2007) 271-290.

[13] Y.Ye, L.Dai, T.Sun, L.P.You, R.Zhu, J.Y.Gao, R.M.Peng,D.P.Yu, and G.G.Qin, High-quality CdTe nanowires Syntheis, characterization, and application in photorespones devices, J.Appl. (2010) Phy 108.

[14] Luu Manh Quynh, Nguyen Hoang Nam, K.Kong, Nguyen Thi Nhung, I.Notingher, M.Henini and Nguyen Hoang Luong, Surface-Enhanced Raman spectroscopic study of 4-ATP on gold Nanoparticles for Basal Cell carinomal Fingerprint Detection, Joural of Electronic Materials, 45(4) (2015), 2563-2568.

[15] Luu Van Thiem, Pham Duc Thang, Dang Duc Dung, Le Tuan Tu and CheolGi Kim, Magnetic behaviors of arrays of Co-Ni-P nanorod: Effects of applied magnetic field", Materials Transactions, 56 (9) (2015) 1327-1330.