



## Surface Atoms Analysis of Silver Nanostructures by X-Ray Photoelectron Spectroscopy

A. ZAHOOR<sup>1,2,\*</sup>, T. QIU<sup>1</sup>, M.A. CHOUDHARY<sup>2,\*</sup> and X. LI<sup>1</sup>

<sup>1</sup>Key Laboratory of Carbon Fiber and Functional Polymer, Ministry of Education, Beijing University of Chemical Technology, Beijing, P.R. China

<sup>2</sup>Department of Chemistry, Mirpur University of Science & Technology, Mirpur, Pakistan

\*Corresponding authors: Tel: +92 5827961100; E-mail: zahoorbuct@hotmail.com

Received: 17 May 2014;

Accepted: 8 July 2014;

Published online: 10 January 2015;

AJC-16657

The binding energy of silver 1D and 3D nanostructures, limited to the surface atoms within the range of 2 nm was analyzed by X-ray photoelectron spectroscopy (XPS). The surface scanning by XPS of silver nanostructures was made possible by polymer encapsulation. The synthesis of nanostructures and their surface encapsulation was obtained in non-aqueous medium under inert and dark environment to avoid the surface oxidation. Experimental data was comparatively analyzed which revealed that binding energy of surface atoms of silver nanoparticles and silver nanowires are comparable, with only intensity difference. The intensity of silver nanoparticles was found much higher as compared to silver nanowires due to their more surface exposition. Moreover, the IR data revealed that bending mode of vibrations are suppressed when polymer layer is thin and appeared well morphed when layer thickness was increased. The morphology of product was confirmed by transmission electron microscope.

**Keywords:** Silver nanostructures, Polymer coating, X-ray photoelectron spectroscopy, Binding energy.

### INTRODUCTION

The research in nano domain is growing exceptionally fast due to the unique and desirable applications of nanomaterials in different fields like bio-detection, electrical sensing, transistor building and wide photon electron interaction<sup>1</sup>. The distinctiveness of nanomaterial is attributed to the quantum confinement of electron, charge tunneling effect and enlarged surface area<sup>2,3</sup>. Moreover, the quantum mechanical approach states that distribution of electron and energy level deep within the bulk crystal differ from their surface. The surface atoms and interior atoms of the bulk crystals always develop some junction and these are also different with reference to their properties<sup>4</sup>. The generation of nanomaterials is thus a strategy to convert bulk materials as a whole into its surface, where there is no E-V junction and study the nature of the surface atoms. The exposition of surface is significant for their catalytic activities in heterogeneous reactions, as for catalysis just the surface atoms of any solid material are required. Thus nanomaterials are good candidate as they provide more surfaces for catalysis and other heterogeneous reactions<sup>5</sup>. Moreover, these are also more appropriate materials to study the nature of surface atoms of any bulk materials.

The XPS is proved to be a suitable technique that can determine the nature of surface atoms of any material except H in solid state. X-ray photoelectron spectroscopy uses X-rays

radiations that can penetrate from 1 to 10 nm deep inside the sample and can eject the core electrons. Thus, these rays are helpful to measure the average characteristic binding energy of surface atoms of any element within the range of 10 nm and their nature<sup>6,7</sup>. However, the binding energy of any metal material is shifted toward higher energy state when it is converted into nano dimension<sup>8,9</sup>. This phenomenon correlates with the loose packing, more charge, reduced size and also with the existence of plasma over the surface of nanostructures.

Herein, the Ag 1D (nanowires) and 3D (nanoparticles) nanostructures have been fabricated using polyol reduction method, using PVP as capping agent<sup>10,11</sup>. The product was sonicated and washed using organic solvents like acetone, ethanol and acetonitrile. The binding energy of as such prepared nanostructures was measured by XPS, which scanned the data upto 10 nm interior of the sample. To obtain the binding energy, limited to the surface atoms of different Ag nanostructures, these were gradually coated by polycarbazole from thickness of 5 to 8 nm, so that the XPS can only be made to probe the binding energy of just surface atoms within the range of 2 nm. The polymer encapsulation was obtained under inert conditions. This strategy was designed for the first time to study the nature of Ag surface atoms from 10-2 nm deep inside of its nanostructures.

Thus the obtained data gave the binding energy of pure Ag nanowires and nanoparticles and also binding energy of

their gradual encapsulated forms. In this way, it enabled us to correlate the binding energy of Ag nanowires and nanoparticles and also their interior and superior atoms. The experimental data revealed that binding energy of Ag nanowires and Ag nanoparticles are comparable. However, the binding energy of nanoparticles is more intense due to more exposure of its surface as compared to nanowires. This study helped to realize that the polymerization under inert environment prevented the surface oxidation, which is major cause of peaks shift in our previous work<sup>10</sup>. This study also proved that metal nanostructures can suppress the bending vibrations of organic polymer due to its own transmission and evolve these bending vibrations, when polymer thickness is increased. Moreover, the experiment is significant to develop a strategy to protect the nano metal's materials against surface oxidation by encapsulating with polymer and increasing its thickness.

### EXPERIMENTAL

Silver nitrate (99.8 %), ethanol (99.8 %), ethylene glycol (96 %), acetonitrile (95 %) and acetone (99.5 %), were purchased from Beijing Shiji. PVP (K30) was bought from Fuchen Chemical Reagent Company, Tianjin. Carbazole monomer (95 %) was bought from Shanghai Zhixin Chemical Industry Co. Ltd., and was recrystallized in 1:1 of *n*-hexane/isopropanol before use. Cupric acetate (98 %) was bought from Beijing Yili Chemical Reagent Company.

The silver nanostructures were prepared by our own designed method<sup>12</sup>, where 10 mL, 0.1M AgNO<sub>3</sub> and PVP solutions were prepared in ethylene glycol and added dropwise into a pre-heated 10 mL ethylene glycol at 160 and 120 °C. The reacting mixture was stirred for 1 h and stopped when grey color of product persisted. The 160 °C temperature was found suitable for synthesis of uniform Ag nanowires and 120 °C temperature was found suitable for synthesis of spherical Ag nanoparticles. The as prepared material was washed using acetone, ethanol and acetonitrile to remove complete PVP and ethylene glycol and observed under electron microscope and recorded their binding energy using XPS.

The as prepared nanostructures were then coated by polycarbazole using surface polymerization of carbazole monomer in dark box and under N<sub>2</sub> environment. In this process, first the Cu<sup>2+</sup> ions were adsorbed onto the nanostructures and then mixed them into 10 mL, 0.1 M of carbazole monomer in acetonitrile. The mixture was stirred from 60-72 h to obtain different thickness of polymer around nanostructures. The product was again washed with ethanol and observed by TEM and HR-TEM to measure the polymer thickness. Moreover, the binding energy of pure Ag nanostructures and their encapsulated forms with polymer of different thickness was determined by XPS.

### RESULTS AND DISCUSSION

The morphology of the silver nanomaterials and its polymer encapsulation was observed by TEM (HI-TACHI-800 operated at 200 kV) and HR-TEM (FEI TECNAI F20). The polymer was characterized by FT-IR (Bruker Tensor37) and Raman (Renishaw plc, UK equipped with a 25 mW (632.8 nm) He-Ne laser). The binding energy of Ag nanostructures from

interior to surface is determined by XPS (Thermo VG Escalab 250).

The morphology of as synthesized material was observed under TEM. The material, which was synthesized at 160 °C, exhibited its morphology as nanowires. According to the Fig. 1a, the nanowires were appeared to be exclusive and uniform product. Their diameter is within the range of 60-80 nm and length is few microns. Similarly the product, which was synthesized at 120 °C is shown as spherical nanoparticles. Fig. 1b displayed the diameter of these nanoparticles within the range of 45-60 nm in diameter. The TEM pictures, displayed in Fig. 1a,b reflected the smooth surface of both nanostructures, which are in form of nanowires and nanoparticles.

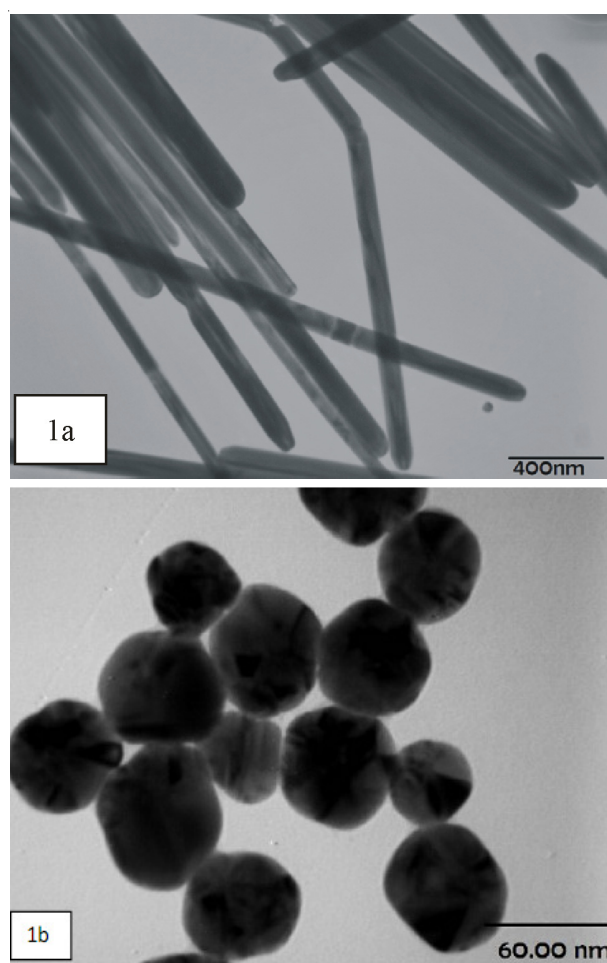


Fig. 1. TEM photograph of (a) Ag nanowires and (b) Ag nanoparticles

Both types of the nanostructures, after 60 h of reactions, were again observed under TEM and HR-TEM and enclosing polymer was displayed in Fig. 2a-c, respectively. The HR-TEM further clearly differentiated the polymer and metal phase and polymer thickness was measured as  $5 \pm 1$  nm. Transmission electron microscope and HR-TEM also revealed almost even growth of polymer which consolidated that surface growth polymerization is good technique for uniform coating. During the growing process polymer also proved helpful to inter connect the nanoparticles, while avoiding their direct contact.

Furthermore, the TEM and HR-TEM data of polymer coating after 72 h of reaction was obtained, which is shown in

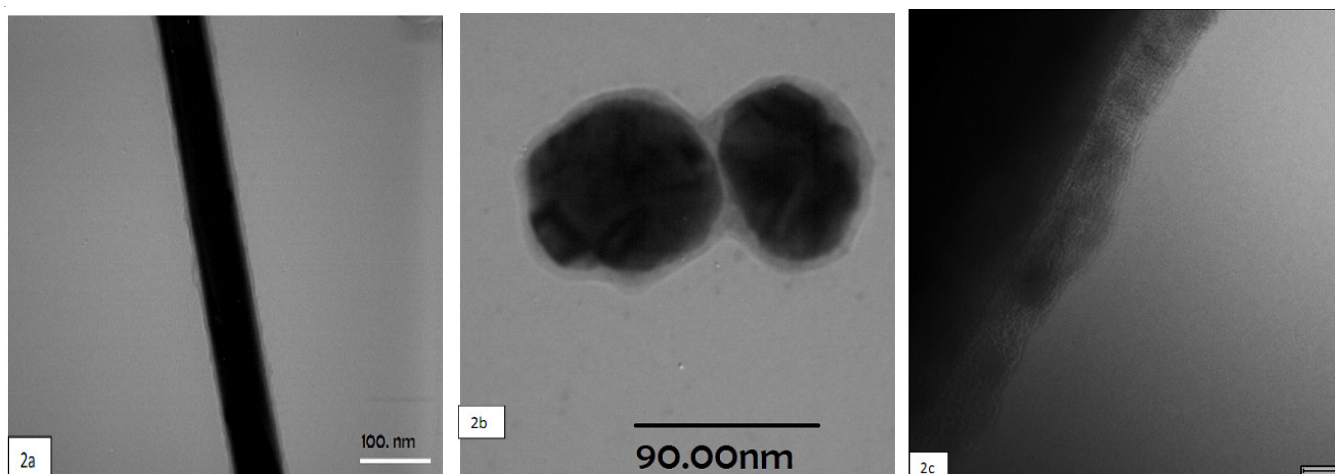


Fig. 2. TEM photograph of showing thin polymer coating over (a) Ag nanowire, (b) Ag nanoparticles and (c) HR-TEM showing polymer thickness over Ag nanostructure

Fig. 3a-c, respectively. Due to the prolongation of time the thickness of polymer coating increased from  $5 \pm 1$  to  $8 \pm 1$  nm as displayed by TEM and measured by HR-TEM. The increased thickness allowed the XPS to scan Ag nanostructure limited about 2 nm. Thus the gradual increase of polymer thickness under inert conditions enabled us to collect and compare the data of binding energy by XPS from 10 to  $\approx 5$  to  $\approx 2$  nm. The polymer thickness of particles as well as wires was comparable, so the HR-TEM pictures of nanowires was shown in Figs. 2c and 3c, which made easy to visualize the polymer thickness.

The coated material was characterized as polycarbazole by FT-IR and Raman spectroscopy and their spectrum is shown Fig. 4a,b, respectively. The FT-IR of composites of nanowires and particles was comparable. The band at  $3427 \text{ cm}^{-1}$  explains N-H stretching vibrations, 13 the band at  $1627$  and  $1406 \text{ cm}^{-1}$  are due to the ring stretching vibrations<sup>14,15</sup>. The band at  $577 \text{ cm}^{-1}$  is due to N-H out of plane bending<sup>16</sup>. The bending vibration is suppressed due to the transmission of core metal therefore, it is nominal when the polymer coating is thin, but became prominent and well morph in thick coating. The behavior of this and other bending vibrations elucidated that increasing polymer thickness are helpful to reduce the metal transmission<sup>12,16</sup>. It also supported the level of polymer thickness which can minimize the metallic interference.

The Raman spectroscopy is very helpful to characterize polymer over its surface due SERS (surface enhanced Raman

spectroscopy) character of nanomaterials<sup>17</sup>. It can magnify and deconvolute the missing and merged bands appeared in FT-IR spectroscopy. The C-C stretching vibration appeared at  $1360 \text{ cm}^{-1}$ , 18 C=C and backbone stretching appeared in the region<sup>19,20</sup> of  $1596$ - $1544 \text{ cm}^{-1}$  and C-N stretching vibration appeared in region<sup>21</sup> of  $1465$ - $1412 \text{ cm}^{-1}$ . The splitting of peak is due to reduced and oxidized form of polymer around silver. The region from  $1285$ - $1149 \text{ cm}^{-1}$  is related to C-N stretching alongwith C-H bending mode 22 and the peak at  $1074 \text{ cm}^{-1}$  gives the information about C-H in plane deformation<sup>19</sup>. The splitting of peaks is due to the oxidized and reduced state of polymer.

The surface atoms of the bulk metal materials are different from their respective interior atoms<sup>11</sup>. The surface atoms are at higher energy state as compared to their interior counterpart. However, materials in nano range usually represent the surface atoms of any bulk metal material that express their catalytic, luminescence and some time memory based properties<sup>18</sup>. Therefore, understanding the nanomaterials can be a way to understand the surface atoms of that material. X-ray photoelectron spectroscopy is the best technique that is helpful to study the range of uniform atoms *i.e.*, atoms having same energy level by measuring their binding energy<sup>6,7</sup>. In this experiment, the binding energy of silver nanowires, nanoparticles and their composite was measured and displayed in Fig. 5a,b, respectively. The as obtained data consolidated that

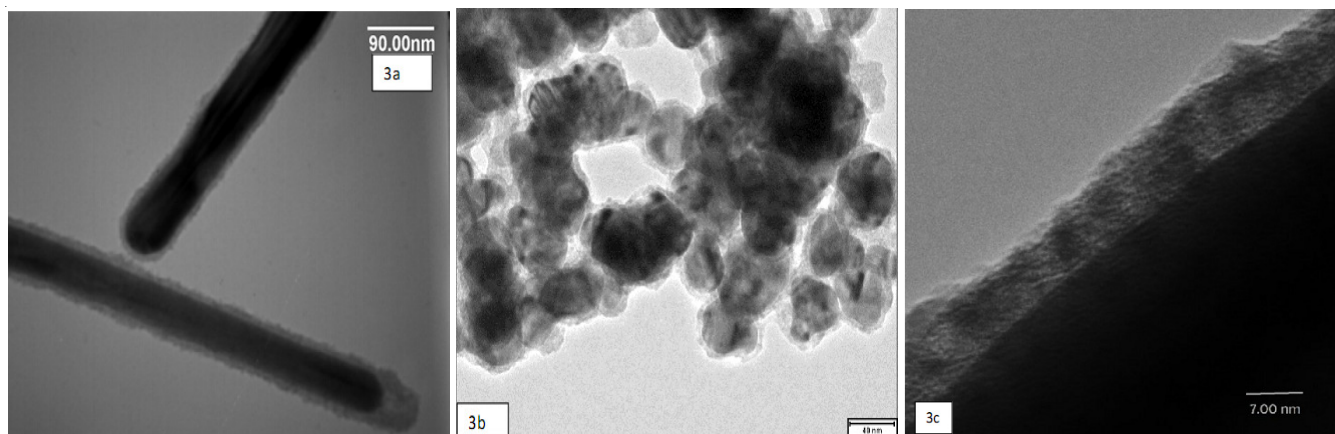


Fig. 3. TEM photograph showing increase in polymer thickness (a) Ag nanowires, (b) Ag nanoparticles and (c) HR-TEM photograph showing the thickness



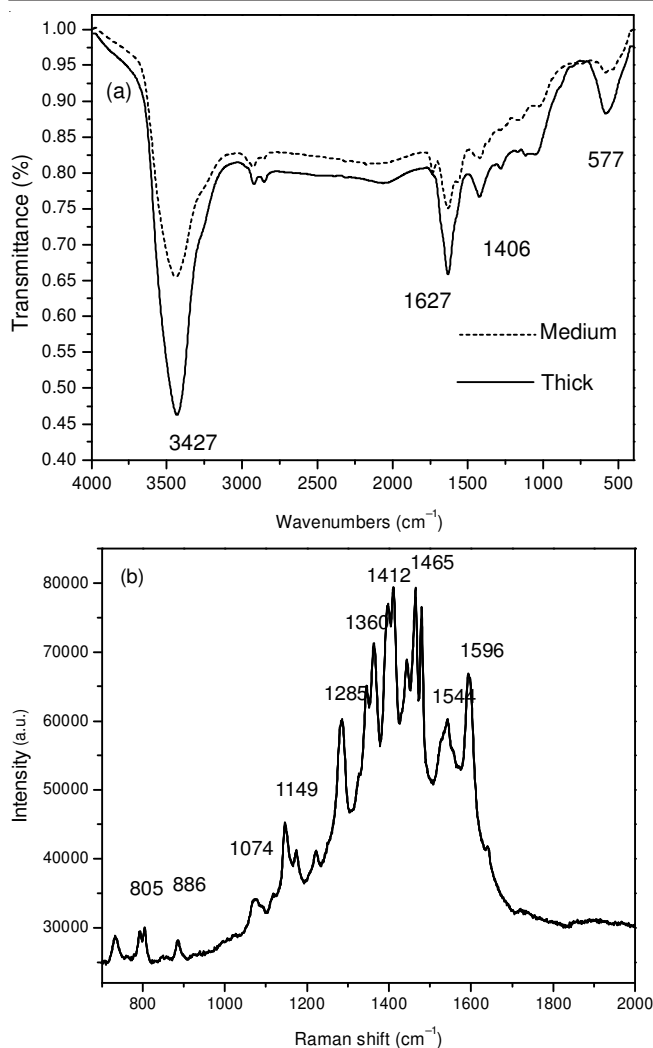


Fig. 4. (a) FT-IR graph of thin and thick PCz coating and (b) Raman graph of PCz over Ag nanostructures

polymer coating is useful to protect Ag nanostructures from oxidation. It also proved helpful to show that atoms of Ag nanostructures have same binding energy from 2-10 nm in range. Moreover, the data displayed that intensity of Ag nanoparticles is more as compared to nanowires, which further supported the idea that smaller the nanostructure have greater the surface area. As the polymer coating is increased over respective nanostructure, the intensity of binding energy decreased accordingly. The 3d doublet at 367.9 and 373.9 eV is due to 3d<sub>5/2</sub> and 3d<sub>3/2</sub>, respectively<sup>23</sup>. Moreover, polymer coating under inert environment just developed the thickness, but not any electronic interaction, thus no shift in binding energy is observed as polymer thickness is increased<sup>24</sup>. From this experiment, it is also seen that intensity of Ag nanoparticle is more as compared to Ag nanowires due to their more surface area. Furthermore, experiment elucidated that polymer coating under inert condition is helpful to protect surface atoms from oxidation even within the range of 2 nm.

### Conclusion

The silver nanowires and nanoparticles were synthesized using polyol reduction method at 160 and 120 °C, respectively. These nanostructures have been coated by polycarbazole for approximate thickness of  $5 \pm 1$  and  $8 \pm 1$  nm under inert

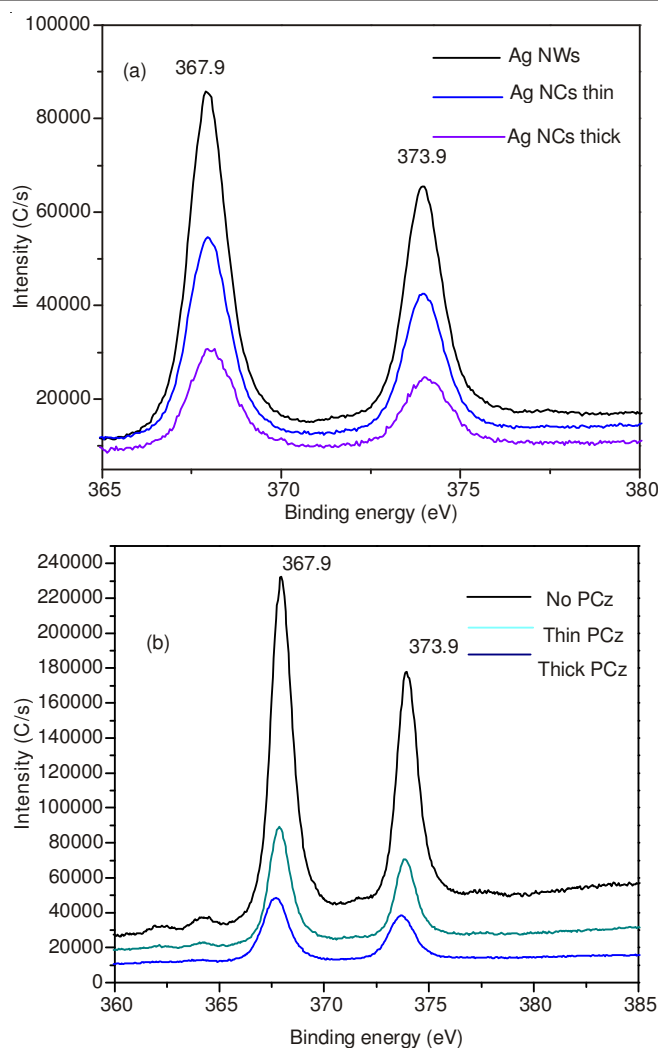


Fig. 5. XPS graph showing binding energy of (a) Ag nanowires and (b) Ag nanoparticles in pure form and, thin and thick polymer coating form

conditions. The material was observed by TEM and polymer thickness was measured by HR-TEM. Polymer coating was confirmed by FT-IR and Raman spectroscopy. The binding energy of pure Ag nanostructures and gradually coated nanostructures was measured by XPS. X-ray photoelectron spectroscopy data was collected from 10 to 2 nm for both nanostructures, which displayed the binding energy of both structures at 367.9 and 373.9 eV for electron of 3d orbital. The XPS data of both nanostructures was comparable and intensity of Ag nanoparticles is more as compared to nanowires. This study proved helpful to elucidate that polyol reduction method is reliable to obtain complete reduced form of Ag nanostructures and almost whole nanostructures have uniform nature of its atoms and there is no heterojunction that develop the potential difference within these nanostructures. Moreover, PCz was proved to be suitable polymer that can develop surface encapsulation without any chemical interaction.

### ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support from NSFC (No. 50673008), Young Teacher Scientific Research Foundation of BUCT (No. QN0611) and HEC, Pakistan.

## REFERENCES

1. L. Gou, M. Chipara and J.M. Zaleski, *Chem. Mater.*, **19**, 1755 (2007).
2. S. Junming, M. Ding, Z. He, L. Xiumei, H. Xiuwen, B. Xinhe, W. Gisela, P. Norbert and S. Dangsheng, *J. Am. Chem. Soc.*, **128**, 15756 (2006).
3. X.C. Song, Y. Zhao, Y.F. Zheng, E. Yang, J. Fu and Y. He, *Cryst. Growth Des.*, **8**, 1823 (2008).
4. A.A. Ryskulov, V.A. Liopo, E.V. Ovchinnikov and E.I. Eismont, *J. Frict. Wear*, **32**, 30 (2011).
5. M. Mihaylov, T. Tsoncheva and K. Hadjiivanov, *J. Mater. Sci.*, **46**, 7144 (2011).
6. J. Yang, A.G. Baker, H. Liu, W.N. Martens and R.L. Frost, *J. Mater. Sci.*, **45**, 6574 (2010).
7. M. Raileanu, M. Crisan, N. Dragan, D. Crisan, A. Galtayries, A. Braileanu, A. Ianculescu, V.S. Teodorescu, I. Nitoi and M. Anastasescu, *J. Sol-Gel Sci. Technol.*, **51**, 315 (2009).
8. M.-C. Bourg, A. Badia and R.B. Lennox, *J. Phys. Chem. B*, **104**, 6562 (2000).
9. J. Zhang, Z. Liu, B. Han, D. Liu, J. Chen, J. He and T. Jiang, *Chem. Eur. J.*, **10**, 3531 (2004).
10. A. Zahoor, T. Qiu, J. Zhang and X. Li, *J. Mater. Sci.*, **44**, 6054 (2009).
11. A. Zahoor, Q. Teng, H. Wang, M.A. Choudhry and X. Li, *Metals Mater. Int.*, **17**, 417 (2011).
12. A. Chen, H. Xie, H. Wang, H. Li and X. Li, *Synth. Met.*, **156**, 346 (2006).
13. H. Taoudi, J.C. Bernede, A. Bonnet, M. Morsli and A. Godoy, *Thin Solid Films*, **304**, 48 (1997).
14. C.-S. Chao, W.-T. Whang and C.-H. Hung, *Macromol. Chem. Phys.*, **202**, 2864 (2001).
15. Z. Wei, J. Xu, G. Nie, Y. Du and S. Pu, *J. Electroanal. Chem.*, **589**, 112 (2006).
16. M. Grigoras and N.-C. Antonoaia, *Eur. Polym. J.*, **41**, 1079 (2005).
17. Z. Deng, M. Chen and L. Wu, *J. Phys. Chem. C*, **111**, 11692 (2007).
18. X.-L. Tang, P. Jiang, G.-L. Ge, M. Tsuji, S.-S. Xie and Y.-J. Guo, *Langmuir*, **24**, 1763 (2008).
19. Y.-C. Liu, *Langmuir*, **18**, 174 (2002).
20. R. Hiyoshi, H. Hiura, Y. Sakamoto, M. Mizuno, M. Sakai and H. Takahashi, *J. Mol. Struct.*, **661-662**, 481 (2003).
21. G.H. Jeong, Y.W. Lee, M. Kim and S.W. Han, *J. Colloid Interf. Sci.*, **329**, 97 (2009).
22. N.R. De Tacconi, Y. Son and K. Rajeshwar, *J. Phys. Chem.*, **97**, 1042 (1993).
23. R. Patakfalvi, A. Oszkó and I. Dékány, *Colloids Surf. A*, **220**, 45 (2003).
24. Y. Zheng, C. Chen, Y. Zhan, X. Lin, Q. Zheng, K. Wei and J. Zhu, *J. Phys. Chem. C*, **112**, 10773 (2008).