

Contents lists available at ScienceDirect

Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jallcom

Nanoscale synthesis and optical features of metallic nickel nanoparticles by wet chemical approaches

Khalid Nouneh^{a,*}, Munetaka Oyama^b, Raquel Diaz^c, Mohammed Abd-Lefdil^d, I.V. Kityk^e, Mosto Bousmina^{a,f}

^a INANOTECH, Institute of Nanomaterials and Nanotechnology, MAScIR Moroccan Advanced Science, Innovation and Research Foundation, ENSET, Av. Armée Royale, Rabat, Morocco

^b Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8520, Japan

^c Department of Física Aplicada C-XII, Universidad Autónoma de Madrid, Madrid, Spain

 $^{\rm d}$ Laboratory of Materials Physics, University Mohammed V, Rabat, Morocco

^e Electrical Engineering Department, Czestochowa University of Technology, Armii Krajowej 17, Czestochowa, Poland

f Hassan II Academy of Science and Technology, Rabat, Morocco

ARTICLE INFO

Article history: Received 11 January 2011 Received in revised form 24 February 2011 Accepted 25 February 2011 Available online 5 March 2011

Keywords: Nickel nanoparticles Wet chemical Surface modification Nanostructured material SPR Indium tin oxide

1. Introduction

ABSTRACT

Nickel nanoparticles (Ni-NPs) were successfully synthesized and attached on indium tin oxide (ITO) substrate by two different methods: from solution reduction process by using sodium borohydride (NaBH₄) as reducing agent in the presence of poly(*N*-vinilpyrrolidone) (PVP) as protective and stabilizing agents and by polyol process under ethylene glycol EG as a solvent. The results indicated that the samples prepared in aqueous solution show the occurrence of face-centered cubic metallic nickel nanoparticles with a medium diameter of ~31 nm and good size dispersion compared to the preparation in EG that revealed large size ~150 nm. The dynamics of the nanoparticle's growth in the solvents and comparison with optical absorption is presented.

© 2011 Elsevier B.V. All rights reserved.

Various techniques have been used to fabricate Ni-NP such as modified polyol method [13], sol-gel with additional annealing treatment [14] and laser ablation technique [15].

On the other side, a variety of reports have focused on the production and/or attaching of Ni-NPs on the conductive substrate. Wu et al. [9] reported fabrication of Ni-NPs by hydrazine reduction in ethylene glycol at 60°C without soluble polymer as a protective agent. These results show that the addition of trace of sodium hydroxide (NaOH) is necessary to produce pure Ni-NP in ethylene glycol and an elevated temperature reaction (at 60 °C) was useful in accelerating the reaction rate. Roy et al. [10] synthesized oxide-coated Ni-NPs with tetragonal crystalline structure by using borohydride reduction method. The effect of the annealing in the as-prepared sample was efficient to observe fcc Ni peak and their subsequent ferromagnetic behavior. Wang et al. [11] prepared Ni-NPs with mean size equal to about 31 nm covered by hydroxyethyl carboxymethyl cellulose (HECMC) layer in solution using hydrazine reduction. In the latest report, Ni NO with monodisperse size (~50 nm) via a modified hydrazine reduction route in ethanol without any surfactant introduced well dispersion were synthesized by Bai et al. [12].

In previous works, refined seed mediated growth method was proved to be the effective way to attach densely precious metal

In the past two decades, considerable attention has been devoted to the synthesis of metal nanoparticles (NP) because their physical and chemical properties differ from those of the bulk phases and are very promising for optoelectronic, biocatalytic activity, different kind of sensing etc. [1,2]. The synthesis of metallic NP with homogenous sizes indicates that control of their size is necessary to evaluate their properties and potential applications in several areas such as microelectronics, optoelectronics, cataly-sis, photocatalysis, magnetic materials, information storage, among others [3–8]. Ni-NPs have also attracted much attention because of their applications as catalysts, conducting and magnetic materials [9–12]. The synthesis of Ni-NP in pure aqueous solutions is attractive due to absence of organic pollution and existence of promising physical and chemical properties.

^{*} Corresponding author at: Institute of Nanomaterials and nanotechnology (INANOTECH), MAScIR, Rabat, Morocco. Tel.: +212 5 37 57 61 80; fax: +212 5 37 57 08 80.

E-mail addresses: k.nouneh@inanotech.mascir.com (K. Nouneh), iwank74@gmail.com (I.V. Kityk).

^{0925-8388/\$ –} see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.jallcom.2011.02.164

on indium tin oxide (ITO) substrate [16–19]. That is, Au, Ag and Pt NP with moderate distribution which can grow on the ITO surface by the method without using any special binder molecular agent.

In the present study, we have found a reproducible synthesis method based on one-step in situ chemical reduction of Ni(OH)^{2–} by using sodium borohydride (NaBH₄) in the presence of trisodium citrate as stabilization. The influence of the parameters on the size of Ni nanoparticles was studied. Such produced samples on ITO are compared with those obtained by using ethylene glycol (EG) as both solvent and reducing agent in presence of NaBH₄. We describe these two methods and we compare the morphology (size, shape and dispersion) and the physical properties of the as-prepared samples.

2. Experimental

The following chemical products were used for synthesis: the nickel nitrate hexahydrate, Ni(NO₃)₂, obtained from Aldrich Co., Ltd. while EG, trisodium citrate, NaBH₄ and NaOH, were obtained from Wako Pure Chemicals, Ltd.

ITO thin conducting film deposited on glass has been used as substrate and it was obtained from Asahi Beer Optical, Ltd. Its sheet resistivity was $150 \Omega/sq$ and their surface sizes are equal to about $1 \text{ cm} \times 1 \text{ cm}$. Before the immersion in Ni precursor complex solution, the ITO thin films were first cleaned by sonication in acetone and in ethanol during 15 min each, respectively. After flashing the different ITO plate by pure water, it was then cleaned by sonication in ultra pure water for 15 min. This procedure was repeated two times in order to remove dust. Finally, the ITO piece was dried with a stream of nitrogen gas before use.

2.1. Growth of nickel by NaBH₄ in aqueous solution

A piece of pre-treated ITO was immersed in Ni precursor complex solution composed of 0.5 ml of 0.01 M Ni(NO₃)₂, 0.1 ml of 0.01 M trisodium citrate and 20 ml H₂O. After stabilizing (~15 min), 1 ml of fresh ice-cold 0.1 M NaBH₄ aqueous solution was added into the Ni precursor complex solution while stirring for 30 s and then keep it for 1 h in 28 °C. The substrate was taken out of the Ni precursor complex solution, thoroughly rinsed with distilled water and dried with nitrogen. Three samples (indicated by A, B, and C) have been modified using the repeated seeding cycles (1, 2 and 3 cycles), respectively by using the same process as described above. Two others samples (indicated by D and E) were immersed during 12 and 24 h, respectively without disturbance. During growth process, the temperature was fixed at 28 °C and we have observed that the Ni precursor complex solution color turned from colorless to black upon reduction.

2.2. Growth of nickel nanoparticles by NaBH₄ in EG

In this case, an appropriate amount of nickel nitrate (0.01 M) hexahydrate was dissolved in 20 ml of capped bottle EG with constant magnetic stirring and heating. Then, an appropriate amount of 0.055 g of poly(*N*-vinilpyrrolidone) (PVP) and 1.0 M NaOH solution (100 μ l) were added in sequence. At a temperature of 60 °C, 1 ml of fresh ice-cold 0.1 M NaBH₄ aqueous solution was added into the Ni precursor complex solution and then after 30 s, the heated system turned off. And the solution cooled to room temperature and kept it for 1 h. The ITO substrate was then immersed in this precursor solution for different growth times (1 h, 2 h, 6 h, 12 h and 24 h). In this case we have observed the attachment only after 24 h growth (sample F).

The size and morphology of the Ni-NP grown on ITO surface were monitored with field emission scanning electron microscopy (FE-SEM, JSM-7400F; JEOL). The optical spectrophotometer, U4100 Hitachi Ltd. with spectral resolution about 0.1 nm, was used to observe the absorption spectra of the Ni-NPs/ITO.

The Grazing X-ray diffraction pattern of Ni-NPs attached ITO was analyzed by Rigaku D/max-2400 diffractometer using CuK_{α}-1 radiation λ = 0.15406 nm in Bragg–Brentano geometry. The background was eliminated in the intensity determination. Silicon powder with a purity of 99.9999% was used as an external standard material to calibrate the peak positions and intensities.

So for the first time we realized in situ attaching Ni-NPs on ITO substrate. We reported the results obtained with two different ways, from solution reduction process by using NaBH4 as reducing agent in the presence of PVP as protective and stabilizing agents and by polyol process under ethylene glycol EG as a solvent. This difference may be caused by different polarizabilities of the particle in the solvants.

3. Results and discussion

Fig. 1A–C shows the FE-SEM images of the Ni-NPs grown on the ITO surfaces, which were prepared using the repeated seeding

cycles (1, 2, and 3 cycles of 1 h, respectively) and under 12 h and 24 h seed (Fig. 1D and E, respectively). With one-cycle in situ seed, the Ni-NPs were found to grow on the surface with a quasi-spherical shape whose size was extended within the range 8-17 nm. This result reflects the limited nucleation Ni after 1 h treatment. We also found that even with increasing in situ time, the attached density was not highly improved due to the high oxidation ability of Ni-NP in the seeded solution. To improve the attached density of Ni-NPs on ITO surface, we proceed to repeat the in situ seeded cycle during 1 h at least two or three times (Fig. 1B and C). When the number of in situ seeded cycles was increased, the density and the grown nanostructures of Ni-NPs had significantly changed, and increase in the grown size of Ni-NPs was observed on the ITO surface keeping a moderate dispersion as shown in Fig. 1D. The size of each Ni-NP has varied within the range of 10-30 nm. In contrast, some gathered clusters of Ni-NPs were observed after six-cycles seeding and if we keep the ITO substrate during 12 h growth, we observe that, the surface morphology has been substantially changed to show the connection or networked nanostructures of Ni-NPs (Fig. 1E). Fig. 1F shows the FE-SEM image of Ni-NPs/ITO produced by NaBH₄ in EG for a growth times of 24 h. It was observed that the attached density of Ni-NPs was relatively low exhibiting a sparse distribution of particles on the surface with a large size distribution of about 200 nm.

The grazing X-ray diffraction (XRD) patterns of the Ni-NPs on ITO samples are shown in Fig. 2A. We should notice that the diffraction peaks of ITO are dominant. Peaks at 2θ =41.89°, 58.95° are assigned to hcp Ni (002) and (012) planes (JCPDS data No. 45-1027), respectively. While a peak at 76.31° is attributed to (220) fcc Ni phase (JCPDS data No. 04-0850). This indicates that both hcp and fcc Ni-NPs were simultaneously synthesized by NaBH₄ in aqueous solution case. In addition, we should note a peak at 2θ =37.65° that can be assigned to hexagonal NiO₂ nickel oxide (006) plane (JCPDS data No. 85-1977). In the case of Ni-NPs prepared in EG, the peaks are less pronounced due to the large thickness of organic films deposited on the ITO substrate.

Chemical composition of Ni-NPs/ITO was analyzed using the X-ray energy dispersive spectrometry order to confirm the presence of Ni (Fig. 2B). Peaks of Si and Ca are originated from the glass substrate on which ITO and Ni were successively deposited. While peaks of In and Sn are due to ITO films.

It is known that the wavelength of surface plasmon resonance λ_{SPR} is sensitive to various parameters like particle size and shape, environment and inter-particle interactions nature of substrate, where the resonance band becomes broader as its refractive index increases [20]. The absorbance spectra of Ni-NP grown on ITO $(150 \Omega/sq)$ under various seeding cycles are reported in Fig. 3. All the spectra present an absorption edge within 374-422 nm spectral range, depending on the sample, which corresponds to the surface plasmon resonance (SPR) of Ni. This is in a good agreement with work of Amekura et al. [21], who reported the convening experimental observation and theoretical analysis of SPR in Ni nanoparticles deposited on silica glass. For nickel (1 cycle, curve A), the SPR energy is quite lower on energy than the other samples, but it is quite higher than the results observed by Yeshchenko on Ni/SiO₂ [14]. In Table 1, we report a comparison between our λ_{SPR} values and the literature. We also notice that the absorbance increases with increasing seeding cycle's number, which can be explained by the increase of the density and the size of the attached Ni-NPs on ITO surface. This is caused by inter-particle interactions which determine the effective masses of electrons and corresponding plasmons. The observed broadening of SPR bands is due to the large damping of free electrons motion in nickel compared to electron motion in noble metals.



Fig. 1. (A–E) The FE-SEM images of the Ni-NPs grown on the ITO surfaces in aqueous solution, which were prepared using the repeated growth cycles of 1 h (A), 2×1 h (B) and 3×1 h (C). (D–E) Ni-films on ITO under 12 h and 24 h, respectively. (F) Ni-NPs on ITO under 24 h growths, prepared in ethylene glycol.

To demonstrate the dynamics of the nanoparticle's growth and absorption on the different stages of the nanocrystallite growth the corresponding data are presented in Figs. 4 and 5. Following these data one can clearly see that the increasing time of the sample's treatment leads to the shift of the average size distribution towards the higher values. And the corresponding absorption spectra do not show any evidence of the maxima typical for the Ni-NP deposited on the surfaces (compare Fig. 3). So the intermolecular interactions within the colloids do not give sufficient contribution to the SPR for the Ni-NP samples.

At the same time due to interaction of the SPR excitations with the lattice phonons of the substrate we have some con-

Table 1 λ_{SPR} wavelength values as reported by other authors and in the present study.

Sample	Average Ni-NPs size (nm)	λ_{SPR} (nm)	Reference
Ni/SiO ₂	1.5	376	[21]
Ni/SiO ₂	20	358-382	[14]
Ni EG	8	355	[15]
Ni/ITO	10-40	374-422	This work



Fig. 2. (A) X-ray diffraction spectra of Ni/ITO prepared in aqueous solution (sample C) and in ethylene glycol (sample F). (B) X-ray energy dispersive spectrometry of the sample Ni/ITO (sample C).



Fig. 3. UV-visible of the Ni-NPs grown on the ITO surfaces in aqueous solution, which were prepared using the repeated growth cycles of 1 h (A), 2×1 h (B) and 3×1 h (C). Curves D and E represent the absorbance for a continuous growth time of 12 h and 24 h, respectively. Curve F represents the case of Ni-NPs produced by NaBH₄ in ethylene glycol under 24 h growth.

tribution to the broadening originating from electron-phonon interactions and in particularly of the anharmonic ones [22]. The relatively large sheet resistance of the ITO creates an effective carrier for the carriers forming the SPR excitations. As a consequence the border between the ITO and Ni-NP is partially polarized forming an effective potential which shift the spec-

Fig. 5. UV-visible of the Ni-NPs in aqueous solution, at different growth times 1 h, 2 h, 3 h, 12 h and 24 h.

tral maximum of the SPR in the spectral wavelengths. One can expect that the proposed materials may be very sensitive to the polarization of the environment and after appropriate referencing they may determine the external polarizabilities. The latter may be promising for nonlinear optical and spintronics applications [22,23]. It is also important that additional broadening is the SPR spectra was observed in the Ag NP [2], which confirm the same origin of the broadening and possible attraction to the ITO substrate.

Fig. 4. Nickel nanoparticles size distribution in aqueous solution, at different growth times 1 h, 2 h, 3 h, 12 h and 24 h.

4. Conclusion

Spherical nickel nanoparticles deposited on ITO surface were successfully fabricated using a wet chemical solution method. For the first time we realized in situ attaching Ni-NPs on ITO substrate. We report the results obtained with two different ways, from solution reduction process by using NaBH4 as reducing agent in the presence of poly(*N*-vinilpyrrolidone) as protective and stabilizing agents and by polyol process under ethylene glycol as a solvent. They were synthesized by reduction of the complex of $[Ni(OH)^{2-}]$ in aqueous solution using sodium borohydride. We realized the control of the nanoparticles size through controlling of various parameters like growth time and nickel ions reduction reaction in different phases. The obtained nickel nanoparticle's have been confirmed by structural analysis. UV-visible spectroscopy curves and wavelength of the surface plasmon resonance were observed to be sensitive to the characteristics of the nanoparticle. All the absorption spectra present an absorption edge at 374-422 nm range, depending on the sample, which corresponds to the surface plasmon resonance of Ni.

Following the study performed for the Ni-NP colloids in the solutions we have found that the increasing time of the sample's treatment leads to the shift of the average sizes towards the higher values. And the corresponding absorption spectra do not show any evidence of the maxima typical for the Ni-NP deposited on the surfaces (compare Fig. 3). So the intermolecular interactions within the colloids do not give sufficient contribution to the SPR for the Ni-NP samples.

Acknowledgements

The financial support from Japan Society for the Promotion of Science (JSPS) program is gratefully acknowledged. This work has

been also done in the framework of the Morocco-Hispano University collaboration by the AECI Project No. A/027536/09. The authors thank also the Hassan II Academy of Science and Technology.

References

- [1] L.N. Lewis, Chem. Rev. 93 (1993) 2693-2730.
- [2] K. Nouneh, M. Oyama, R. Diaz, M. Abd-Lefdil, I.V. Kityk, M. Bousmina, J. Alloys Compd. 509 (2011) 2631.
- [3] K.R. Gopidas, J.K. Whitesell, M.A. Fox, Nano Lett. 3 (2003) 1757-1760.
- [4] J. Jortner, C.N.R. Rao, Pure Appl. Chem. 74 (2002) 1491–1506.
- [5] D.J. Maxwell, J.R. Taylor, S. Nie, J. Am. Chem. Soc. 124 (2002) 9606–9612.
- [6] P.V. Kamat, J. Phys. Chem. B 106 (2002) 7729-7744.
- [7] E.C. Walter, K. Ng, M.P. Zach, R.M. Penner, F. Favier, Microelectron. Eng. 61 (2002) 555-561.
- [8] M.M. Oliveira, E.G. Castro, C.D. Canestraro, D. Zanchet, D. Ugarte, L.S. Roman, A.J.G. Zarbin, J. Phys. Chem. B 110 (2006) 17063–17069.
- [9] S.H. Wu, D.H. Chen, J. Colloid Interface Sci. 259 (2003) 282-286.
- [10] A. Roy, V. Srinivas, S. Ram, J.A. De Toro, U. Mizutani, Phys. Rev. B 71 (2005) 184443-184453.
- [11] H. Wang, X. Kou, J. Zhang, J. Li, Bull. Mater. Sci. 31 (2008) 97-100.
- [12] L. Bai, F. Yuan, Q. Tang, Mater Lett. 62 (2008) 2267-2270.
- [13] G.G. Couto, J.J. Klein, W.H. Schreiner, D.H. Mosca, A.J.A. de Oliveira, A.J.G. Zarbin, J. Colloid Interface Sci. 311 (2007) 461–468.
- [14] O.A. Yeshchenko, I.M. Dmitruk, A.A. Alexeenko, A.M. Dmytruk, J. Phys. Chem. Sol. 69 (2008) 1615–1622.
- [15] J. Zhang, C.Q. Lan, Mater Lett. 62 (2008) 1521-1524.
- [16] M. Oyama, A. Orimo, K. Nouneh, Electrochem. Acta 54 (2009) 5042– 5047.
- [17] D. Nkosia, J. Pillaya, K.I. Ozoemena, K. Nouneh, M. Oyama, Phys. Chem. Chem. Phys. 12 (2010) 604–613.
- [18] G. Chang, M. Oyama, K. Hirao, J. Phys. Chem. B 110 (2006) 20362–20368.
- [19] K. Ozga, T. Kawaharamura, A. Umar, M. Oyama, K. Nouneh, A. Slezak, S. Fujita, M. Piasecki, I.V. Kityk, Nanotechnology 19 (2008) 185709–185715.
- [20] G. Xu, M. Tazawa, P. Jin, S. Nakao, Appl. Phys. A 80 (2005) 1535-1540.
- [21] H. Amekura, Y. Takeda, N. Kishimoto, Nuclear Instrum. Meth. Phys. Res. B 222 (2004) 96.
- [22] I.V. Kityk, J. Ebothe, I. Fuks-Janczarek, A.A. Umar, K. Kobayashi, M. Oyama, B. Sahraoui, Nanotechnology 16 (2005) 1687.
- [23] M. Idrish Miah, Phys. Lett. 13 (2010) 4247.