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Synthesis and characterization of gold nanoparticles via submerged arc discharge based on a seed-mediated approach

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Abstract

Gold nanoparticles were prepared via liquid arc discharge technique using a seed-mediated approach in solution and characterized by dynamic light scattering, UV-vis spectroscopy, X-ray diffraction, optical imaging, and atomic force microscopy. A surface plasmon resonance was observed around 520 nm based on optical absorption spectroscopy of as-prepared samples at 15 A arc current in HAuCl_4 solution. It was found that sodium citrate acts as a stabilizer and surface capping agent of the colloidal nanoparticles. It was found that the intensity of the plasmonic peak of as-prepared gold nanoparticles in 1 min arc duration gradually increases due to seed mediation up to 6 h. The formation time of gold nanoparticles in higher seed concentrations is less than the lower seed concentrations.

Keywords: Submerged discharge, Gold nanostructures, Seed mediation, Physiochemical properties

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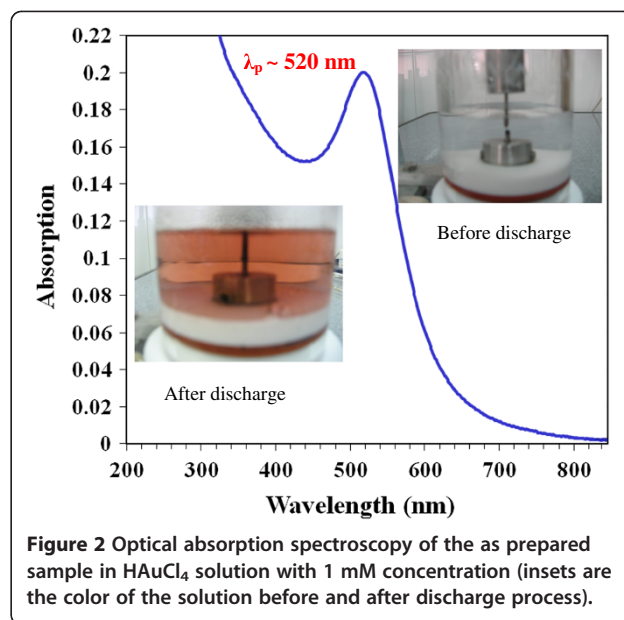
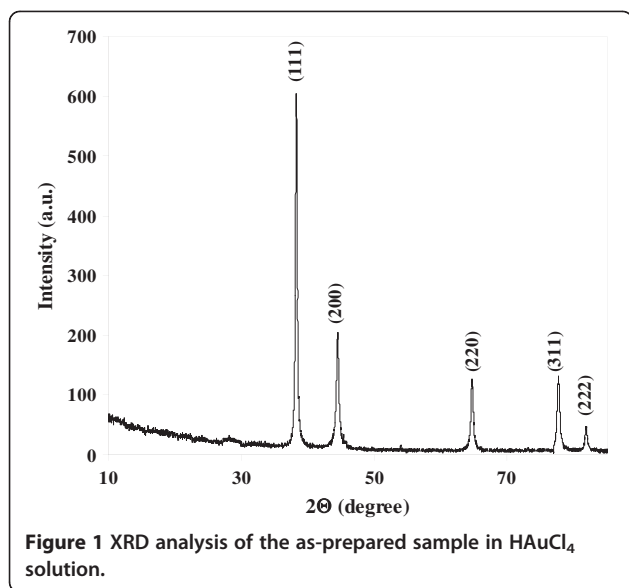
Background

Metal nanoparticles, particularly gold, have attracted much attention because of their potential applications in surface SERS [1-4], biosensors [5,6], biological labeling [7,8], nanoelectronic and optoelectronic [9,10], and photocatalysts materials [11,12]. In this regard there has been large efforts on the synthesis of gold nanoparticles by different methods such as photochemical [13-15], electrochemical [16,17], chemical reduction [18], ion irradiation [19,20], and plasma processing [21]. Most of the mentioned methods are based on chemical and physical reduction using weak and strong reducing agents such as ascorbic acid and sodium borohydride, respectively. Compared with other techniques, the electrical arc discharge in liquid is attractive because the apparatus is simple to build, there is no need for vacuum equipments, and the source materials are cheap. The simplicity of this method also allows scaling up for mass

production as we described in details in our previous work [22].

In the conventional arc discharge method in liquid, two gold electrodes are used to obtain gold nanoparticles. Lung and co-workers have synthesized gold nanoparticles by arc discharge in aqueous solutions [23]. In their study two gold electrodes were melted by high temperature caused by plasma discharge and converted into gold nanoparticles. They obtained nanoparticles with diameters from 7 to 40 nm. This distribution is too broad compared to the distribution obtained using the chemical reduction methods. Although, they could achieve smaller particle size by using anhydrous ethanol instead of pure water recently [24] but, in the present work, we do not use gold electrodes to produce gold nanoparticles. In all previous reports, the electrodes play a direct role in the formation of final nanoparticles, whereas in this work we do not utilize gold electrodes to produce the gold nanoparticles. In fact, we have used the electron-rich source of plasma region produced by a discharge between two titanium electrodes in HAuCl_4 solution to reduce the HAuCl_4

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into Au nanoparticles according to these reduction equations:



In the current work, we have prepared gold nanoparticles by electrical arc discharge between titanium electrodes in HAuCl₄ solution. The formation processes were monitored both through UV-vis spectroscopy and optical imaging. We have also evaluated the effect of primarily gold seeds on the formation of gold nanoparticles in 15 A arc current and 1 min arc duration. The main advantage of this method is the formation of gold nanoparticles by adding some seeds through the discharge process without any physical or chemical reactions.

Results and discussion

XRD analysis of the products

X-ray diffraction (XRD) analysis was taken out to find the crystalline phase of the final product as depicted in Figure 1. The result for the as-prepared sample shows formation of gold nanoparticles. The obtained spectrum reveals main peaks of gold phase at $2\theta = 38.3, 44.5, 64.7, 77.7,$ and 82.3 , which is in close agreement with the 004-0784 standard card from the JCPDS. The as-prepared powder was annealed at 350°C in order to remove the sodium citrate from the sample. Single crystalline domain, determined by Debye-Scherrer formula, was approximately 3 nm according to (111) crystalline plane from the XRD pattern.

Optical properties

The optical absorption spectroscopy of the as-prepared sample obtained from the discharge between titanium electrodes in HAuCl₄ solution with 1 mM concentration was demonstrated in Figure 2. By applying a discharge process between titanium electrodes in HAuCl₄ solution, the color of the solution gradually changes to red (which was pale yellow and almost transparent before discharge process) which indicates formation of gold nanoparticles. After the discharge process, the color of the solution completely changes to red which ascribes to the formation of spherical gold nanoparticles, as depicted in the inset of Figure 2. The absorption peak around 520 nm corresponds to the characteristic plasmonic peak of gold nanoparticles and shows formation of gold nanoparticles. Also the shape and location of the plasmonic peak reveal formation of spherical nanoparticles with aspect ratio close to 1.

Microscopic studies

Atomic microscope analysis (AFM) analysis was taken out to find the size and shape of the resulting gold nanoparticles (Figure 3a). Results revealed that particles with average diameter of almost 12 nm were formed during seed-mediated growth process (Figure 3b). Due to the artificial effects in AFM technique, the accurate size determination is a little difficult. AFM images are usually composed of probe and sample geometry and vary depending upon the tip shape. When both the sample geometry and the geometry of the imaging portion of the tip are unknown, an AFM image contains little quantitative information. But, according to our previous results, we expect

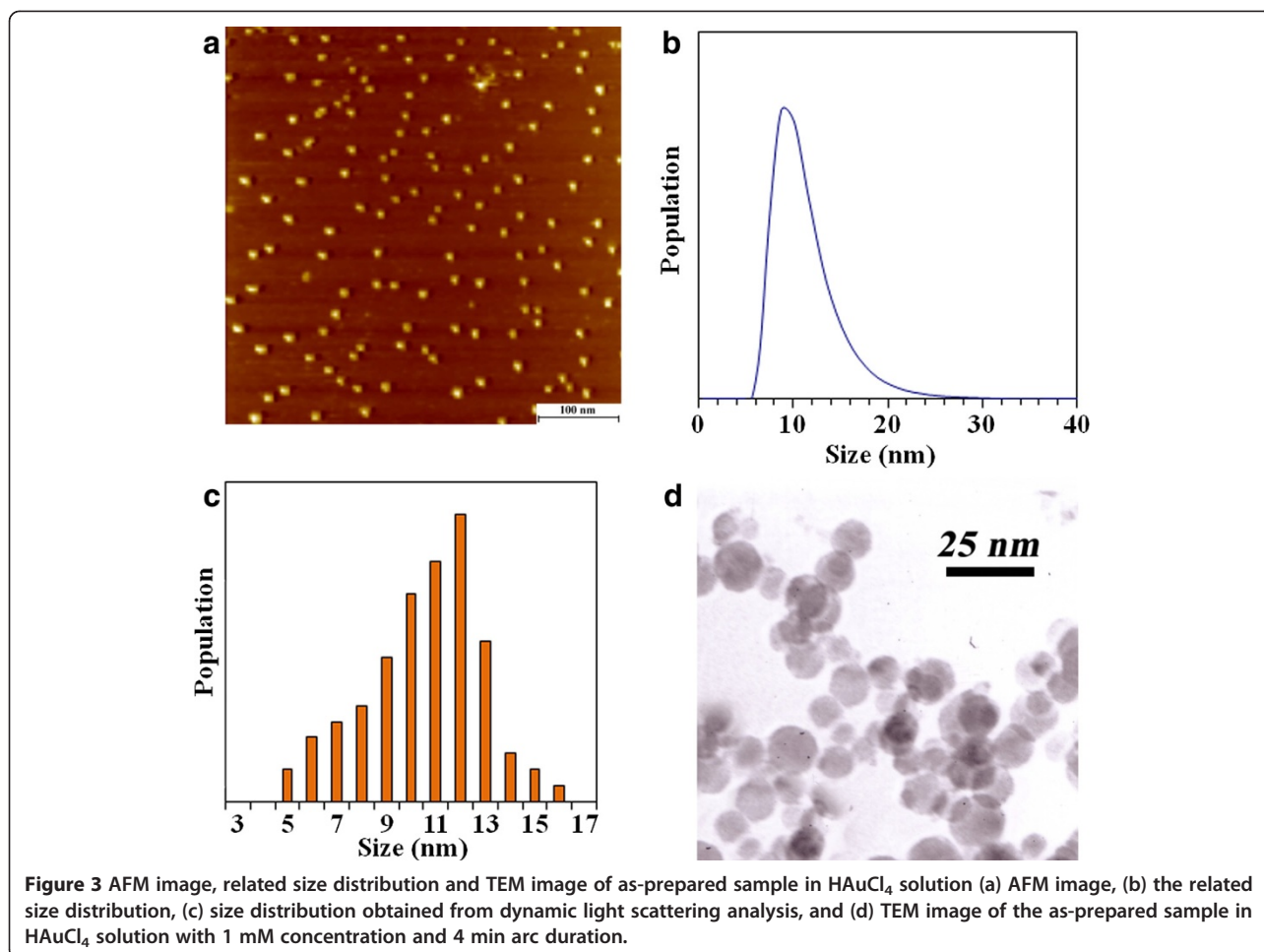


Figure 3 AFM image, related size distribution and TEM image of as-prepared sample in HAuCl_4 solution (a) AFM image, (b) the related size distribution, (c) size distribution obtained from dynamic light scattering analysis, and (d) TEM image of the as-prepared sample in HAuCl_4 solution with 1 mM concentration and 4 min arc duration.

almost spherical gold nanoparticles in seed-mediated growth procedure. The AFM image also exhibit rather good monodispersity of the formed gold nanoparticles, as illustrated in Figure 3a. Therefore, transmission electron microscope (TEM) was used to verify the size distribution and mean particle size. Figure 3d shows a typical TEM image of gold nanoparticles obtained from the discharge between titanium electrodes in HAuCl_4 solution with 1 mM concentration. This TEM image confirms the AFM result and reveals rather monodispersed nanoparticles.

As we have described in details in our previous work [22], gold nanoparticles of 8 nm diameter (detected by TEM) were formed during the reduction of HAuCl_4 in the plasma discharge zone. This is also in close agreement with AFM results. The produced gold nanoparticles precipitated after about 2 weeks in DI water, and we found that sodium citrate acts as a stabilizer and surface capping agent of the colloidal gold nanoparticles. In 1:13 volume ratio for the HAuCl_4 /sodium citrate with 1 mM concentration, the gold nanoparticles were stable for

several months. We have found that all the HAuCl_4 molecules will reduce after about 4 min arc duration and in 15 A arc current. By increasing the arc current, the erosion rate of titanium electrode increases as well as the amount of HAuCl_4 reduction.

UV-vis spectroscopy

The interesting phenomena that we have observed in our experiments was the increasing intensity of the plasmonic peak of as-prepared gold nanoparticles in 1 min arc duration and in 15 A arc current up to 6 h (Figure 4a). We have observed that for samples prepared at 15 A arc current and 1 min arc duration, the intensity of the plasmonic peak gradually increases, and the color of the as-prepared solution which was pale red changes to red then dark red, which is due to reduction of gold ions by sodium citrate. As we showed in optical absorption spectroscopy, the amount of electrons injected from discharge zone to the solution in 1 min arc duration is not enough to reduce all gold ions to gold nanoparticles [22]. The optical image

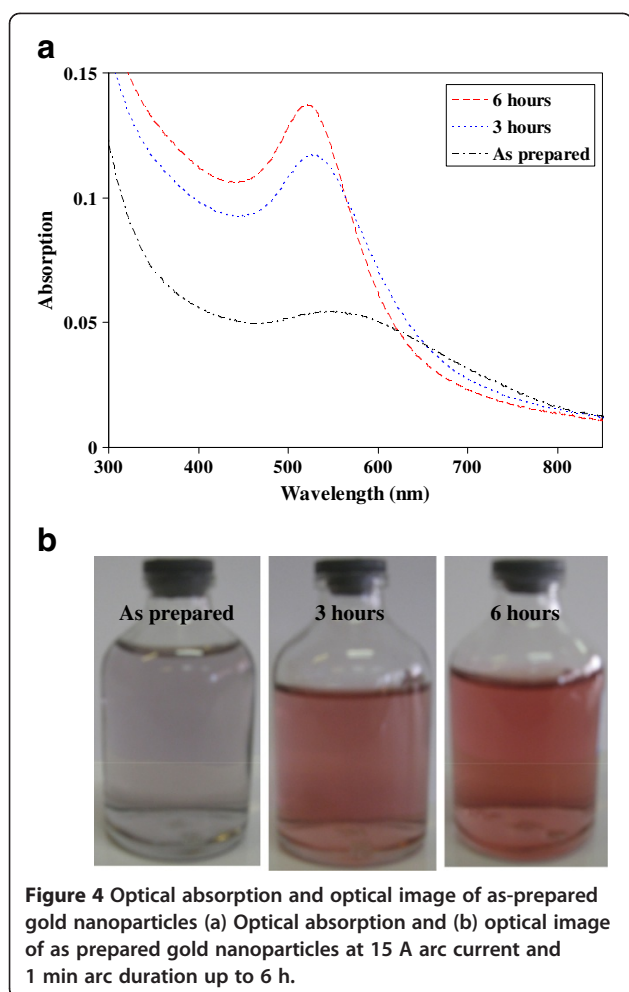


Figure 4 Optical absorption and optical image of as-prepared gold nanoparticles (a) Optical absorption and (b) optical image of as prepared gold nanoparticles at 15 A arc current and 1 min arc duration up to 6 h.

of as-prepared samples at 15 A arc current and 1 min arc duration, which is pale red, also verifies this result (Figure 4b). Optical spectroscopy and images of this sample reveal that gradually, the intensity of the plasmonic peak increases, and the color of the solution completely changes to red. This shows that even though the discharge process has ended, the formation of gold process has continued (Figure 4a,b). Therefore, there may be some gold ions that remained in the solution and reduced to gold nanoparticles. In fact, the primarily formed gold seeds in 1 min arc duration serve as nucleation sites for the reduction of gold ions which results in the formation of gold nanoparticles and also in the increase of the intensity of the plasmonic peak.

Seed mediation mechanism

The main concept of seed-mediated growth of nanoparticles is that small nanoparticles seeds serve as nucleation centers to grow nanoparticles to a desired size [25,26]. We have examined this common assumption

for shorter arc durations such as 30 and even 10 s. Figure 5a,b shows optical absorption spectroscopy of as-prepared samples prepared at 15 A arc current and 30 and 10 s arc durations, respectively. As is clear from the absorption spectra, the intensity of the plasmonic peak in as-prepared samples is not so sharp, indicating less formation of gold nanoparticles. This is also obvious from the optical images of those samples. We have found that the intensity of the plasmonic peak increases gradually up to 4 days and after that, there are no remarkable changes in the intensity of the plasmonic peak. The optical images of as-prepared samples indicate more formation of gold nanoparticles up to 4 days, too. In fact, after 4 days the color of the solution completely changes to red and remains stable for several months (Figure 5c).

Conclusions

In summary, we studied the seed-mediated reduction of gold salt by the electrical arc discharge between titanium electrodes in water. The optical absorption of the as-prepared sample exhibits a plasmonic peak around 520 nm, which corresponds to the surface plasmon resonance of gold nanoparticles. We observed that all the HAuCl_4 molecules will reduce to gold nanoparticles after about 4 min in 15 A arc current. Optical absorption of the samples prepared at 15 A and 1 min arc duration at different time intervals shows an increase of the plasmonic peak due to seed mediation up to 6 h. In lower arc durations, the saturation time was 4 days due to the lower concentration of seeds. But in higher arc durations, the intensity of the plasmonic peak saturates within a few hours.

Methods

Synthesis of gold nanoparticles

The preparation system consists of two main parts as we have reported in our previous works [27-31]: a high current DC power supply and a reactor including anode, cathode, and a micrometer which moves the anode towards the cathode. In this work a 15-A arc current was applied between two titanium electrodes in HAuCl_4 solution. The voltage was dropped to about 3 V during the arc while the current was fixed at the desired amount. Both anode and cathode were titanium, wire-shaped, 2 mm in diameter, and 99.99% purity. In this arc current, which was the threshold current for discharge between titanium electrodes, only discharge happens between the electrodes, and there is negligible erosion for titanium based on energy dispersive X-ray spectroscopy (EDX) analysis as depicted in Table 1. Initially, we bring the two electrodes into touch leading to a small contact cross-section and, thus, to a high current density. As a result arc discharge happens between titanium electrodes, and HAuCl_4

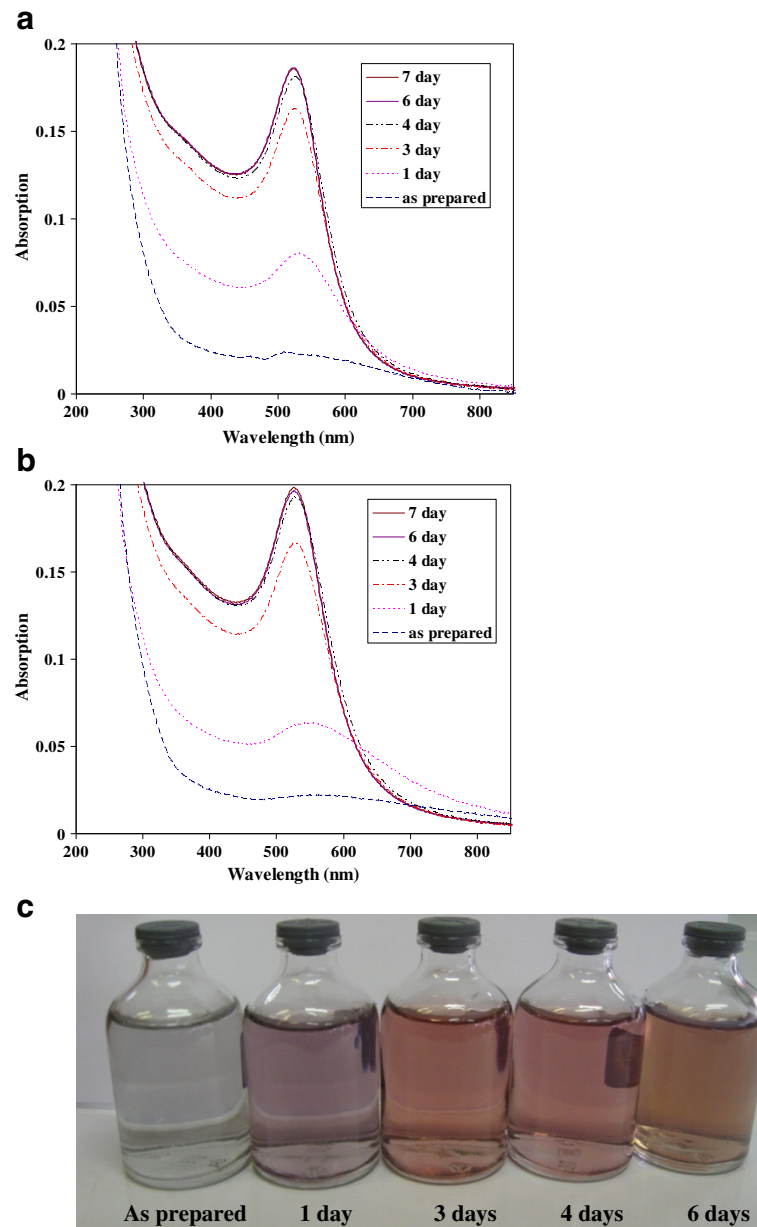


Figure 5 Changes in the optical absorption of gold nanoparticles prepared at 15 A arc current at (a) 30 s arc duration and (b) 10 s arc duration and (c) the corresponding optical images up to 1 week.

Table 1 EDX analysis of as prepared sample after discharge process between titanium electrodes in HAuCl_4 solution

Number	Type of element	Weight percentage in solution (wt.%)
1	Gold	99.60
2	Titanium	0.40
3	Total	100.00

reduces to gold nanoparticles by means of electrons coming from the plasma zone.

Characterization

EDX analysis was done by a Philips XL30 instrument (Royal Philips Electronics, Amsterdam, The Netherlands) at 20 kV accelerating voltage. Size distribution of nanoparticles was determined by a Zetasizer Nano ZS from Malvern Company (Malvern, Worcestershire, UK). The analysis of the crystalline structure was performed by a XRD diffractometer (X'pert Philips, Royal Philips

Electronics, Amsterdam, The Netherlands) with wavelength of Cu K α radiation being 1.5406 Å in 2 θ range from 10° to 80° by 0.05° sec⁻¹ steps. The UV–vis spectroscopy of the samples was taken out by a Lambda 950 spectrophotometer (PerkinElmer Inc., Waltham, MA, USA) from 200 to 1100 nm wavelengths. AFM images were taken by a Veeco autoprobe instrument (Veeco Instruments, Plainview, NY, USA) in non-contact mode and the results were analyzed by SPIP software (version 4.5, Le Monde diplomatique, France).

Competing interests

The author declares that he/she has no competing interests.

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References

1. Toderas, F, Baia, M, Baia, L, Astilean, S: *Nanotechnology* **18**, 255702 (2007)
2. Hossain, MK, Kitahama, Y, Huang, GG, Kaneko, T, Ozaki, Y: *Appl. Phys. B* **93**, 165 (2008)
3. Wang, Y, Chen, H, Wang, E: *Nanotechnology* **19**, 105604 (2008)
4. Zou, X, Ying, E, Dong, S: *Nanotechnology* **17**, 4758 (2006)
5. Castaneda, MT, Merkok, A, Pumera, M, Alegret, S: *Biosens. Bioelectron.* **22**, 961 (2007)
6. Rosi, NL, Mirkin, CA: *Chem. Rev.* **105**, 1547 (2005)
7. Gardea-Torresdey, JL, Parsons, JG, Gomez, E, Peralta-Videa, J, Troiani, HE, Santiago, P, Yacaman, MJ: *Nano Lett.* **2**, 397 (2002)
8. Daniel, MC, Astruc, D: *Chem. Rev.* **104**, 293 (2004)
9. Souza, RF, Alentar, MARC, Silva, EC, Meneghetti, MR, Hickmann, JM: *Appl. Phys. Lett.* **92**, 201902 (2008)
10. Shen, H, Cheng, B, Lu, G, Ning, T, Guan, T, Zhou, Y, Chen, Z: *Nanotechnology* **17**, 4274 (2006)
11. Haruta, M: *Nature* **437**, 1098 (2005)
12. Haruta, M: *Gold Bulletin* **37**, 27 (2004)
13. Zhu, J, Shen, Y, Xie, A, Qiu, L, Zhang, Q, Zhang, S: *J. Phys. Chem. C* **111**, 7629 (2007)
14. Pal, A: *Mater. Lett.* **58**, 529 (2004)
15. Meyre, ME, Delapierre, MT, Faure, C: *Langmuir* **24**, 4422 (2008)
16. Knake, R, Fahmi, AW, Tofail, SAM, Clohessy, J, Mihov, M, Cunnane, VJ: *Langmuir* **21**, 1001 (2005)
17. Zhou, M, Chen, S, Zhao, S, Ma, H: *Physica E* **33**, 28 (2006)
18. Pырpassopoulos, S, Niarchos, D, Nounesis, G, Boukos, N, Zafiropoulou, I, Tzitzios, V: *Nanotechnology* **18**, 485604 (2007)
19. Mohapatra, S, Mishra, YK, Avasthi, DK, Kabiraj, D, Ghatak, J, Varma, S: *J. Phys. D: Appl. Phys.* **40**, 7063 (2007)
20. Kazemian Abyaneh, M, Paramanik, D, Varma, S, Gosavi, SW, ulkarni, SK: *J. Phys. D: Appl. Phys.* **40**, 3771 (2007)
21. Kim, SM, Kim, GS, Lee, SY: *Mater. Lett.* **62**, 4354 (2008)
22. Ashkarran, AA: *J. Cluster Sci.* **22**, 233 (2011)
23. Lung, JK, et al.: *J. Alloys Compd.* **434–435**, 655 (2007)
24. Tseng, KH, Huang, JC, Liao, CY, Tien, DC, Tsung, TT: *J. Alloys Compd.* **476**, 446 (2009)
25. Jana, NR, Gearheart, L, Murphy, CJ: *Chem. Mater.* **13**, 2313 (2001)
26. Gole, A, Murphy, CJ: *Chem. Mater.* **16**, 3633 (2004)
27. Ashkarran, AA, Irajizad, A, Ahadian, MM, Mahdavi Ardakani, SM: *Nanotechnology* **19**, 195709 (2008)

28. Ashkarran, AA, Irajizad, A, Mahdavi, SM, Ahadian, MM: *Mater. Chem. Phys.* **118**, 6 (2009)
29. Ashkarran, AA: *Curr. Appl. Phys.* **10**, 144 (2010)
30. Ashkarran, AA, Ahmadi Afshar, SA, Aghigh, SM, Kavianipour, M: *Polyhedron* **29**, 1370 (2010)
31. Ashkarran, AA, Kavianipour, M, Aghigh, SM, Ahmadi Afshar, SA, Saviz, S, Irajizad, A: *J. Cluster Sci* **21**, 753 (2010)

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