

U. PAL^{1,✉}
J.F. SANCHEZ RAMIREZ²
R. SIVLA GONZALEZ¹
J.R. DIAZ-ESTRADA³

Organization of metal nanoclusters on fatty amine films using ion-dipole interaction

¹ Instituto de Física, Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla, Pue. 72570, México

² Facultad de Química, ICUAP, Universidad Autónoma de Puebla, 14 Sur, Pue. 72570, México

³ Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colon esq. Paseo Tollocan, Apdo. Postal A-20, Toluca, 50120, México

Received: 28 June 2004/Accepted: 20 September 2004

Published online: 3 November 2004 • © Springer-Verlag 2004

ABSTRACT A new technique for the organization of metallic nanoparticles on fatty amine films is demonstrated. A selected polymer (PVP) is used which can both control the size of metal clusters in colloidal form and can help the clusters to be attached with the fatty amine films for a wide range of pH limit of the colloidal solution. The amount of metal clusters incorporated on the fatty amine surface can be controlled by controlling the time of exposure and pH of the colloidal solution. The ion-dipole interaction between the kyton group of PVP and the amino group of the amine is utilized for the incorporation of PVP capped metal clusters on the amine substrate. The same technique can be utilized for the organization of any metal particle on any substrate. Mechanism and optimum incorporation conditions are studied by microscopy and spectroscopic techniques.

PACS 82.70.Dd; 82.65.Yh; 61.82.Rx; 61.46.+w; 68.65.+g

1 Introduction

Nanoparticle research became a thrust area of interest among the scientific community extending from physics to medical science due to the potential applications of this “neglected dimension” of matter [1, 2] in almost all the fields of science and technology. While the synthesis of these nanoparticles is an important aspect of the research, the organization of the particles is important for device applications. Organic matrices are being investigated for the controlled growth of small particles either at the air-water interface [3] or by chemical insertion into Langmuir-Blodgett (LB) films [4]. Utilizing electrostatic immobilization process, multilayer lamellar films of nanoclusters have also been grown by LB technique on Langmuir monolayers [5, 6]. Mayya et al. [7] could transfer the lamellar multilayer gold colloidal particle

films onto the solid supports by the LB method using the electrostatic interaction between the ionized amine group of solid support and the carboxylic group of thiol used for capping of Au particles. The use of thiol or carboxylic acid groups to produce self-assembled monolayers (SAMS) on metal cluster surface as the bifunctional polymer compound are rather common [7–11] and been utilized effectively for several applications like bio sensors [12]. However, sometime, the use of such aromatic or aliphatic compounds as SAMS inhibit their application in catalysis. On the other hand the conventional organic capping like PVP sometime accelerates the catalytic properties of nanocluster metal particles [13, 14].

In the present communication, we report on the use of conventional capping agent PVP both for the controlled size growth and for organization of metal particles on fatty amine films. In

general, use of carboxylic group for the attachment of metal particles in fatty amines (using the electrostatic interaction of the ionized thiol and amine groups) is restricted by the control of the pH of the colloidal solutions. But in our approach, we demonstrate that the use of PVP as the capping agent can eliminate such a strict pH restriction for the attachment of metal particles in fatty amine films. Such organized colloidal metal nanoparticles on polymer substrates produce high activity for surface enhanced Raman scattering [15, 16].

2 Experimental

The Au/Pd colloidal bimetallic nanoparticles were synthesized by the simultaneous reduction of corresponding metal ions in presence of poly(N-vinyl-2-pyrrolidone) (PVP) in a water/methanol (1:1) solvent. The details of the preparation technique is described elsewhere [17]. By changing the volumetric ratio of the two ions in the mixture solution, bimetallic nanoparticles of different compositions were prepared. The obtained colloidal dispersions presented a reddish-violet color and of pH 4.9.

Thin films of octadecylamine (ODA) of about 300 nm thick were deposited on quartz glass substrates by thermal evaporation. The attachment process of the metallic particles on amine surface was realized simply by immersing the amine films in the colloidal dispersions at different values of pHs (4,6,7,8 and 10) at room temperature. The pH of the colloidal dispersions was varied by adjusting the amount of NaOH or HCl in the colloidal solutions. For a particular

✉ Fax: +52-222-2295611, E-mail: upal@sirio.ifuap.buap.mx

pH value of the colloidal solution, the extent of metal particle incorporation in the ODA films was controlled just by controlling the time of immersion of the films in the colloidal solution. After removal from the colloidal solutions, the films were washed with methanol several times and dried in N_2 flow before their further characterization.

Transmission electron microscopy (TEM) measurements of the colloidal dispersions were realized using a JEOL-JEM200 electron microscope operating at 200 keV. For the evaluation of morphology of the metal particle incorporated amine films a JEOL-JSM5400LV scanning electron microscope operating at 10 keV and a DI SPM Nanoscope4 in tapping mode were used. The optical absorption measurements in the UV-Vis spectral range of the colloidal dispersions and of the cluster incorporated amine films were realized utilizing a Shimadzu UV-3101PC double beam spectrophotometer. A Fourier transform infrared (FTIR) (Nicolet) spectrophotometer was used for recording the IR absorption spectra of the metal particle incorporated amine films.

3 Results and discussion

A typical TEM micrograph of the bimetallic (Au/Pd = 12/1) colloids and its optical absorption spectrum are shown in Fig. 1. The size distribution of the bimetallic colloids is presented as the inset in Fig. 1a. The absorption spectrum of the colloidal Au/Pd particles revealed a surface plasmon resonance (SPR) band with a peak at about 521 nm (Fig. 1b). Figure 2 shows the UV-Vis absorption spectra of the amine films after immersion in colloidal solutions for 48 hrs at different pH values. It can be observed that the intensity of the SPR absorption band decreases with the increase of the pH value of the colloidal solution. In the inset of Fig. 2 we presented the variation of the SPR band intensity with the variation of the pH of the colloids. We can see that the variation is almost linear in the range of pH 4–8. However, the position of the SPR band shifts towards higher wavelengths by decreasing the pH of the colloidal solutions indicating the flocculation (the term flocculation is used as we are not sure whether union of smaller clusters to form bigger clusters is due to

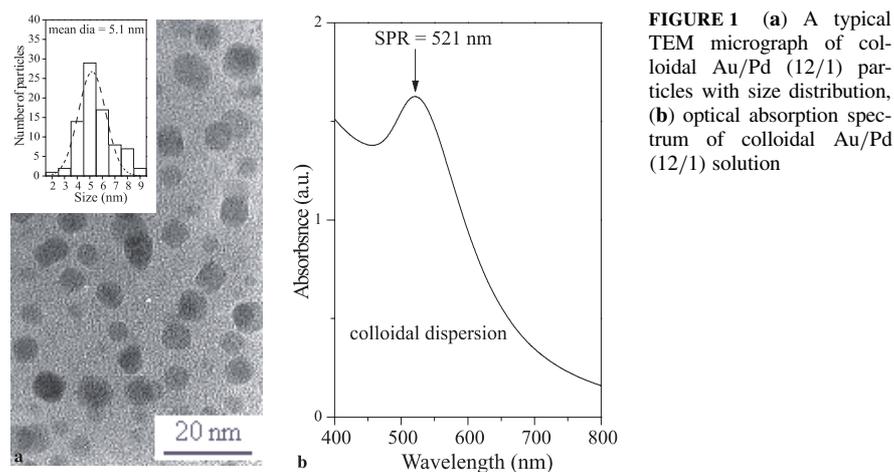


FIGURE 1 (a) A typical TEM micrograph of colloidal Au/Pd (12/1) particles with size distribution, (b) optical absorption spectrum of colloidal Au/Pd (12/1) solution

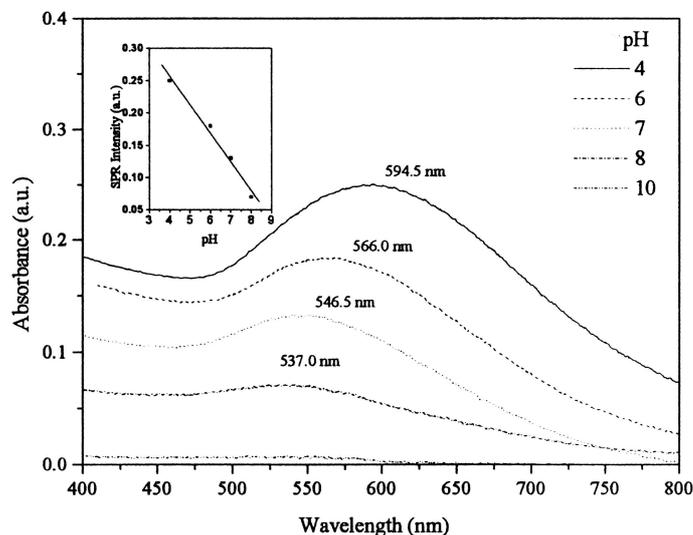


FIGURE 2 Optical absorption spectra of ODA films after incorporation of Au/Pd clusters at different pH values (for 24 hrs). The *insert* shows the variation of SPR absorption intensity with pH values

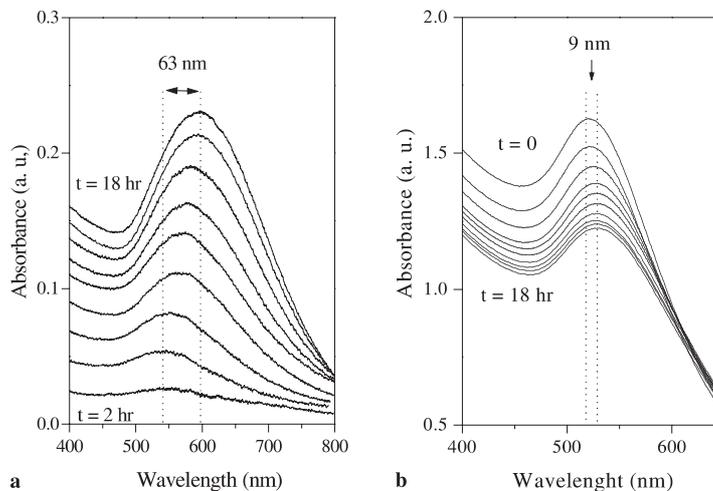


FIGURE 3 Optical absorption spectra of (a) ODA films after every 2 hrs of immersion in colloidal solution and (b) colloidal cluster solution of Au/Pd at every 2 hrs after preparation

aggregation or agglomeration) of metal clusters for lower pH values. As the flocculation process may occur even in the colloidal solution of the metal

clusters, we performed the optical absorption measurements on the colloidal metal clusters and also on the metal cluster incorporated amine films with

time. In Fig. 3, the optical absorption spectra of the colloidal metal clusters after different hours of preparation and the same for the metal cluster incorporated amine films after several hours of immersions in metal colloids are shown. We can see that after 18 hrs, the shift of the SPR peak position for metal colloids is about 9 nm, whereas, the shift of SPR peak position after immersion of the amine film in metal colloids is about 63 nm. From the observation, we can conclude that the flocculation process occurs mainly on the amine film surface. To visualize the flocculation process, we performed the SEM measurements of the carbon coated metal cluster incorporated amine films. In Fig. 4 the SEM images for the amine films after immersing them into the metal colloid solutions for 24 hrs at different pH values are shown. We can see the formation of big along with small metal clusters on the surface of the amine film immersed in the metal colloidal solution of pH = 4. Though the morphology of the film immersed in the colloidal solution of pH = 10, seems to be more uniform, it was difficult to comment on the process of flocculation from the images as the surfaces of the evaporated ODA were not very uniform. However, as our optical results revealed the incorporation of more clusters in the films for lower pH values (increase of SPR intensity with decreasing pH), we assume that for lower pH values, due to strong ionization of amine (NH_2) groups, some of the incorporated clusters might have penetrated the amine surface to the interior of the film. Though the shift of SPR peak position (ref. Figure 2) towards higher wavelengths on decreasing pH values is indicative of flocculation of clusters in the films, we could not confirm whether the flocculation process occurs only on the surface of the amine film or throughout the film thickness. To have a better idea of the flocculation process, we annealed a few ODA films at 50 °C for 10 min. in argon atmosphere to make the film surfaces uniform. The annealed films were used to incorporate Au/Pd (1/1) colloidal clusters at pH = 4 for different immersion times. In Fig. 5, the atomic force microscopic (AFM) images of the films immersed in the colloidal solution for 12 and 48 hrs are shown along with the image of an annealed film. We can see a smooth sur-

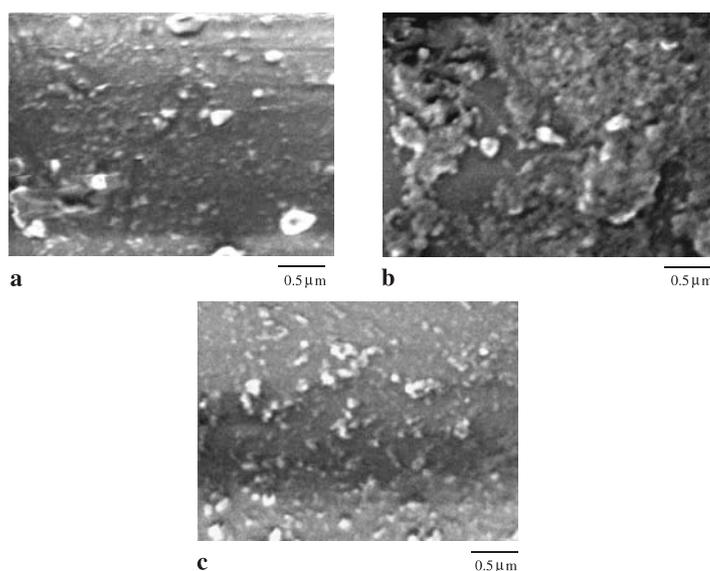


FIGURE 4 Typical SEM micrographs of the ODA films after Au/Pd cluster incorporation at (a) pH = 4, (b) pH = 6 and (c) pH = 10

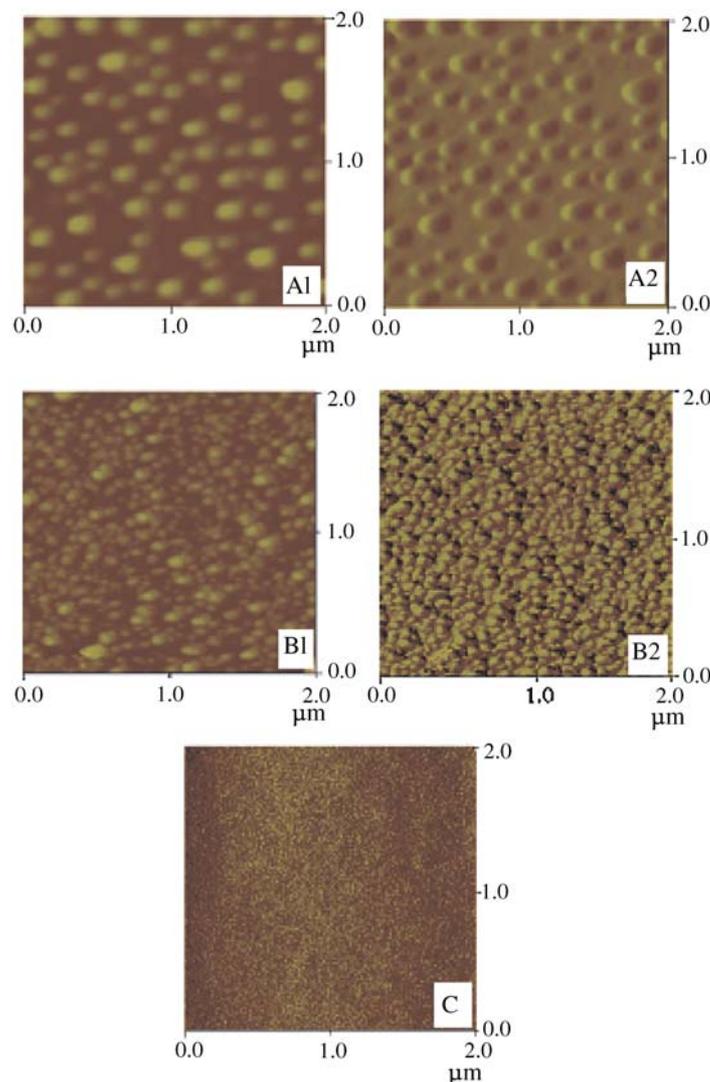


FIGURE 5 AFM images of ODA films (A) after incorporation of Au/Pd clusters for 48 hrs, (B) after incorporation of Au/Pd clusters for 12 hrs and (C) without incorporation of Au/Pd clusters. (1) and (2) correspond to height contrast and phase contrast images respectively

face morphology for the annealed ODA film (Fig. 5C). Homogeneous distributions of bimetallic clusters on the amine film surfaces are observed for the samples prepared by immersing them for 12 and 48 hrs in the colloidal solution (pH = 4) (Fig. 5A and B). For the sample prepared by immersing for 12 hrs, we can see the formation of clusters of about 88 nm average size with high density. Whereas, for the sample prepared by immersing for 48 hrs, the average size of the clusters is about 150 nm and the density is low.

As the average size of the clusters in colloidal solution was about 5 nm (ref. Fig. 1a), formation of bigger clusters in the ODA films is indicative of flocculation of clusters on their surface.

The process of incorporation of the metal clusters is even clearer from the IR absorption spectra of the metal cluster attached amine films. In Fig. 6, the IR absorption spectra of the amine films immersed for 24 hrs in the bimetallic colloidal cluster solutions of different pH values are shown. In the $3500\text{--}3200\text{ cm}^{-1}$ spectral range. There appeared an absorption band at about 3332 cm^{-1} for the amine film, which corresponds to the antisymmetric vibration frequency of the NH_2 as observed by other researchers [18], (Ganguly et al. 1993; Sastry et al. 1997). Generally this band shifts towards lower frequency on the formation of salts (Bardosova et al. 1995). From the figure, we can observe a shift of this band towards lower frequency on incorporating the metal clusters into the amine films. The band shifted towards lower frequency gradually on decreasing the pH value of the colloidal solution and disappeared for the $\text{pH} < 8$. The disappearance of the band indicates that on immersing the amine films into the colloidal solution of $\text{pH} < 8$, almost all the NH_2 groups on the amine film surface ionized completely to form the bonds with the polar $\text{C}=\text{O}$ groups of the PVP layer on the metal clusters.

The process of attachment of the metal clusters on the amine surface is demonstrated through the diagram given in Fig. 7. As the pK_A of ODA is 10.5, all the NH_2 groups are expected to be ionized fully for $\text{pH} < 8$, the ion-dipole interaction between the NH_3^+ groups and kytion groups of PVP is strong. So, the incorporation of metal

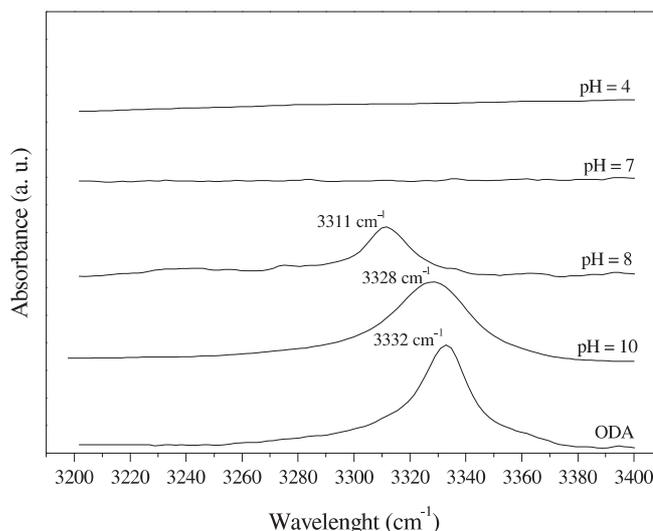


FIGURE 6 FTIR spectra of Au/Pd cluster-incorporated ODA films at different pH values of the colloidal solution

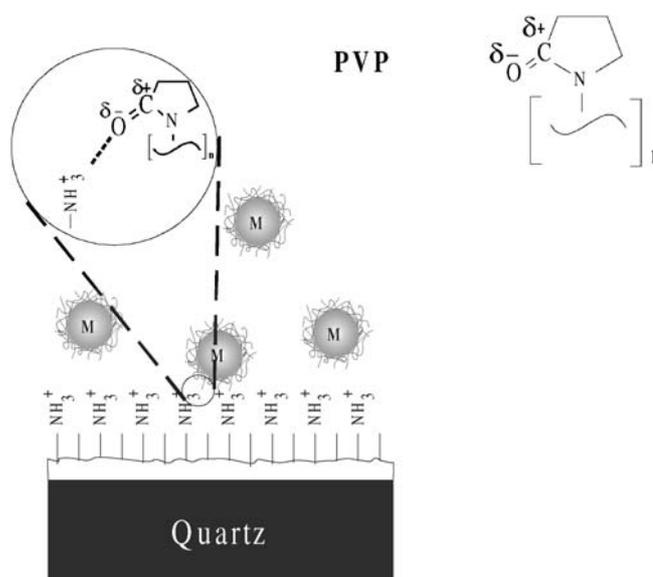


FIGURE 7 Schematic illustration of the incorporation mechanism of PVP capped metal clusters in ODA film

colloids on the amine surface is rapid, causing the formation of big and dispersed (about 35% of average size) metal clusters on the amine surface. On the other hand, on increasing the pH of the colloidal solution, the amine groups of the ODA films ionize partially and the process of incorporation of metal clusters on the surface is slow.

Therefore, we can control the size distribution and the amount of clusters on the amine film surface just by controlling the pH of the metal colloid solution and the time of immersion. In this process of metal particle assembly as there is no ion-ion/electrostatic interaction between the NH_3^+ ions of amine film and the ions from capping layer

(e.g., carboxylic ions), there is no strict necessity to control the pH of the colloidal solution for the optimum incorporation of metal particles on the amine surface. We can control the amount of metal cluster on the amine surface for a wide range of pH value just by controlling the time of immersion. The same procedure can be utilized for the organization of metal nano-clusters on any kind of solid surface by making a thin layer of amine on the solid surface.

4 Conclusions

By using the ion-dipole interaction between the ionized amine groups of fatty amine films and the car-

boxyl groups of PVP, we could incorporate metal particles in fatty amine films for a wide range of pH values of the metal colloid solution. By adjusting the pH of the colloidal solution and the time of immersion, the amount of metal particle incorporation in the fatty amine films and their size could be controlled. The same procedure can be utilized for the incorporation of any metal cluster on any kind of surfaces.

REFERENCES

- 1 P.H. Abelson: *Science* **271**, 11 (1996)
- 2 J.I. Bauman: *Science* **271**, 889 (1996)
- 3 J. Yang, F.C. Meldrum, J.H. Fendler: *J. Phys. Chem.* **99**, 5500 (1995)
- 4 R.S. Urquhart, D.N. Furlong, T. Gengenbach, N.J. Geddes, F. Grieser: *Langmuir* **11**, 1127 (1995)
- 5 M. Sastry, K.S. Mayya, V. Patil, D.V. Paranjape, S.G. Hegde: *J. Phys. Chem. B* **101**, 4954 (1997)
- 6 M. Bardosova, R.H. Tredgold, Z. Ali-Adib: *Langmuir* **11**, 1273 (1995)
- 7 K.S. Mayya, V. Patil, M. Sastry: *Langmuir* **13**(9), 2575 (1997)
- 8 A. Ulman: *An Introduction to ultrathin organic film Langmuir-Blodgett to self-assembly* (Academic press, New York 1991)
- 9 R.G. Freeman, K.C. Grabar, K.J. Allison, R.M. Bright, J.A. Davis, A.P. Guthrie, M.B. Mommer, M.A. Jackson, P.C. Smith, D.G. Walter, M.J. Natan: *Science* **267**, 1629 (1995)
- 10 C.S. Weisbecker, M.V. Merritt, G.M. Whitesides: *Langmuir* **12**, 3763 (1996)
- 11 K.C. Grabar, K.J. Allison, B.E. Baker, R.M. Bright, K.R. Brown, R.G. Freeman, A.P. Fox, C.D. Keating, M.D. Musick, M.J. Natan: *Langmuir* **12**, 2353 (1996)
- 12 J. Jia, B. Wang, A. Wu, G. Cheng, Z. Li, S. Dong: *Anal. Chem.* **74**, 2217 (2002)
- 13 L.D. Rampino, F.F. Nord: *J. Am. Chem. Soc.* **63**(10), 2745 (1941)
- 14 J.U. Kohler, J.S. Bradley: *Langmuir* **14**, 2730 (1998)
- 15 Y. Maeda, H. Yamamoto, H. Kitano: *J. Phys. Chem.* **99**, 4837 (1995)
- 16 K.C. Grabar, P.C. Smith, M.D. Musick, J.A. Davis, D.G. Walter, M.A. Jackson, A.P. Guthrie, M.J. Natan: *J. Am. Chem. Soc.* **118**, 1148 (1996)
- 17 J. F. Sánchez-Ramírez, G. Díaz, A. Vázquez, U. Pal: *J. New Mater. Electrochem. Appl.* 2004 (in press)
- 18 P. Ganguly, D.V. Paranjape, M. Sastry: *J. Am. Chem. Soc.* **115**, 793 (1993)
- 19 M. Sastry, V. Patil, K.S. Mayya: *Langmuir* **13**, 4490 (1997)