J. Chem. Sci., Vol. 117, No. 4, July 2005, pp. 311–316.

Synthesis of Pt, Pd, Pt/Ag and Pd/Ag nanoparticles by microwave-polyol method

KIRTI PATEL,[1] SUDHIR KAPOOR,[2]* DEVILAL PURSHOTTAM DAVE[1] and
TULSI MUKHERJEE[2]
[1]Department of Chemistry, The Institute of Science, Mumbai 400 032, India
[2]Radiation Chemistry & Chemical Dynamics Division, Bhabha Atomic Research Centre,
Mumbai 400 085, India
e-mail: sudhirk@apsara.barc.ernet.in

MS received 25 February 2005; revised 31 May 2005

Abstract. Pt, Pd, Pt-Ag and Pd-Ag bimetallic nanoparticles were synthesized in ethylene glycol and glycerol using the microwave technique in the presence of a stabilizer poly(N-vinylpyrrolidone) (PVP). It has been observed that PVP is capable of complexing and stabilizing nanoparticles. Mixed clusters were formed by simultaneous reduction of the metal ions. The clusters were characterized using UV–Vis spectra, XRD and dynamic light scattering. To understand the mechanism of formation of mixed nanoparticles, several experimental parameters such as *in situ* irradiation of mixed metal salts and mixing of individual sols were attempted.

Keywords. Mixed particles; microwave; optical absorption.

1. Introduction

Metallic nanoparticles of definite size are easily synthesized via a “bottoms-up” approach and surface-modified with special functional groups. Nanoparticles exhibit new optical properties which are not observed either in the individual molecules, or in the bulk metals.[1–3] One particular example is the presence of a strong absorption band in the visible region. This arises due to the surface-plasmon-oscillation modes of the conduction electrons that are coupled through the surface to external electromagnetic fields.[4–8] As a result of such plasmon absorption bands the optical properties of copper, silver and gold nanoparticles in solution have received considerable attention. It has been shown that the colour of noble metal nanoparticles depends on the size and the shape of the particles, as well as on the refractive index of the surrounding medium.[4,7,9] In addition, it has been documented that bimetallic nanoparticles generally show different physicochemical properties as compared to their individual particles. In the past few decades considerable efforts have been devoted to bimetallic nanoparticles owing to their different catalytic properties,[10] magnetic properties[11] etc. Owing to all the above special properties that are brought about by the changes on surface and structure caused by alloying or due to core–shell, control of composition distribution of bimetallic nanoparticles is crucial to the improvement of particle properties. In general, bimetallic nanoparticles can be prepared by simultaneous reduction or by successive reduction of two metal ions in the presence of suitable stabilizer. The atoms of the less noble metal systematically transfer an electron to the ions of the more noble metal and this relay process favours the complete reduction of latter into monometallic clusters before the other ions can be reduced at their surfaces. The result is, therefore, bimetallic clusters with segregation into a core–shell structure whose properties depend on the thickness of the external metal. A number of methods has been used to prepare bimetallic nanoparticles including alcohol reduction,[12] citrate reduction,[13,14] polyol process,[15] borohydride reduction,[16] photolytic reduction,[17] radiolytic reduction[18] and laser ablation.[19,20]

Pt-containing nanosized composite particles, with the second metal being usually Au or Pd or Rh, have attracted significant attention due to their specific catalytic activity and selectivity in hydrogenation and visible light induced hydrogen evolution.[21–28]

---

*For correspondence

Microwaves are electromagnetic waves. Microwave heating is well known in the food industry and of late has found a number of applications in chemistry, especially in organic chemistry. It is also being used for the development of different materials. In microwave application, heating is caused by the interaction of the permanent dipole moment of the molecule with the high frequency electromagnetic radiation. In comparison with conventional heating, this novel method shortens reaction time by a factor of approximately 20. Also, heating is not only quick but also uniformly spread through the entire bulk of the reaction mixture. This may result in narrow distribution of particle sizes. In the present article, we report on the preparation of metallic Pt, Pd, Pt/Ag and Pd/Ag particles in ethylene glycol and glycerol in the presence of stabilizer poly(N-vinylpyrrolidone) (PVP).

2. Experimental

All reagents were of the highest purity. $AgNO_3$ (BDH), Na_2PdCl_4, Na_2PtCl_4, ethylene glycol (Spectrochem, India), glycerol (Spectrochem, India) and poly(N-vinylpyrrolidone) (PVP) (Sigma) were used as received.

Solutions were freshly prepared to avoid any photochemical reactions. All experiments were carried out in air. The total metal ion concentration was 5×10^{-4} mol dm^{-3} in all the experiments. The reactions were carried out in a domestic microwave oven (Kenstar, MO-9706A, power supply 230 V/50 Hz, consumption 1200 W, output power 800 W, frequency 2450 MHz) operating in a cyclic mode (ON 15 s, OFF 5 s) to prevent intense boiling of solvents as well as aggregation of metals.

Absorption measurements were carried out on a UV 160-A Shimadzu spectrophotometer. The spectra were recorded at room temperature using 1 × 1 cm quartz cuvettes. X-ray diffraction patterns were taken using a Phillips Analytical automated powder diffractometer employing CuK$_a$ radiation. Dynamic light scattering experiments were done on a Malvern 4800 Autosizer employing a 7132 digital correlator. The intensity correlation function was analysed by the method of cumulants, using the mean and the variance of the distribution on the fitted variable. The diffusion coefficient (D) of the particle is related to the average decay rate (Γ) of the correlation function by $\Gamma = Dq^2$ where q is the magnitude of the scattering vector (given by $q = (4pn/l)\sin q/2$, l is the wavelength of light, n is the refractive index and q is the scattering angle). The mean hydrodynamic coefficient of the particles was obtained from the diffusion coefficient using the Stokes–Einstein relationship. The light source was an Ar^+ ion laser operated at 514·5 nm and scattering angle $q = 90°$.

3. Results and discussion

3.1 *Formation of Pt and Pd nanoparticles*

Figure 1 shows the absorption spectra of Pt and Pd particles prepared in ethylene glycol in the presence of 0·1% PVP after irradiation for 60 s. Similar results were obtained when glycerol was used in place of ethylene glycol. The observed spectra are similar to that reported in literature for nanoparticles of Pt and Pd.[29] The phase structure of the prepared particle is characterized by X-ray diffraction (XRD) as shown in figure 2. All the XRD peaks can be indexed as face centered cubic (FCC) structure. No peaks of any other planes are detected, indicating the high purity of the product. The average size of the particles can be derived from the peak width using the Scherrer equation,

$$d = \frac{0{\cdot}94\,l}{\mathrm{FWHM}(2q)\cos q}, \tag{1}$$

where d is the diameter of the crystalline core of the particle and q is the Bragg's angle of the peak considered. The particle sizes obtained are tabulated in table 1.

3.2 *Formation of Pd/Ag bimetallic nanoparticles*

Figure 3 shows the absorption spectra of microwave-irradiated reduced solutions for Pd, Ag and mixed particles of Pd/Ag. It can be seen that the silver spectrum shows a surface plasmon band at 420 nm.

Table 1. Colloidal Pt and Pd dispersions obtained in polyols. Particle sizes are determined from XRD peaks.

Metal salt, 0·5 mmol/l	Medium	PVP (wt %)	Mean size (nm)
Pt	Ethylene glycol	0·1	30
Pt	Glycerol	0·1	25
Pd	Ethylene glycol	0·1	30
Pd	Glycerol	0·1	22

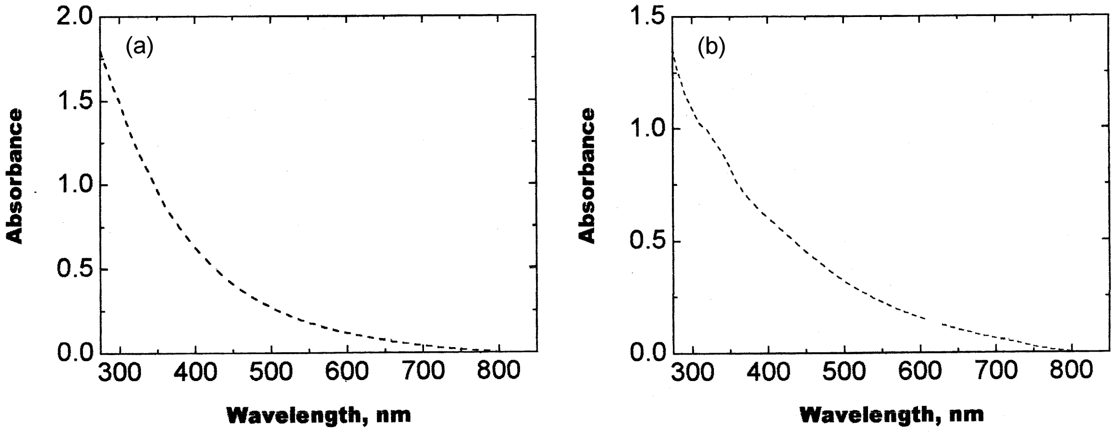

Figure 1. UV/Vis absorption spectra of (**a**) Pt and (**b**) Pd nanoparticles in ethylene glycol after 60 s of irradiation of 5×10^{-4} mol dm^{-3} metal salt in the presence of 0·1% PVP.

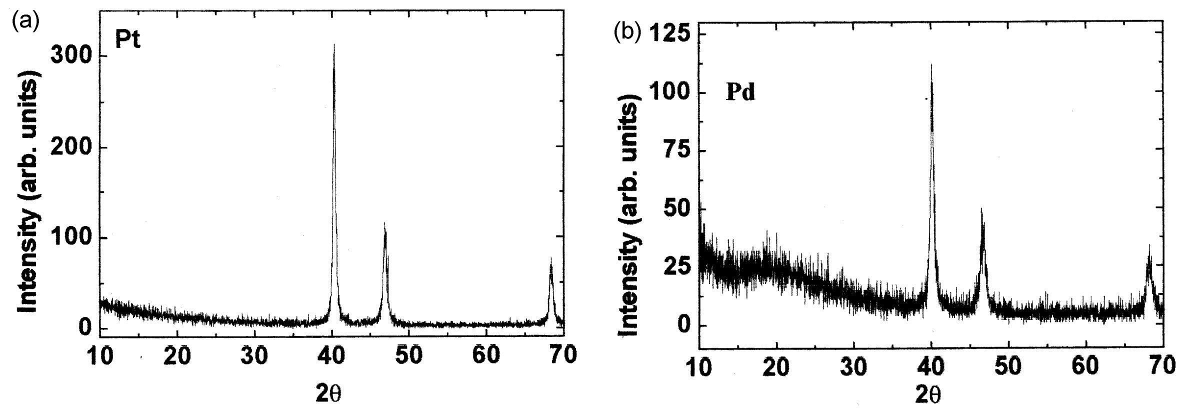

Figure 2. XRD diffraction pattern for (**a**) Pt and (**b**) Pd nanoparticles. Other conditions for spectra of Pd-Ag bimetallic nanoparticles at 1 : 1 molar ratio as in figure 1.

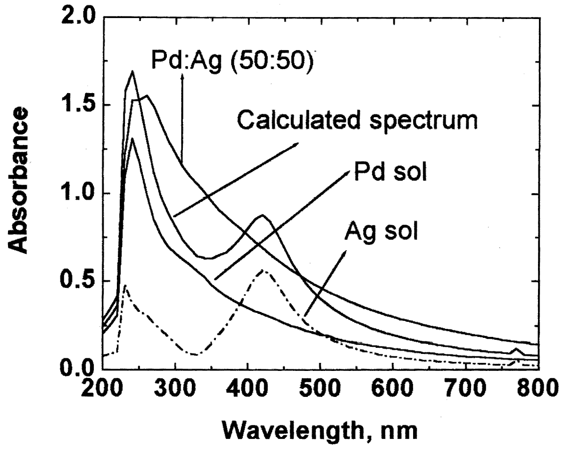

Figure 3. UV/Vis absorption spectra of individual and mixed particles (at ratio 1 : 1) of Pd and Ag prepared by microwave irradiation in ethylene glycol. Other conditions as in figure 1.

For mixed clusters studied at different molar ratios of Pd^{2+}/Ag^{+} ions (Pd^{2+} = 5% to 50%) the plasmon band of silver disappears almost completely at all the ratios. A representative case is shown in figure 3. For comparison, the calculated spectrum obtained by adding absorbance of Pd and Ag sol (at the same percentage, that is, 50%) for mixed Pd and Ag particles is also shown in the figure. It can be noted that the calculated spectrum obtained differs drastically from the experimentally observed spectrum for mixed particles. Similar phenomenon was observed at other compositions. This shows that damping of the silver spectrum occurs even in presence of minor quantities of Pd. The absence of even a shoulder at the absorption maximum for the silver plasmon band rules out a preferential reduction of silver. The similarity in the shape of the spectrum and the absence of any shift of the maximum at all the ratios studied also exclude preferential reduction of Pd ions followed by the reduction of silver which would have lead to silver-coated Pd clusters with a maximum at 420 nm. The obtained particles were quite stable and could not be precipitated. Therefore, the size of the particles was determined using dynamic light scattering experiments and is tabulated in table 2.

In order to have better knowledge of mixed particles sol, we have prepared separately a pure silver sol and a pure Pd sol which were then mixed in the ratio of 50 : 50 and compared with that of mixed particle sol prepared by simultaneous reduction of metal salts (figure 3). It was noticed that the observed spectrum was similar to that obtained in figure 3. As no additivity of the individual spectra was seen even in the present case, it clearly shows that there is substantial interaction between the particles. It is important to mention here that no care has been taken to reduce metal ions completely. Therefore, there exists a possibility of electron transfer from the metal to unreduced ions. An electron transfer explains the segregation of metals into the core-shell structure from the less noble metal to the ions of the more noble metal. Under such conditions core is systematically constituted of the more noble metal. However, there should be progressive change in the optical absorption of more noble metal in the presence of less noble metal ions.

It is pertinent to confirm whether the alloying process is diffusion controlled or not. Therefore, the mixed clusters were also prepared in glycerol. Figure 4 shows the evolution of spectra obtained on mixing Ag and Pd sol in glycerol. It can be noted that the spectrum obtained just after mixing shows features of silver plasmon band with substantial broadening. As discussed above, if the electron transfer is the only phenomenon occurring on mixing sol, we should not have observed the broadening of the peak. Due to high viscosity of glycerol, diffusion processes of the metal sol decreases and making it possible to monitor the changes spectrophotometrically. This strongly supports the conclusion that intimately alloyed clusters are formed.

3.3 *Formation of Pt/Ag bimetallic nanoparticles*

To further substantiate the above observation we have carried out studies for Pt/Ag mixed particles which were prepared by irradiating mixtures of 5×10^{-4} mol dm^{-3} Na_2PtCl_4 and 5×10^{-4} mol dm^{-3} $AgNO_3$ solutions at various molar ratios. However, overall metal ion concentration was kept constant at 5×10^{-4} mol dm^{-3}. Figure 5 shows the plasmon absorption band of particles obtained on microwave irradiation of Ag^+/Pt^{2+} ions at 1 : 1 ratio along with individual sols and calculated spectrum for Ag^+/Pt^+ ions at 1 : 1 molar ratio. Before and after irradiation, the solutions were free of precipitates. No scattered light was observed in the UV–Vis spectra of samples prior to irradiation. This ruled out the formation of AgCl that could have resulted from adding a chlorine-containing compound like Na_2PtCl_4 and solution containing Ag^+ ions. The sizes of the particles at 1 : 1 ratio were determined using light scattering experiments and are tabulated in table 2. It was observed that at all the studied Pt^{2+}/Ag^+ ions molar ratios (Pt^{2+} = 5% to 50%) the plasmon band at 420 nm vanishes instantly and is eventually replaced by monotonic decay of Pt particles. It is clear that the presence of Pt particles even in small quantities strongly affects the spectrum of Ag. No linear shift in the surface plasmon band of Ag was observed with increasing content of Pt metal.[30] However, this does not rule out the possibility of the formation of

Table 2. Colloidal dispersions obtained in ethylene glycol on co-reduction of $AgNO_3$ with different metal ions at 1 : 1 ratio after 60 s of irradiation. Total metal ion concentration is $0{\cdot}5 \times 10^{-3}$ mol dm^{-3}. Particle sizes determined by light scattering.

$AgNO_3$ + metal ion	PVP (wt %)	Mean size (nm)
Na_2PdCl_4	0·1	18
Na_2PtCl_4	0·1	16

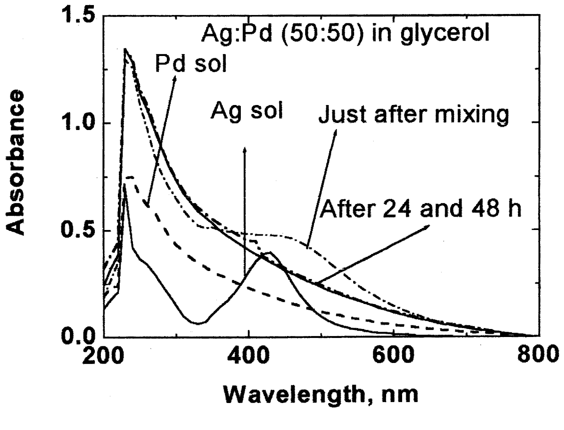

Figure 4. Evolution of the UV/Vis absorption spectra of the physical mixture of individual Pd and Ag nanoparticles in glycerol.

$(Ag)_{core}(Pt)_{shell}$ type of particles under our experimental conditions.

The optical absorption spectra rule out the possibility of the presence of isolated Ag clusters, which would otherwise give rise to Ag surface plasmon absorption peak. Although helpful, optical absorption measurement could not establish whether Ag and Pt form a homogenous alloy or if the nanoparticles have a core–shell structure. The surface plasmon absorption peak of Ag nanoparticle is in fact extremely sensitive to the presence of the transition metals and vanishes rapidly when Pt is added to Ag nanoparticles, independent of cluster structure and degree of alloying.[21]

To further confirm whether alloying of Pt/Ag particles occur on co-reduction of Ag and Pt salts under microwave irradiation, we have prepared individual sols of Ag and Pt. The individual sols were then mixed in various ratios. The observed spectra obtained after mixing were roughly similar to that obtained on irradiation of individual metal salt ions (data not shown). The small difference between the spectra obtained by individual mixing of sols or by irradiation of mixed salt solutions is attributed to the interfacial changes associated during formation of the particles. The possible faster reduction of Ag^+ can be explained on the basis of electrochemical arguments. The reduction of $Pt^{II}Cl_4^{2-}$ to Pt metal occurs at potential $E^o = +0{\cdot}74$ V. The reduction potential of Ag^+ to Ag metal in acidic solutions is $E^o = +0{\cdot}79$ V. Thus, Ag^+ is more noble species in our solutions. During irradiation, transfer of charge from less noble (Pt) to more noble Ag can take place. Thus, clusters of more noble metal (Ag in our case) form first. Under such conditions, on mixing individual sol the overall optical absorbance should have shown the features of silver plasmon band only. However, we have observed that metal salts irradiated simultaneously or on mixing individual sol results in almost similar spectra, which were neither equivalent to pure Ag nor Pt. This further confirms that the formed particles in figure 5 are due to alloy formation.

For the formation of alloy, it is necessary that the reduction of both metal ions take place simultaneously. Therefore, equal concentrations of metal ions were taken for making the mixed particles. However, the mechanism of alloying of small particles is still not clear. Kinetic considerations indicate that, for the two metals to mix, the diffusion coefficients need to be many orders of magnitude larger than those of the bulk materials.[31] It is suggested that, in addition to the collisional energy and the striking coefficient, the rates of nucleation and growth were determined mainly by the collisions between the atoms.[32–34] The reduction rate in microwave irradiation was so large that most of the ions were reduced before the formation of the nuclei and therefore the probability of the effective collisions between the atoms was higher. Due to this the probability of alloying increases and the resultant particles would have more mono-dispersity. As mentioned above for alloy formation inter-diffusion of metal sol should occur. Hence, this may be dependent on the viscosity of the medium. Indeed, when we attempted to prepare Ag/Pt sol in glycerol, we could observe a spectrum which was roughly similar to the additive spectrum

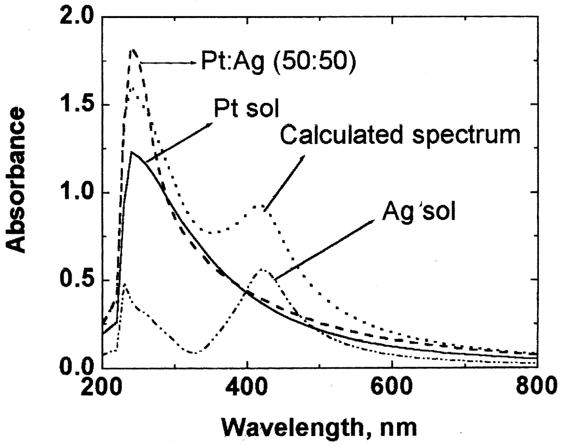

Figure 5. UV/Vis absorption spectra of Pt-Ag bimetallic nanoparticles at 1 : 1 molar ratio prepared by microwave irradiation in ethylene glycol. Other conditions as in figure 1.

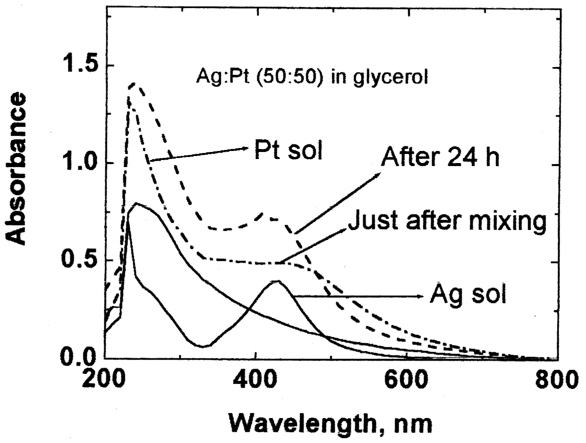

Figure 6. Evolution of the UV/Vis absorption spectra of the physical mixture of individual Pt and Ag nanoparticles in glycerol.

of the individual sols (figure 6). This shows that the solvent also plays some role in the formation of the particles.

4. Conclusions

The microwave irradiation allows the synthesis of Pd, Pt, Pd/Ag and Pt/Ag nano-aggregates. The UV–Vis absorption spectrum of such particles are noticeably different from those obtained with pure metals. The results suggest a substantial rate of inter-diffusion of particles at room temperature. Also, it appears that inter-diffusion is a function of viscosity of the medium. The interesting aspect of the present study is that we have shown that mixed metal nanoparticles can be prepared either by mixing of individual sols or by co-reduction of metal salts.

References

1. Daniel M C and Astruc D 2004 *Chem. Soc. Rev.* **104** 293
2. Schmid G 1992 *Chem. Rev.* **92** 1709
3. Lewis L N 1993 *Chem. Rev.* **93** 2693
4. Underwood S and Mulvaney P 1994 *Langmuir* **10** 3427
5. Hostetler M J, Zhong C J, Yen B K H, Anderegg J, Gross S M, Evans N D, Porter M and Murray R W 1998 *J. Am. Chem. Soc.* **120** 9396
6. Belloni J, Amblard J, Marignier L and Mostafavi M 1994 *Cluster of atoms and molecules* (ed.) H Haberland (New York: Springer-Verlag) vol. 2, p. 290
7. (a) Henglein A 1989 *Chem. Rev.* **89** 1861; (b) Henglein A and Meisel D 1998 *J. Phys. Chem.* **B102** 8364
8. Mulvaney P 1996 *Langmuir* **12** 788
9. Dimitrijevic N M, Bartels D M, Jonah C D, Takahashi K and Rajh T 2001 *J. Phys. Chem.* **B105** 954
10. Harada M, Asakura K, Ueki Y and Toshima N 1993 *J. Phys. Chem.* **97** 5103
11. Sun S, Murry C B, Weller D, Folks L and Moser 1989 *Science* **287** 2000
12. Yonezawa T and Toshima N 1995 *J. Chem. Soc., Farady Trans.* **91** 4111
13. Link S, Wang S Z L and El-Sayed M A 1999 *J. Phys. Chem.* **B103** 3529
14. Esumi K, Shiratori M, Ishizuka H, Tano T, Torigoe K and Meguro K 1991 *Langmuir* **7** 457
15. Silvert P Y, Vijaykrishnan V, Vibert P, Herrera-Urbina R and Elhsissen K T 1996 *Nanostruct. Mater.* **7** 611
16. Liz-Marzan L M and Philipse A P 1995 *J. Phys. Chem.* **99** 15120
17. Sato T, Kurado S, Takami A, Yonezawa Y and Hada H 1991 *Appl. Organomet. Chem.* **5** 261
18. Marignier J L, Belloni J, Delcourt M O and Chevalier J P 1985 *Nature* (*London*) **317** 344
19. Hodak J H, Henglein A, Giersig M and Hartland G V 2000 *J. Phys. Chem.* **B104** 11708
20. Chen Y and Yeh C S 2000 *Chem. Commun.* 371
21. Remita S, Mostafavi M and Delcourt M O 1996 *Radiat. Phys. Chem.* **47** 275
22. Belloni J, Mostafavi M, Remita S, Marignier J L and Delcourt M O 1998 *New J. Chem.* 1239
23. Wang Y and Toshima N 1997 *J. Phys. Chem.* **B101** 5301
24. Schmid G, West H, Malm J O, Bovin J O and Grenthe C 1996 *Chem. Eur. J.* **2** 1099
25. Toshima N, Yonezawa T and Kushihashi K 1993 *J. Chem. Soc., Faraday Trans.* **89** 2537
26. Yonezawa T and Toshima N N 1993 *J. Mol. Catal.* **83** 167
27. Toshima N and Hirakawa K 1997 *Appl. Surf. Sci.* **121/122** 534
28. Torigoe K, Nakajima Y and Esumi K 1993 *J. Phys. Chem.* **97** 8304
29. Creighton J A and Eadon D G 1991 *J. Chem. Soc., Farady Trans.* **87** 3881
30. Doudna C M, Bertino M F, Blum F D, Tokuhiro A T, Lahiri-Dey D, Chattopadhyay S and Terry J 2003 *J. Phys. Chem.* **B10**7 2996
31. Yasuda H and Mori H 1992 *Phys. Rev. Lett.* **69** 3747
32. Mostafavi M, Marignier J L, Amblard J and Belloni J 1989 *Radiat. Phys. Chem.* **34** 605
33. Wong W, Efrima S and Regev O 1989 *Langmuir* **14** 602
34. (a) Petit C, Lixon P and Pileni M P 1993 *J. Phys. Chem.* **97** 12974; (b) Pileni M P 1997 *Langmuir* **13** 3266; (c) Pileni M P 1993 *J. Phys. Chem.* **97** 6961