

Paramagnetic silica-coated gold nanoparticles

Corneliu Ghica · Petre Ionita

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Abstract Water soluble gold nanoparticles, obtained by the reduction of the gold (III) chloride with sodium borohydride in the presence of citric acid or thioctic acid, were covered with a paramagnetic silica layer using the Stober method, yielding a hybrid metallic-inorganic nanomaterial (gold nanoparticles, with an average size of 5 nm, embedded into silica nanoparticles, with an average size of 100 nm). The paramagnetic silica layer was formed by copolymerization of a paramagnetic silica precursor (derived from 3-aminopropyltrimethoxysilane) with tetramethoxyorthosilicate. The paramagnetic silica precursor was obtained by coupling 3-aminopropyltrimethoxysilane with 3-carboxy-proxyl free radical. TEM pictures show that each silica nanoparticle of about 100 nm in size embedded about 10 gold nanoparticles. These hybrid nanoparticles are quite stable and exhibit the expected paramagnetic characteristics, as seen by electron paramagnetic resonance. The accessibility of methanol through the silica layer was also studied. Depending on the capping ligands of the gold nanoparticles (citric or thioctic acid), different silica networks are formed, as seen by the mobility of the spin-label inside the silica layer. The EPR spectra showed that the paramagnetic silica layer is very robust and the mobility of the spin-probe inside the silica layer is very little affected by methanol. However, if spin-labeled thioctic acid protected gold nanoparticles were used in the material synthesis, the mobility of the spins

attached to the gold surface is quite high in the presence of methanol, while the spins embedded into the silica layer remains immobilized.

Introduction

Inorganic and metallic nanoparticles are one of the most robust nano-objects which can be obtained in high yield and large quantities. There is a constant interest in the study of such tiny objects, due to their possible technical applications as catalyst, colloids, templates, probes, carriers, etc [1–5].

Gold nanoparticles, as well as silica ones, have extreme stability and robustness, and their characteristics can be easily tailored to fit requested properties. This is also possible due to the endless functionalization surface approaches [6, 7].

Investigation of the advanced materials requires quite different techniques; for example, electron paramagnetic resonance (EPR) is suitable for studying systems that contains unpaired electrons. Organic stable free radicals covalently linked to nanostructures have been previously used to provide information about the dynamics and structure of such systems, as well as about the exchange mechanism and rate of the ligands exchange on the nanoparticle surface [8–10]. The line width and the shape of the EPR spectra are strongly dependent on the tumbling rate of the spin-label; besides, if the spin-labels are close to each other, a supplementary interaction between spins occurs, which can allow, in some cases, the accurate determination of the distance between adjacent spins [11–14].

Our previous work on spin-labeled gold nanoparticles [8, 14], as well as on spin-labeled silica materials [9],

C. Ghica
National Institute for Materials Physics, PO Box MG-7,
Bucharest-Magurele 077125, Romania

P. Ionita (✉)
Institute of Physical Chemistry, 202 Spl. Independentei,
Bucharest 060021, Romania
e-mail: pionita@icf.ro

showed that the free radicals attached to the nanostructure provide data that cannot be achieved easily by other methods, such as information about polarity, viscosity, and dynamics of the surrounding space of the spin-label, as all these dramatically affect the recorded EPR parameters. A stable free radical immobilized to the surface will provide useful information about processes which occur at the border between the adjacent phases.

For spin-labeled silica, as well for some gold nanoparticles, literature data showed that these materials can be used as oxidants for several types of substrates (i.e. alcohols) [15–19]. In the case of hybrid nanoparticles, such as gold nanoparticles embedded into bigger silica nanoparticles, to obtain information about the accessibility of some species through the silica layer toward the metallic core (where the catalytic reaction is supposed to take place), seems to be an insurmountable problem. In order to achieve any information about this process, we designed a study strategy which involves the covering of the gold core with a paramagnetic silica layer. The free stable radical covalently linked (and also embedded) into the silica layer will provide useful information about the accessibility of some other species from the outside of the hybrid nanoparticles towards the metallic core. This study has importance about understanding the catalytic effect of metal nanoparticles embedded into inorganic matrix. Moreover, for a system which contains spin-labeled gold nanoparticles embedded into spin-labeled silica layer, interesting features may result, as the two types of spins are in completely different environments.

Experimental

All chemicals and solvents were purchased from Aldrich, Merck, or Chimopar. TEM pictures were achieved on a Jeol 200 CX microscope operated at 200 kV. EPR spectra were recorded at room temperature using a Jeol spectrometer (typical settings: frequency 8.99 GHz, field 3,330 G, sweep width 100 G, sweep time 60 s, time constant 30 ms, gain 50, modulation frequency 100 kHz, modulation width 1 G).

Synthesis of gold nanoparticles

Citrate- [6] and thioctic acid- [7] protected water soluble gold nanoparticles were synthesized as literature data showed, by reduction of gold (III) chloride with sodium borohydride in the presence of a stabilizing agent (citric- or thioctic-acid). TEM pictures showed that nanoparticles with an average size of ~ 5 nm were mainly obtained [6, 7].

Synthesis of the silica spin-labeled precursor

The procedure is similar to that reported previously [20], for obtaining the spin-labeled silica precursor known as doxyl-TMOS (N-propyltrimethoxysilane-5-doxylstearamide): to 1 mmol of 3-aminopropyl-trimethoxysilane dissolved in 5 mL methanol was added 1.2 mmol of 3-carboxypropyl free radical in 5 mL methanol and 1.2 mmol of EEDQ (2-ethoxy-1-ethoxycarbonyl-1,2-dihydroquinoline). The reaction mixture was left for 2 days at room temperature and used directly for the synthesis of the silica-coated gold nanoparticles (the pure compound was not separated from the reaction mixture because the acidic aqueous work up required for separation causes the polymerization of the precursor [13]). $C_{15}H_{31}N_2O_5Si$, $M = 347$. ESI-MS: 370 (M+Na)⁺. EPR (MeOH): $a_N = 15.44$ G.

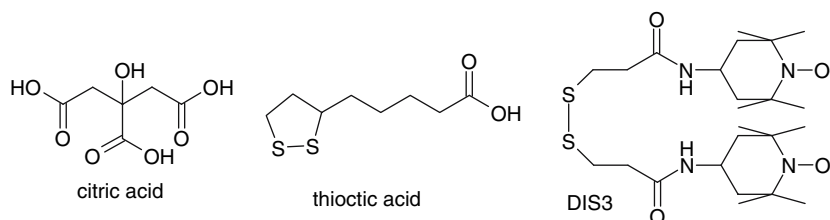
Synthesis of the spin-labeled gold nanoparticles

As prepared citrate and thioctic acid protected gold nanoparticles have been subjected to the spin-labeling procedure involving a disulfide diradical (DIS3, Fig. 1) [8, 14], in an exchange ligands type reaction. Typically, a mixture of gold nanoparticles and the DIS3 ligand (Fig. 1), in a 1–10 ratio, in aqueous methanol, were stirred overnight, then the solvent was partially removed under vacuum at no more than 50 °C; the mixture was filtered, and the solution subjected to dialysis. Using this procedure, it was possible to spin-label thioctic protected gold nanoparticles (as EPR showed), but not citrate protected ones. All our different attempts to label the citrate protected gold nanoparticles (changing solvents, reaction time, ratio between reactants, etc.) failed; in the presence of the disulfide diradical, the red solution turns to blue and aggregation occurs.

Coating with silica the gold nanoparticles

The general procedure is similar to that ones described in literature [1, 21, 22]: 1 mL 5×10^{-5} M of gold nanoparticles was mixed with 4 mL isopropanol, and under stirring, 0.5 mL of concentrated ammonia (25%) was added, followed by 0.5 mL 10^{-2} M TMOS and 0.05 mL 0.1 M of silica spin-labeled precursor; the last two steps were repeated hourly for 7 times, then the mixture was left overnight. Next day the solution was filtered through a 20 μ m filter, centrifugated, and the solid redispersed in methanol, followed by re-centrifugation (a total of 10 times repeated); afterwards the solid was dried in vacuum.

Fig. 1 Chemical structure of citric acid, thiocetic acid, and the disulfide diradical DIS3



Measuring the EPR rotational correlation time

The EPR parameter which usually characterizes the dynamics of the spin-label tumbling is the rotational correlation time τ , which can be calculated from Eq. 1, if the recorded EPR spectrum is in the so called slow regime mode (when the tumbling of the spin is restricted).

$$\tau = 6.5\Delta H \left(\sqrt{\frac{h_0}{h_{-1}}} + \sqrt{\frac{h_0}{h_{+1}}} - 2 \right) 10^{-10} \quad (1)$$

ΔH is the peak-to-peak line width (in Gauss) of the central line, and h_0 , h_{+1} , and h_{-1} are the heights of the low field, middle and high field lines of the ^{14}N hyperfine components.

If the recorded EPR spectrum is close to the so called rigid regime mode, the rotational correlation time τ may be approximated from Eqs. 2 and 3.

$$\tau = a(1 - S)^b \quad (2)$$

$$S = 2A'_{ZZ}/2A_{ZZ} \quad (3)$$

$2A_{ZZ}$ is the extreme separation in the rigid limit spectrum and $2A'_{ZZ}$ is the separation at temperature T . Considering a Brownian diffusion model and an intrinsic line width of 3 G, the values of a and b are 5.4×10^{-10} s and -1.36 , respectively [23].

Results and discussion

Water soluble gold nanoparticles

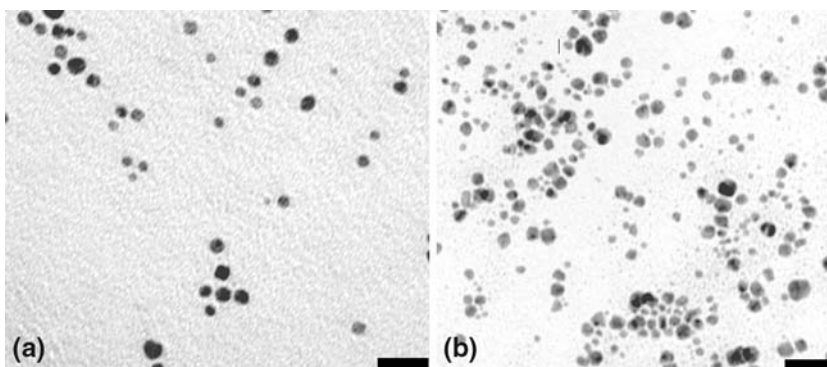
Water soluble gold nanoparticles were obtained by the well known methods [6, 7]: mainly, the gold salt is reduced with sodium borohydride in the presence of capping ligands (in our case, citric- or thiocetic acid). Figure 2 shows the TEM images of the synthesized gold nanoparticles, as seen by transmission electron microscopy (TEM). The average size of the gold nanoparticles is about 5 nm.

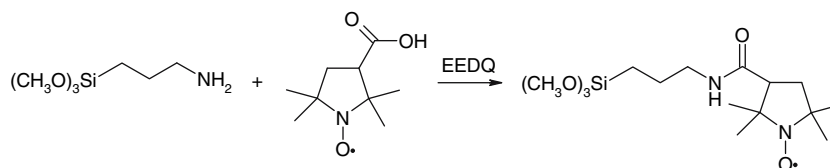
The spin-labeled silica precursor

The spin-labeled aminopropyl-silica precursor was obtained by a classical coupling reaction, which have the advantages of high yield; thus, 3-carboxy-proxyl free radical reacts in the presence of EEDQ with (3-aminopropyl)trimethoxysilane, yielding the desired compound (Scheme 1).

ESI-MS and EPR analysis of the reaction mixture confirm the formation of the new compound: (i) in the ESI-MS spectrum, the peak at 370 corresponds to the $(M+\text{Na})^+$; (ii) the EPR spectrum (Fig. 3) shows the expected triplet of the unpaired electron, with the hyperfine coupling constant $a_N = 15.44$ G; moreover, the third line (high field) is smaller than the other two, indicating the slow tumbling of the molecule, due to the attachment of the spin-label to the

Fig. 2 TEM pictures of water soluble gold nanoparticles used in this study: **a**—citrate protected; **b**—thiocetic acid protected; scale bar: 20 nm





Scheme 1 The synthesis of the spin-labeled silica precursor

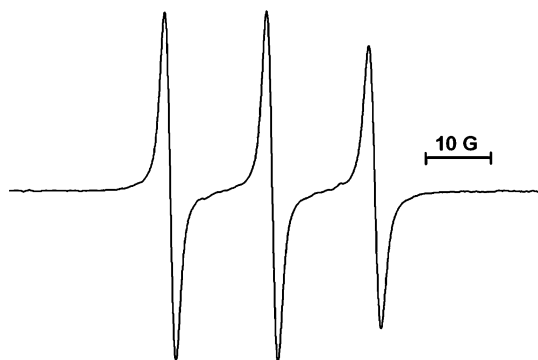


Fig. 3 EPR spectrum of the spin-labeled silica precursor

silane moiety [20]. The rotational correlation time τ calculated from Eq. 1 is 1.17×10^{-10} s.

The spin-labeled thioctic acid protected gold nanoparticles

The spin-labeled thioctic acid protected gold nanoparticles were obtained by the common exchange ligands reaction [8, 14], using a ratio of 10 between the incoming DIS3 ligand (Fig. 1) and the gold nanoparticles; this ratio was necessary in order to achieve a good EPR signal of the spin labeled gold nanoparticles (Fig. 4), which seems to be more difficult to be labeled in this way, due to the fact that

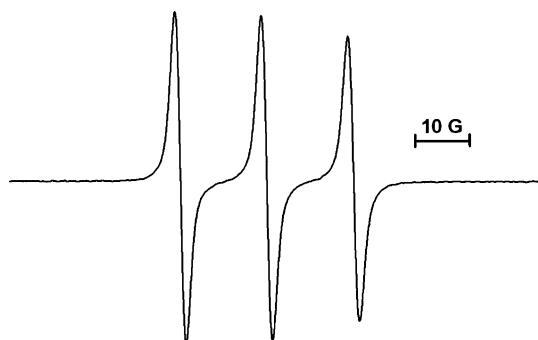


Fig. 4 EPR spectrum of the spin-labeled thioctic acid protected gold nanoparticles

there are two sulfur atoms which bond to the gold surface, or said in the other way, there are two bonds which should break to free the outgoing ligands. The rotational correlation time (τ) (calculated from Eq. 1 is 0.81×10^{-10} s, very similar with that of the spin-labeled silica precursor. As usual for the spin labeled gold nanoparticles, the third line (high field) is smaller than the other two, indicating the same slow tumbling of the supramolecular assembly, due to the attachment of the spin-label to the gold surface [8, 14].

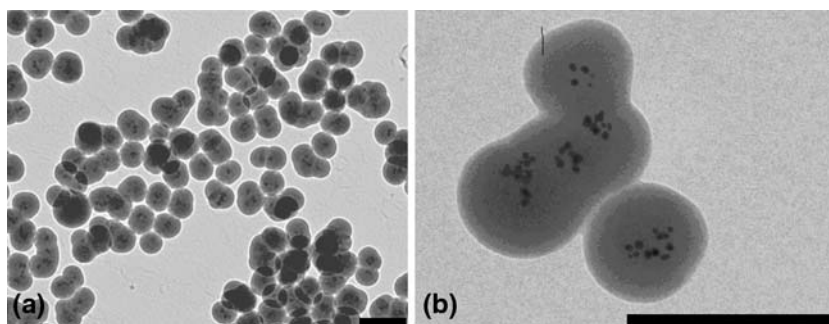
As we said also in experimental part, we were not able to spin-label the citrate protected gold nanoparticles using this procedure, even after several different attempts; probably the citrate ligands are quite easily to be removed by the disulphide (which have a strong adherence to the gold surface), and led to aggregation of the starting gold nanoparticles (color changes to blue).

Hybrid nanoparticles

Hybrid metallic-inorganic nanoparticles were obtained using the water soluble gold nanoparticles as seeds in the formation of the larger silica nanoparticles [1]. Thus, gold nanoparticles are covered with a silica layer, which is formed by slowly hydrolysis of the silica precursors (the spin-labeled precursor and TMOS). TEM pictures (Fig. 5) show the complete embedding of the gold nanoparticles into the silica layer; however, we noticed that each silica nanoparticle contains more than one gold nanoparticle (usually around ten, Fig. 5b). This behavior can be explained by the formation in the first instance of well separated silica nanoparticles which contain each only one seed of gold nanoparticle, and during time they aggregate, yielding finally bigger silica nanoparticles which embed several gold nanoparticles.

Our attempt to visualize the initial formation of separated mono-seeded silica nanoparticles by collecting probes at different time reaction failed. Literature data showed that it is possible that the mono-seeded silica nanoparticles to (self) assembly into bigger aggregates [24]; several attempts were also performed in order to reduce the possible aggregation [25].

Fig. 5 Typical TEM picture of gold nanoparticles embedded into silica nanoparticles (a); detailed view of the gold nanoparticles embedded into silica layer (b); scale bar: 200 nm



EPR spectra of the paramagnetic hybrid nanoparticles

The silica layer, formed on gold nanoparticles, contains the paramagnetic probe, the stable free radical (the proxyl moiety). This spin-label, embedded also into the silica layer (being covalently linked to silica), provide information about the micro-environment, at molecular level. The recorded EPR spectra of the solid dry samples are shown in Fig. 6.

At the first glance, the two EPR spectra are quite different. Comparing them, we can directly say that for the first one (citrate protected gold nanoparticles embedded into spin-labeled silica), the spin-label is very immobilized (with an estimated rotational correlation time 1.5×10^{-7} s), while for the second one (thioctic acid protected gold nanoparticles embedded into spin-labeled silica), the spin-label is much more mobile (with an estimated rotational correlation time 2.3×10^{-8} s). The mobility of the covalently linked spin-label gives information about the silica layer structure.

Normally, the differences between the two synthesized hybrid nanomaterials should be correlated only with the differences between the embedded gold nanoparticles, namely their size and their capping ligands. Their size difference or their polydispersity is too small to have such major impact, comparatively with the big differences regarding the capping ligand (citric or thioctic acid, Fig. 1). The following differences might be found between them: (i) thioctic acid binds extremely strong to the gold surface, comparatively with the citric acid (the later can be easily

removed by transferring the nanoparticles into an organic solvent); (ii) the capping layer thickness is different, the molecule of thioctic acid being longer; (iii) the packing of the capping agent is different (due to different molecular hindrance). At this point, we do not have a full explanation of the differences in the EPR spectra, but we suppose that the different capping agent induces a different silica network formation around the gold nanoparticles.

Literature data showed also that changes in pH, ionic strength, polarity of the solvent mixture, etc. may greatly affect the stability of the nanoparticles [26]. Different ways were tried to initialize the formation of the hybrid nanoparticles and to stabilize them [27–29].

Our further experiment was to monitor the accessibility and diffusion of methanol through the dry silica layer which covers the gold nanoparticles; this can be easily achieved by EPR spectroscopy, as the motion of a spin probe covalently linked to a dry solid change if a liquid is added. Unexpectedly, the EPR spectra change very little when the solid dry material was suspended in methanol; literature data showed that, in some cases, the mobility of a spin-probe linked to a dry solid increase dramatically in the presence of methanol [9, 12, 13]. The recorded EPR spectra showed a small increase in the mobility of the spin probe, with an estimated rotational correlation time of 4.5×10^{-8} s and 1.9×10^{-8} s, respectively (Fig. 7).

The only possible explanation for this case is that the spin-label is captured in a very rigid silica network, which is fully cross-linked and does not leave much space for mobility of the spin label, even after addition of methanol.

Fig. 6 EPR spectra of the dry hybrid nanoparticles: left-EPR spectrum of citrate protected gold nanoparticles embedded into spin-labeled silica; right-EPR spectrum of thioctic acid protected nanoparticles embedded into spin-labeled silica

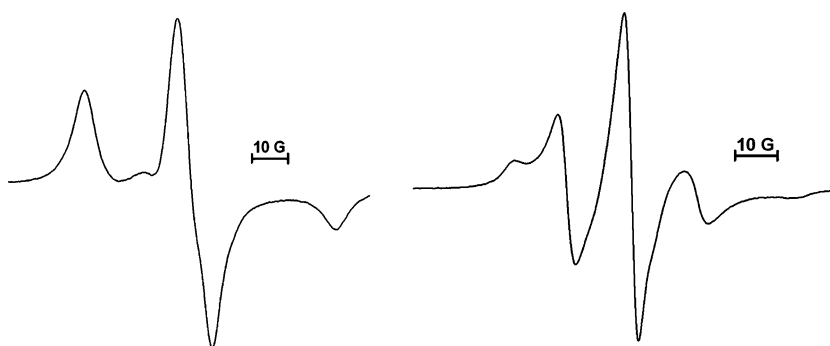


Fig. 7 EPR spectra of the hybrid nanoparticles suspended in methanol: left-EPR spectrum of citrate protected gold nanoparticles embedded into spin-labeled silica; right-EPR spectrum of thioctic acid protected nanoparticles embedded into spin-labeled silica

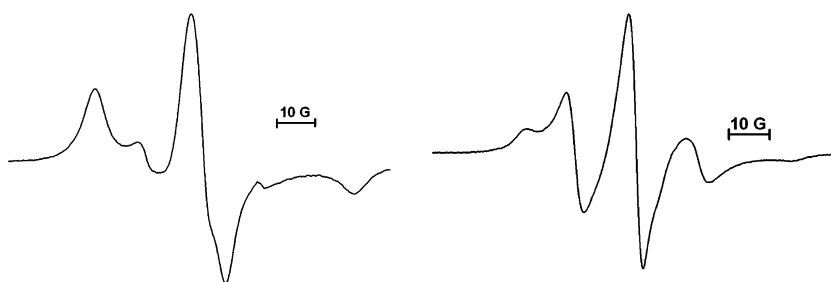
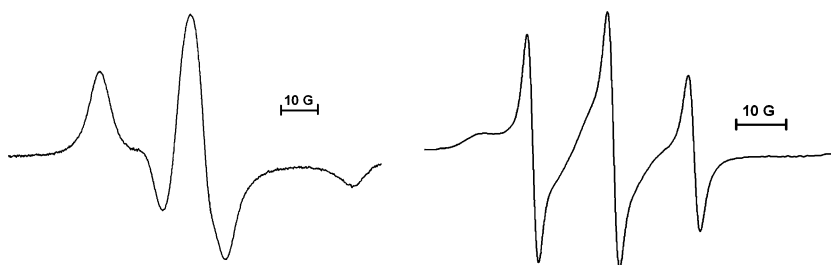


Fig. 8 EPR spectra of the hybrid nanoparticles which contain spin-labeled gold nanoparticles embedded into the silica layer; left-dry sample; right-in the presence of methanol



Using a silica imprinting approach [30], it was demonstrated that at the core-shell interface only siloxy (Si–O–Si and Si–OH) groups are present. Gold nanoparticles introduced only in structured silica channels seems to confirm this result [31]. The EPR spectra recorded for nitroxyl radicals immobilized on ultra-fine silica are similar to ours [32].

EPR spectra of the hybrid nanoparticles which contain spin-labeled gold nanoparticles embedded into the silica layer

The next step in our study was to try to use spin-labeled gold nanoparticles [8] instead of gold nanoparticles; as was mentioned before, we succeeded to label only the thioctic acid protected gold nanoparticles, and not the citrate-protected ones. EPR spectrum of the dry sample (Fig. 8, left) is different from the previous one (Fig. 6), with an estimated rotational correlation time of 6.8×10^{-8} s; addition of methanol dramatically changes the EPR spectrum (Fig. 8, right). In the presence of methanol, the EPR spectrum looks like a two component spectrum, with the well known broad signal for immobilized spins, superposed to a sharp triplet, common to mobile spins. We suppose that these two types of superposed EPR signals arise from the two different spins, which are in two different environments. The spins embedded into the rigid silica layer give the broad lines, as they have very little or no mobility, while the spins attached to the gold surface have a much higher mobility, as they are embedded into the organic layer.

Conclusions

Paramagnetic silica-coated gold nanoparticles with an average size of 100 nm were obtained. Each silica nanoparticles embedded inside about or more than 10 gold nanoparticles. Depending on the capping ligands of the gold nanoparticles (citric or thioctic acid), different silica networks are formed, as seen by the mobility of the spin-label inside the silica layer. The EPR spectra showed that the paramagnetic silica layer is very robust and the mobility of the spin-probe inside the silica layer is very little affected by methanol. Using spin-labeled gold nanoparticles as seeds for the formation of hybrid gold-silica nanoparticles, we noticed that, in the presence of methanol, the mobility of the spins attached to the gold surface is extremely high, comparatively with that ones embedded into the silica layer.

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References

- Liu S, Han M (2005) *Adv Funct Mater* 15:961
- Kim J, Lee JE, Jang Y, Kim DW, An K, Yu JH, Hyeon T (2006) *Angew Chem Int Ed* 45:1
- Zhelev Z, Ohba H, Bakalova R (2006) *J Am Chem Soc* 128:6324
- Guari Y, Thieuleux C, Mehdi A, Reye C, Corriu RJP, Gallardo SG, Philippot K, Chaudret B (2003) *Chem Mat* 15:2017
- Alonso B, Clinard C, Durand D, Veron E, Massiot D (2005) *Chem Commun* 1746
- Grabar KC, Allison KJ, Baker BE, Bright RM, Brown KR, Freeman RG, Fox AP, Keating CD, Musick MD, Natan MJ (1996) *Langmuir* 12:2353

7. Roux S, Garcia B, Bridot JL, Salome M, Marquette C, Lemelle L, Gillet P, Blum L, Perriat P, Tillement O (2005) *Langmuir* 21:2526
8. Chechik V, Wellsted HJ, Korte A, Gilbert BC, Caldararu H, Ionita P, Caragheorgheopol A (2004) *Faraday Discuss* 125:279
9. Ionita P, Tudose M, Constantinescu T, Balaban AT, Appl Surf Sci (accepted)
10. Wheeler KE, Lees NS, Gurbiel RJ, Hatch SL, Nocek JM, Hoffman BM (2004) *J Am Chem Soc* 126:13459
11. Ottaviani MF, Mollo LJ (1997) *Colloid Interface Sci* 191:154
12. Ruthstein S, Frydman V, Goldfarb D (2004) *J Phys Chem B* 108:9016
13. Baute D, Frydman V, Zimmermann H, Kababya S, Goldfarb D (2005) *J Phys Chem B* 109:7807
14. Ionita P, Caragheorgheopol A, Gilbert BC, Chechik V (2004) *Langmuir* 20:11544
15. Ionita P, Gilbert BC, Chechik V (2005) *Angew Chem Int Ed* 44:3720
16. Kashiwagi Y, Chiba S, Anzai J (2003) *New J Chem* 27:1545
17. Ciriminna R, Blum J, Avnir D, Pagliaro M (2000) *Chem Commun* 1441
18. Fey T, Fischer H, Bachmann S, Albert K, Bolm C (2001) *J Org Chem* 66:8154
19. Ciriminna R, Bolm C, Fey T, Pagliaro M (2002) *Adv Synth Catal* 344:159
20. Caldararu H, Caragheorgheopol A, Savonea F, Macquarrie DJ, Gilbert BC (2003) *J Phys Chem B* 107:6032
21. Graf C, Dembski S, Hoffman A, Ruhl E (2006) *Langmuir* 22:5604
22. Hall SR, Davis SA, Mann S (2000) *Langmuir* 16:1454
23. Goldman S, Bruno G, Freed JJ (1972) *Phys Chem* 76:1858
24. Nooney RI, Thirunavukkarasu D, Chen Y, Josephs R, Ostafin AE (2003) *Langmuir* 19:7628
25. Bagwe RP, Hillard LR, Tan W (2006) *Langmuir* 22:4357
26. Osterloh F, Hiramatsu H, Porter R, Guo T (2004) *Langmuir* 20:5553
27. Kobayashi Y, Katakami H, Mine E, Nagao D, Konno M, Marzan LML (2005) *J Colloid Interface Sci* 283:392
28. Chen W, Cai WP, Liang CH, Zhang LD (2001) *Mat Res Bull* 36:335
29. Santos IP, Juste JP, Marzan LML (2006) *Chem Mat* 18:2465
30. Poovarodom S, Bass JD, Hwang SJ, Katz A (2005) *Langmuir* 21:12348
31. Gu JL, Shi JL, You GJ, Xiong LM, Qian SX, Hua ZL, Chen HR (2005) *Adv Mat* 17:557
32. Tsubokawa N, Kinoto T, Endo T (1995) *J Mol Catal* 101:45