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[11] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-173106 (**1**), CCDC-173107 (**2**), and CCDC-173108 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). Diffraction experiments were performed on a Siemens SMART System CCD diffractometer and solved by employing the SHELX-TL software package. **1**: Space group: $Pa\bar{3}$; $a = 14.6083(10)$ Å, $V = 3117.4(4)$ Å^3, $Z = 4$, $R = 0.0424$, $R_w = 0.1156$, GOF = 0.901. **2**: Space group: $Pa\bar{3}$; $a = 14.324(6)$ Å, $V = 2939(2)$ Å^3, $Z = 4$, $R = 0.0764$, $R_w = 0.1683$, GOF = 0.890. **3**: Space group: $P2/n$; $a = 11.727(3)$, $b = 8.370(2)$, $c = 27.150(8)$ Å, $\beta = 97.414(5)^\circ$, $V = 2642.5(13)$ Å^3, $Z = 2$, $R = 0.0502$, $R_w = 0.1390$, GOF = 1.048.

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A Nanoscale Hybrid System Based on Gold Nanoparticles and Heteropolyanions**

Cédric R. Mayer, Sophie Neveu, and Valérie Cabuil*

The preparation of hybrid organic–inorganic systems has witnessed major growth in the last few years.[1] Increasingly sophisticated nanocomposites with greater added value have been obtained. The interest in such systems lies in the synergy that arises through association of organic and inorganic moieties. An especially interesting class of materials are hybrids based on nanoparticles.[2] These are expected to find many applications as sensors or in the fields of magnetism, electronics, and optics. Gold nanoparticles are often involved in the synthesis of nanoscale hybrid systems. An interesting example is the formation of dimer and trimer nanocrystals by exploiting the recognition between oligonucleotide-functionalized Au nanoparticles.[3] The stability of such hybrids is strongly related to the irreversibility of the functionalization of the nanoparticles. In the case of Au, Ag, and CdS, alkylthiol groups provide a strong link to the particles.[3]

Smaller than gold nanoparticles and intermediate between the colloidal and molecular ranges, the polyoxometalates (POMs) have recently received increasing attention.[4–8] Polyoxometalates based on Mo or W constitute a full class of nanobuilding blocks. These metal oxo clusters play a role in many areas.[4] Their applications are due to a combination of several valuable properties,[5] and to their ability to behave as fully oxidized/(photo)reducible compounds.[4c] Their involvement in hybrid organic–inorganic materials is of great interest, and attention was recently paid to the development of ordered assemblies of POMs in such hybrid systems.[6] Although numerous studies deal with hybrids including POMs, only a few describe the preparation of hybrids with strong interactions between the organic and inorganic entities. One of these is a hybrid polymer in which organoimido polyoxomolybdates are pendant groups on polystyrene chains.[7] Some of us recently described the synthesis of new hybrid networks based on hydrosoluble polymer chains (polyacrylamide) cross-linked by hydrosoluble tetrafunctionalized polyanions.[8]

Here we report the synthesis of a new nanoscale hybrid system in which gold nanoparticles (4–12 nm) are associated with the prefunctionalized polyoxometalate γ-$[\mathrm{SiW_{10}O_{36}(RSi)_2O}]^{4-}$ ($\mathrm{R = HSC_3H_6}$), designated here as $[\mathrm{POM(SH)_2}]^{4-}$. The organic part R plays two main roles: it forms a covalent link to gold particles through the thiol group

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and a covalent link with the polyanion through the trimethoxysilane group.

The mixing of functionalized nanoparticles and POM is governed by the necessity to avoid reduction of the POM; therefore, it is added in the last step. Hence, a suitable strategy for obtaining POM–Au nanosystems is to synthesize the functionalized POM first, and to adsorb it onto the surface of particles in a second step.[9] In the synthesis, the ratio of the concentration of $[POM(SH)_2]^{4-}$ to that of $HAuCl_4$ was fixed at 1/6. This ratio was chosen to ensure that the surface area of the particles is sufficient to avoid the presence of unadsorbed POM in solution.

$[POM(SH)_2]^{4-}$ consists of a divacant γ-$[SiW_{10}O_{36}]^{8-}$ polyanion onto which a dimeric siloxane RSiOSiR is grafted through four Si-O-W bridges (Figure 1 a). This polyanion was chosen for its easy functionalization with organosilyl groups. Moreover the tetrabutylammonium (TBA^+) countercation associated with $[POM(SH)_2]^{4-}$ provides the POM species with solubility in mixtures such as CH_3CN/H_2O or CH_3CN/toluene.

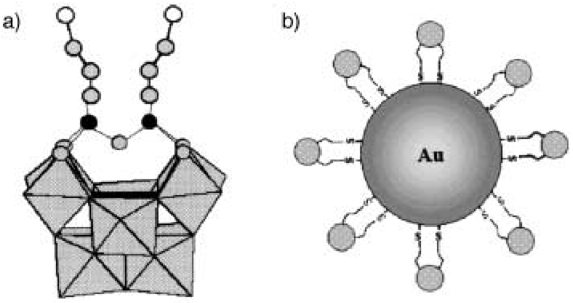

Figure 1. a) Polyhedral representation of the difunctionalized polyanion γ-$[SiW_{10}O_{36}(RSi)_2O]^{4-}$ ($R = HSC_3H_6$). b) Idealized picture of $[POM(SH)_2]^{4-}$ linked through R-S-Au bridges to an Au nanoparticle.

Many studies have been devoted to the preparation of Au nanoparticles, especially by chemical reduction. We used methods described elsewhere[1, 11] to obtain particles with average diameters of 4, 8, and 12 nm. In the first method, which leads to large particles, an aqueous solution of $HAuCl_4$ was reduced by $NaBH_4$ in the presence of trisodium citrate as a stabilizer.[11] The hybrid system was then obtained by pouring the aqueous dispersion of gold particles into a solution of $[POM(SH)_2]^{4-}$ in acetonitrile. The functionalized gold nanoparticles were recovered as a purple solid and could be dispersed in organic solvents such as acetonitrile, DMF, and DMSO (Figure 2 a).

In the second method, leading to smaller particles, $HAuCl_4$ was reduced in toluene with various amounts of tetraoctylammonium bromide ($NOct_4Br$). A ratio of $[NOct_4]^+/[AuCl_4]^-$ of 4.44/1[2] leads to particles 4–5 nm in diameter (Figure 2 c). At a lower ratio (1.11/1), the particles were larger (8 nm; Figure 2 b). As in the previous method, a solution of polyanion in acetonitrile was added. The POM-coated particles were then recovered after various treatments and were dispersible in acetonitrile.

The nanohybrids synthesized by these two methods are stable in solution for several months. They were fully characterized by various spectroscopic methods. Powder X-ray diffraction, transmission electron microscopy (TEM), and UV/Vis spectroscopy were used to characterize the Au particles. The powder X-ray diffraction pattern of gold particles obtained from the aqueous solution showed the characteristic 111, 200, 220, 331, 222, and 400 reflections of fcc gold.[12] The TEM of hydrosols allowed the particle diameter to be estimated (see Figure 2). The UV/Vis spectra show a broad, particle-size-dependent band which shifts from $\lambda_{max} =$ 520 (4–5 nm) to $\lambda_{max} = 530$ nm (12 nm; Figure 3).

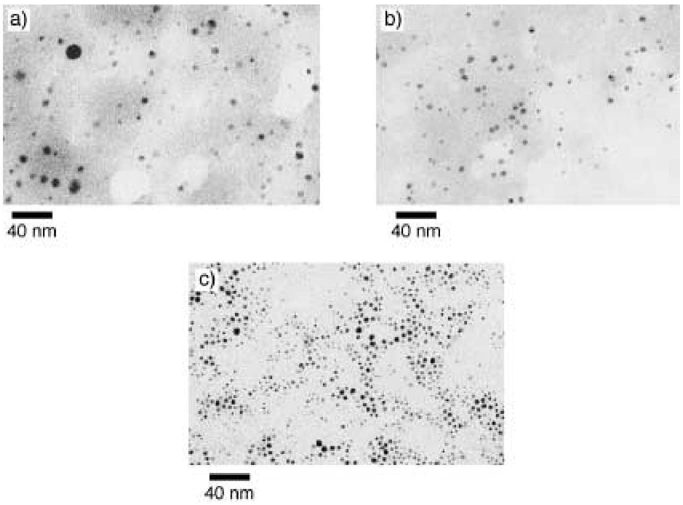

Figure 2. TEM images of hybrid nanoparticles derived from colloidal Au particles of diameter a) 12, b) 8 and c) 4–5 nm.

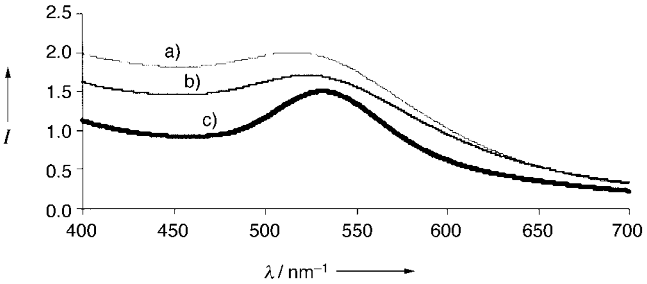

Figure 3. UV/Vis spectra of colloidal solutions of Au nanoparticles of diameter a) 4–5, b) 8, and c) 12 nm.

IR and ^{183}W NMR spectroscopy were used to characterize the $[POM(SH)_2]^{4-}$ moieties. The latter confirmed the presence of POM in the nanosystems: A solution of $POM(SH_2)$–Au nanoparticles obtained from a hydrosol led to three lines with relative intensity of 2:1:2 (see Supporting Information) and the same chemical shifts as ungrafted $[POM(SH)_2]^{4-}$. These ^{183}W NMR signals are in good agreement with those of the functionalized POM γ-$[SiW_{10}O_{36}(RSi)_2O]^{4-}$.[10]

The presence of a covalent link between the two nanobuilding blocks POM and Au was confirmed by IR spectroscopy, in particular by studying of the vibrational band of the thiol groups. For all samples, the IR spectrum shows the same $\nu_{asym}(W{=}O_{ter})$ and $\nu_{asym}(W\text{-}O_b\text{-}W)$ stretching bands as that of the starting polyanionic framework, but it no longer exhibits the characteristic $\nu_{asym}(SH)$ band in the region of 2563 cm^{-1} (Figure 4). This confirms the participation of all the thiol groups in the attachment of POM to gold nanoparticles.

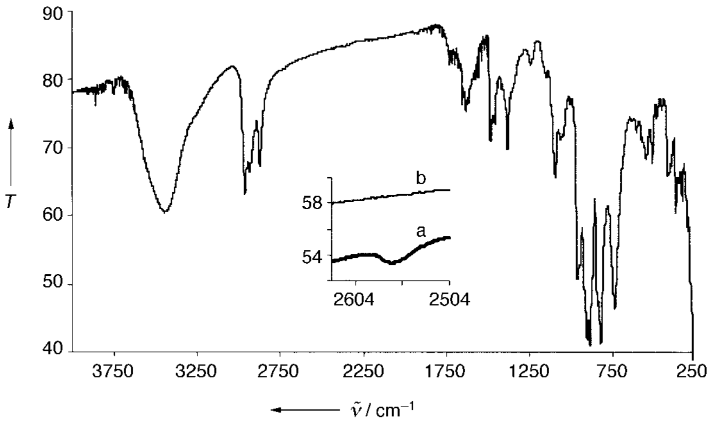

Figure 4. IR spectrum of $POM(SH)_2$ – Au nanoparticles of 12 nm diameter and abscissa (transmission T) expansion of the region of the $\nu_{asym}(SH)$ band showing a) the presence of the vibrational band in the starting POM and b) its absence in the hybrid material.

Further evidence for a covalent link between the POM species and the Au nanoparticles through the thiol groups is given by the following experiment: We tried to fix a functionalized polyanion without thiol groups, namely, γ-$[SiW_{10}O_{36}(ClC_3H_6Si)_2O]^{4-}$ ($[POM(Cl_2)]^{4-}$), solved in acetonitrile, on Au particles synthesized in water. Evaporation of the acetonitrile led to separation of the polyanion and the Au nanoparticles, which were dispersed in aqueous solution. Similar results were obtained with Au particles synthesized in toluene: irreversible aggregation of nanoparticles was observed after the evaporation of toluene, as described by Brust et al.[13] The behavior of the product obtained with such polyanions is thus completely different from what is observed with $[POM(SH)_2]^{4-}$. This confirms the specific ability of the latter to link covalently to Au nanoparticles through its thiol groups.

The attachment of POM on the particles surface results in particular TEM images (see Figure 2). Even when grids contain many particles (Figure 2c) they always seem to be well separated. This could be due to the presence of POM spacers which induce a steric repulsion between the nanoparticles. The TBA^+ counterions associated with $[POM(SH)_2]^{4-}$ remain associated with the POM – Au nanoparticles, and this allows them to be dispersed in organic media.

In contrast to the observations in our previous work on maghemite nanoparticles in coexistence with POM in a hybrid network,[14] here we find the $[POM(SH)_2]^{4-}$ directly linked to nanoparticles. To our knowledge, this is the first nanoscale hybrid system based on Au nanoparticles and POM species with a covalent link between the two nanobuilding blocks (Figure 1b). Thus, it also differs from the Rh nanoparticles functionalized by another POM ($[P_2W_{15}Nb_3O_{62}]^{9-}$) through electrostatic interactions between POM and nanoparticle, described by Finke et al.[15] In our case, the (sulfanylpropyl)silyl ligand avoids the desorption of $[POM(SH)_2]^{4-}$ from the particles. Thus, these nanosystems are potentially promising for catalyst applications. Likewise, they can be used as nanobuilding blocks for the realization of hybrid materials because it is also possible to use functionalized counterions of the polyanion. Such a material would have a valuable combination of the properties of both the POM and the Au species.

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