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Gold Nanoparticles in Organic Capsules: A Supramolecular Assembly of Gold Nanoparticles and Cucurbituril

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Abstract: Gold nanoparticles (≤1 nm) have been encapsulated inside cucurbit[7]uril (CB[7]) by vapor deposition or chemical reduction in aqueous solutions. CB[7] has unique host properties compared with CB[5] and CB[6]. The particle size distribution obtained with CB[5] and CB[6] is similar to that obtained in the absence of CBs and the particles obtained are much too large to be incorporated inside the organic capsules. When gold nanoparticles are prepared inside CB[7] the resulting supramolecular assembly has shape-selective properties for gold interactions with amines, cyanide, and quaternary ammonium ions. Thus, CB[7] has the potential to be used in applications such as selective adsorption, sensing, and catalysis.

Keywords: capsules • cucurbiturils • gold • nanoparticles • supramolecular chemistry

Introduction

Although it was known that gold(III) acted as a Lewis acid to catalyze cycloisomerizations,[1] Haruta et al. showed that metallic gold particles are also very efficient at promoting the low-temperature oxidation of CO and that the size of the particle is one of the key parameters that controls the catalytic activity.[2] This work triggered intense research into the preparation of gold nanoparticles on various solid supports so that the newly discovered catalytic activity of gold could be used in other reactions.[3–10]

A general problem of metal nanoparticles is their tendency to undergo agglomeration, which increases their particle size, and therefore, dramatically reduces the catalytic activity.[5,11] Two general strategies have been developed to stabilize the particle size of the metal, namely, supporting the metal nanoparticles on suitable solid surfaces or by using suitable ligands.[3,4,12–16] New possibilities for gold catalysis could be developed if one could stabilize gold nanoparticles by encapsulating them in a structured host to combine the unique catalytic properties of gold nanoparticles with reaction shape-selectivity effects.

Organic capsules would be suitable hosts to improve the stability and solubility of gold nanoparticles in common solvents. In this context, nanoparticles have recently been encapsulated in cyclodextrins by means of laser ablation of colloidal gold suspensions in the presence of cyclodextrins.[17] However, owing to their conical shape, cyclodextrins cannot ensure permanent encapsulation of the incorporated nanoparticle, and as a result of the larger dimensions of the capsule entrance, nanoparticles are free to exit the host and diffuse into the solution in which they agglomerate. In this work, we have achieved permanent encapsulation and stabilization of gold nanoparticles (≤1 nm) in a cucurbituril (CB) that contains seven glycoluril units (CB[7]).

CBs are organic capsules that are shaped like a pumpkin with a larger diameter in the center of the capsule than at the rims.[18–20] In addition, the two portals of CBs are flanked by polar carbonyl groups that exert a strong influence on access to the interior of the capsule and also on the association constant through electrostatic interactions.[21–26] By using these capsules we have encapsulated gold nanoparticles that are highly stable in the presence of a large variety of ligands and reagents. The resulting supramolecular assembly of gold nanoparticles encapsulated in CB are promising

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for applications in gold-catalyzed reactions and in nanotechnology.[13,27,28]

Results and Discussion

Encapsulation of gold nanoparticles within CB[7] was achieved by gas-phase adsorption of gold atoms onto dry powders by using a 1:1 molar ratio of gold/CB[7] in a vapor deposition chamber. Alternatively, gold nanoparticles can be encapsulated by using a liquid-phase process that involves solutions of CBs in a 1:1 mixture of water/ethanol and the reduction of $HAuCl_4$ by $NaBH_4$. All CBs were soluble at 10^{-4} M in this solvent mixture. Importantly, irrespective of the preparation procedure employed, visual differences in color were observed that depended on the size of CB used, that is, whether it was CB[5], CB[6], or CB[7]. Figure 1 shows a photograph of the solutions after addition of $NaBH_4$ in the presence of CBs of different sizes. It can be anticipated that these color variations are related to changes in the particle size distribution of gold in the nanometer length scale because it is well known that λ_{max} and the shape of the surface plasmon band in the visible region, which are characteristic for gold nanoparticles, depend on the particle size.[5]

Figure 1. Photograph of suspensions of colloidal gold particles in H_2O/EtOH 1:1, which were formed in the presence of (from left to right) no CB, CB[5], CB[6], and CB[7].

The size of the gold nanoparticles was measured by TEM. Figure 2 shows selected images of the gold nanoparticles formed by gas adsorption or liquid-phase reduction in the absence and in the presence of CB[7]. For Au@CB[7], obtained either by gas-phase adsorption or by $NaBH_4$ reduction, the particle size distribution was significantly narrower and with an average size that was considerably smaller than when the process was repeated in absence of CB[7]. The CB[7] samples obtained have been labeled Au@CB[7]GP for the sample obtained by gas-phase adsorption and Au@CB[7]BH_4 for the sample obtained by $NaBH_4$ reduction. These data suggest that for CB[7], gold atom diffusion inside the capsule or effective interaction between CB[7] and $AuCl_4^-$ has occurred to control the size of the gold nanoparticles. The particle size distributions for Au@CB[7]GP and Au@CB[7]BH_4 were determined by statistical analysis of ≈200 particles. Figure 3 shows the particle size distribution for some of the samples prepared. Au@CB[7]GP and Au@CB[7]BH_4 had a large percentage of nanoparticles that were sufficiently small enough to be included inside the CB[7] capsule (≤1.0 nm). For Au@CB[7]BH_4, about 20 % of Au particles are much too large to occupy internal positions.

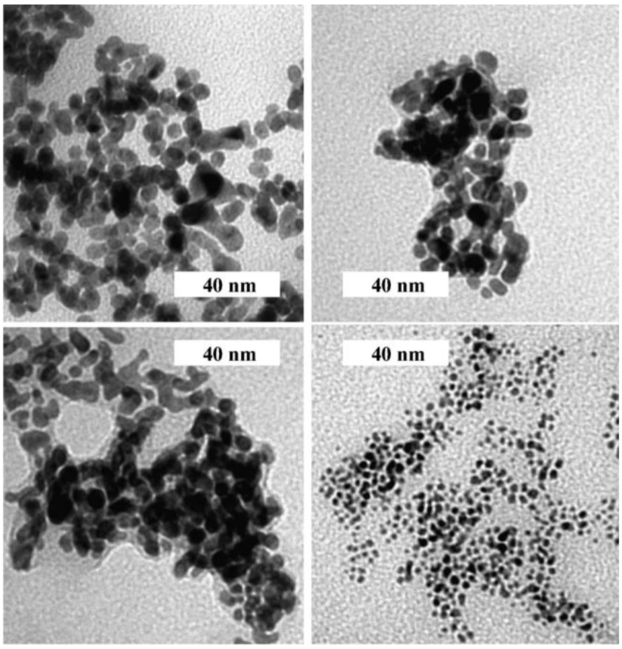

Figure 2. TEM images of gold nanoparticles obtained in the absence of CB (top, left) and in the presence of CB[5] (top, right), CB[6] (bottom, left), and CB[7] (bottom, right).

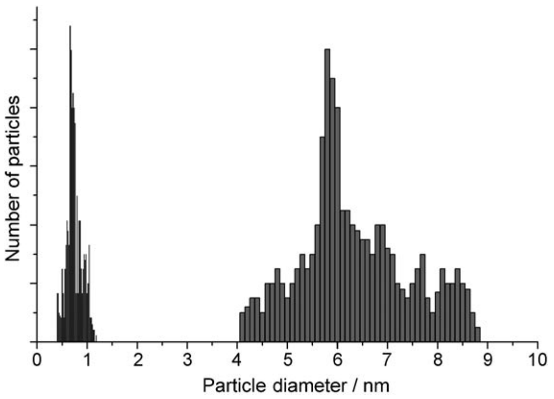

Figure 3. Size distribution of gold nanoparticles prepared by $AuCl_4^-$ reduction in the absence (right) and presence (left) of CB[7].

For Au@CB[7]GP, about 50 % of the gold atoms form clusters that were sufficiently small enough to be accommodated within CB[7], whereas the rest of the particles were too large to go inside the organic capsule.

Additional high-angle annular dark field (HAADF) imaging studies of the samples prepared in the presence of CB[7] confirm the presence of a majority of gold nanoparticles with diameters below 1.5 nm (Figure 4, left). Likewise high-resolution electron microscopy (HREM) images reveal that these nanoparticles are crystalline with regular fcc structures (Figure 4, right).

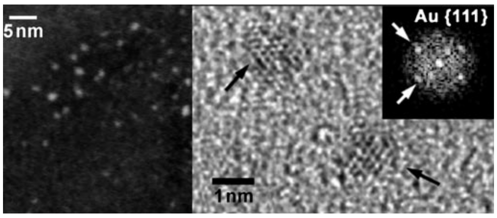

Figure 4. Left: HAADF image obtained on Au@CB[7]BH_4 that shows Au nanoparticles (white dots) in the order of 1 nm in diameter. Right: HREM detail of these Au nanoparticles. Note the presence of {111} type planes of the fcc structure in both the image and the corresponding digital diffractogram (inset).

The generality of the above finding that particle size could be controlled by forming the nanoparticles in the presence of CBs of the appropriate diameter was addressed by using the positively charged $[Au(NH_3)_4]^{3+}$ complex to form colloidal gold. CBs interact with cations through the negative carbonyl groups of the portals[22,24] and it is possible that negatively charged $AuCl_4^-$ as a precursor behaves differently from the positive $[Au(NH_3)_4]^{3+}$ complex. However, we have also observed that $NaBH_4$ reduction of $[Au(NH_3)_4]^{3+}$ in the presence of CBs gave similar results to those obtained when $AuCl_4^-$ was used.

Interestingly, when CB[5] and CB[6], which have smaller entrances to their cavities than CB[7] (2.4 and 3.9 Å, respectively, relative to 5.4 Å for CB[7]),[29] were used to encapsulate gold, TEM images of the resulting samples show that the majority of the gold particles are equal or larger than 4.0 nm and have the same particle distribution as those prepared in the absence of cucurbiturils. These results suggest that gold is not encapsulated in CB[5] and CB[6], and smaller particles are not stabilized by CB[5] and CB[6] (Figure 5).

The reason for this contrasting behavior between CB[7] and CB[5] and CB[6] cannot be owing to different abilities to stabilize small gold nanoparticles. It is more likely that the different behaviors are observed because it is more difficult to include gold atoms or their precursors inside CB[5] and CB[6] than inside CB[7]. On the other hand, it is possible that stabilization of gold nanoparticles can occur by encapsulation within the cavities of CB[7] and/or by stabilization of externally formed gold nanoparticles by CB to prevent particle growth because CB surrounds and interacts with the external surface of the particle. Considering the size of the cavity in CB[7], only particles with a diameter of 1.0 nm or less can be accommodated inside, which corresponds to the results shown in Figure 3, and applies to 80% of the total number of gold atoms.

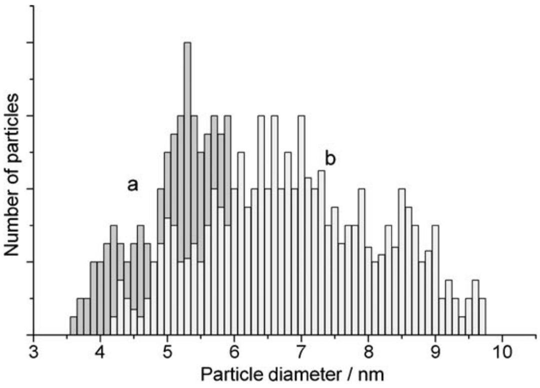

Figure 5. Size distribution of gold nanoparticles prepared by $AuCl_4^-$ reduction in the presence of a) CB[5] and b) CB[6].

To investigate the possibility of diffusing gold atoms through the pores of different CBs, we have carried out semiempirical calculations at the MM2 level. The energy changes that occur when a single gold atom follows a trajectory in which it approaches a CB molecule perpendicular to the portal planes, passes through the center of the organic capsule, and exits through the opposite portal have been estimated. These calculations were performed for CB[5], CB[6], and CB[7], and the results are summarized in Figure 6. For CB[5], only a shallow minimum is estimated for the gold atom located outside the CB and interacting close to the carbonyl oxygen atoms of the portals. Notably, a huge energy barrier is predicted for the gold atom to enter the cavity. In other words, the situation in which a gold atom is inside the CB[5] cavity appears to be energetically unfavorable with respect to the situation in which the gold atom is outside the cavity. Analogously, for CB[6], when the gold atom interacts with the carbonyl oxygen atoms outside the portal or at the center of the capsule, clear minima in energy are estimated. According to the theoretical model, the problem for CB[6] occurs when the gold atom crosses through the portals for which energy barriers of about 7 kcal

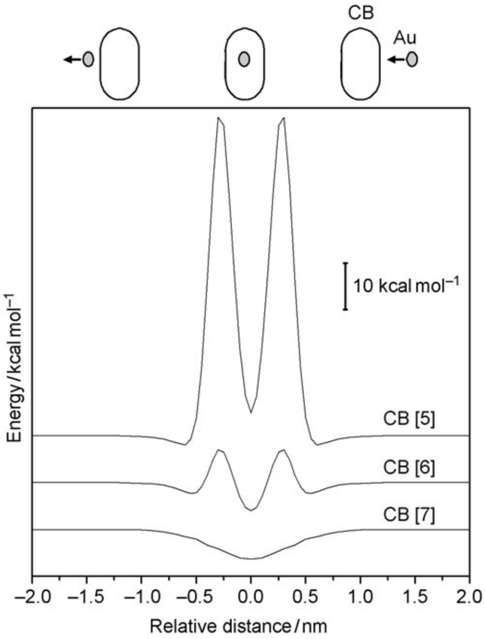

Figure 6. Energy variations estimated by MM2 calculations of a system that consists of a gold atom and a CB capsule as a function of the distance between the centers of the atom and CB.

mol^{-1} are estimated. The situation for CB[7] is completely different than for CB[5] and CB[6]. Importantly, the energy barrier for the penetration of a gold atom into the cavity disappears, and the situation in which a gold atom is at the geometrical center of CB is exothermic by 6 $\mathrm{kcal\,mol}^{-1}$. Therefore, the theoretical calculations support the experimental results in the sense that for CB[5] and CB[6] encapsulation of gold atom should be disfavored, whereas CB[7] can, in principle, accommodate gold atoms without passing any energy barrier because the gold atom at the center of the capsule is in a clear energy minima with respect to the energy of the atom outside CB[7]. A simple calculation based on the volumes of CB[7] (0.279 nm^3) and gold atoms (0.013 nm^3) indicates that undeformed CB[7] can host up to a few tens of atoms, which corresponds to a cluster of the size expected to fit inside the CB[7] capsule. This number of gold atoms agrees relatively well with the count that can be made from the HREM image (see Figure 4).

The same type of semiempirical calculations show that AuCl^{4-} has no opportunity to enter any of the CB molecules studied. Thus, the most reasonable rationalization of gold cluster encapsulation when AuCl^{4-} is used as a precursor is that reduction of AuCl^{4-} by $\mathrm{BH_4}^-$ to form gold atoms must occur prior to entering the capsule.

To address the internal versus external location of gold nanoparticles for CB[7], we carried out extraction of gold nanoparticles from the aqueous phase into a toluene phase for aqueous solutions that contained CB[5], CB[6], CB[7], and those without CB by using tetraoctylammonium bromide (TOABr) as a phase transfer agent following the procedure described for the two-phase preparation of gold nanoparticles.[5] The results show that all of the gold can be transferred from the aqueous solutions that do not contain CB and those containing CB[5] or CB[6] into the toluene phase, whereas 90 % of the gold remains in the aqueous solution when it contains CB[7] because the particle size distribution of the sample is very similar to the distribution before treatment with tetraoctylammonium bromide. Migration of gold nanoparticles to toluene from aqueous solutions that contain CB[5] and CB[6] is reflected by the remarkable change in the UV-visible spectra of the aqueous solutions before and after treatment with TOABr. In addition, Figure 7 shows that there was a blueshift in $\lambda_{\max}$ for the surface plasmon band for Au@CB[7] relative to gold nanoparticles in the presence of CB[5] or CB[6]. Figure 7 shows selected spectra that illustrate the dramatic variations in the spectra for CB[5] and CB[6] after extraction with toluene, and also the fact that there is almost no change for CB[7]. These results firmly indicate that there is a strong interaction between the small gold nanoparticles and CB[7] to keep the nanoparticles in the aqueous phase.

To provide further evidence for the stabilization of gold nanoparticles by CB[7], we subjected Au@CB[7]$\mathrm{BH_4}$ to treatment with an excess of tetrabutylammonium cyanide. The ability of CN^- to form a strong complex with gold ions is well established. Subsequently, gold nanoparticles that had been formed in the absence of CBs or in the presence of CB[5] and CB[6] totally disappeared and were dissolved in water in the presence of CN^-. Again Au@CB[7] showed contrasting behavior and remained almost unaltered after this harsh treatment, as shown by UV-visible spectroscopy.

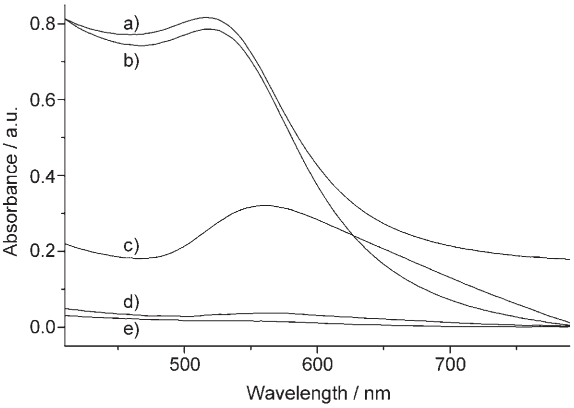

Figure 7. UV-visible transmission spectra of aqueous colloidal gold nanoparticles before and after treatment with the phase transfer agent TOABr. a) Au@CB[7]$\mathrm{BH_4}$ before, b) Au@CB[7]$\mathrm{BH_4}$ after treatment, c) Au/CB[6] before treatment, d) Au/CB[6] after treatment, and e) colloidal Au solution in the absence of CBs treated with TOABr in toluene.

Phase separation of gold occurs when aqueous solutions that do not contain CBs or in solutions that contain CB[5] and CB[6] are heated at reflux. However, aqueous solutions that contain Au@CB[7] were stable after the solutions had been heated at reflux for prolonged periods.

Careful nanoanalytical experiments by scanning transmission electron microscopy were also conducted to obtain further direct evidence on the encapsulation of gold particles inside the CB[7] capsule. In particular, electron energy loss spectra (EELS) were obtained from purely surface locations of the smaller fraction of gold nanoparticles, the sizes of which could fit the CB[7] internal space. To avoid any interference from the underlying holey carbon grid in the EELS signal of these particles, only those particles that were clearly in positions over holes on the grid were considered for analysis. This configuration is depicted in the experimental HREM image of Figure 8 (top). On particles like these, a 0.5 nm electron probe was placed on the surface on the hole side, at a distance of at least three to four times the probe width from the grid. By using very short acquisition times, in the order of one second, and under conditions in which there was no sample drift, EELS spectra were obtained that showed a very weak carbon K-edge signal (Figure 8, bottom right). This result can be considered unequivocal evidence for the presence of an organic layer that surrounds the smaller metal nanoparticles. Owing to the much slower cross section of the nitrogen K-edge relative to the carbon K-edge, and the smaller number of nitrogen atoms present in CB[7], it was not possible to detect this element in the EELS spectra acquired under our experimental conditions. After acquisition of the EELS spectra, the nanoparticles were analyzed by X-ray energy dispersive spectroscopy (XEDS) to avoid any subtle modification in structure of the

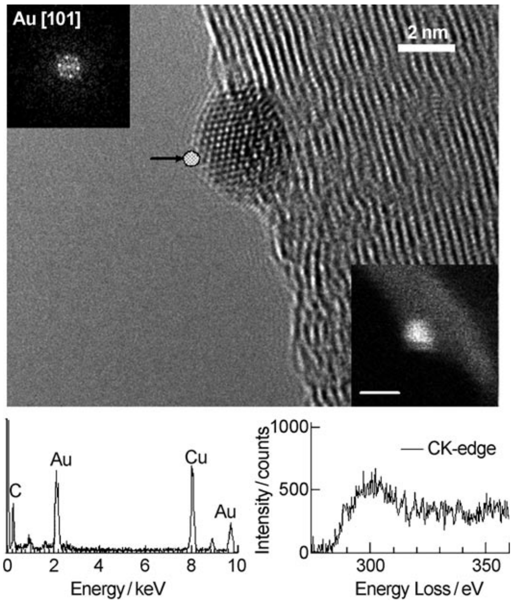

Figure 8. HREM image (top) of a gold nanoparticle that depicts the geometrical configuration used to perform the EELS nanoanalysis experiments. Note that a portion of the surface projects into the vacuum (no support interference). The arrow and dashed circle indicate the location and approximate probe width used to record the EELS spectra. The HAADF image inset shows an Au particle (ca. 1 nm) on which the EELS spectrum (bottom right) was obtained. XEDS results (bottom left) obtained on the particle show Au signals and a Cu signal from the grid.

surface by the electron beam. Importantly, XEDS analysis indicates that, within the detection limits, gold is the only element present in these particles (Figure 8, bottom left). Thus, we have been unable to detect chlorine in the samples, which indicates that the gold atoms are zerovalent. This result is in good agreement with the observations obtained by HREM.

To observe some kind of shape selectivity effect, we treated the Au@CB[7]BH_4 with amines of various sizes. It was expected that, depending on their size, gold nanoparticles could interact with smaller amines and become inaccessible to larger amines. Therefore, an aqueous solution of Au@CB[7]BH_4 was treated with ethylendiamine, methylamine, and triphenylamine, such that the amount of amine equaled that of the Au in solution. Results from Figure 9 clearly show that there is a relationship between the disappearance of the surface plasmon band and the nature of the amine. Indeed, triphenylamine interacts with Au nanoparticles considerably less than smaller amines, which is expected for protected Au nanoparticles.

With regards to the specific properties of CBs compared with other organic capsules, and in particular cyclodextrins (CDs), we attempted to perform similar studies with Au@CDs as those presented above for CBs. However, although vapor deposition and $NaBH_4$ reduction of $AuCl_4^-$ in the presence of CDs were apparently also successful for including gold nanoparticles inside α, β, and γ-CD capsules, massive agglomeration of Au takes place when the solutions are allowed to stand. The colloidal gold suspensions are unstable and do not persist under these conditions. TEM images of Au@CDs show the presence of very large gold particles (average size over 20 nm). Thus, we interpret this instability and particle growth by assuming that even though gold nanoparticles could have been incorporated inside CDs in the formation step, these conical capsules cannot retain the nanoparticles and migration outside the organic host upon standing for prolonged periods or heating the aqueous solution occurs, owing to the larger dimensions of one of the CD portals. Under these conditions, the gold nanoparticles that are released will easily agglomerate to form large Au nanoparticles. On the other hand, the very special pumpkin shape and dipolar structure of CBs would be responsible for effective encapsulation of gold nanoparticles and their corresponding stability.

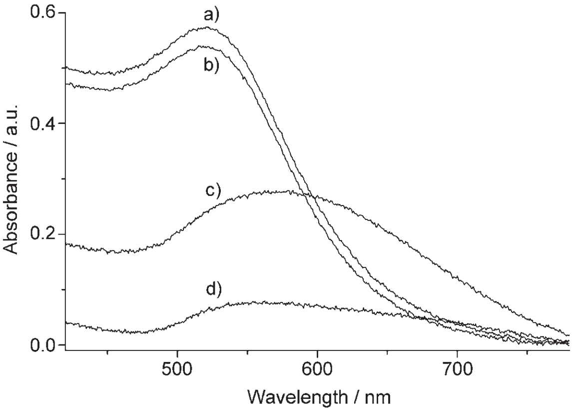

Figure 9. UV-visible transmission spectra of an aqueous colloidal solution of Au@CB[7]BH_4 before (a) and after addition of equimolar amounts (Au/probe = 1) of triphenylamine (b), methylamine (c), or ethylendiamine (d).

Conclusion

In conclusion, in the present work we have shown that the size of metal nanoparticles can be controlled by encapsulation in CB[7], which shows unprecedented behavior at stabilizing very small gold nanoparticles. Gold clusters can be incorporated by adsorption from the gas phase or by reduction of $AuCl_4^-$ in solution. We have found that gold nanoparticles stabilized by CB[7] do not interact with cyanide or large amines, and cannot be extracted by tetraoctylammonium bromide. Prolonged heating does not lead to gold agglomeration. CB[7] is also unique at stabilizing gold nanoparticles compared with cyclodextrins, which upon standing or heating lead to phase separation of gold from aqueous solutions.

Experimental Section

Preparation of gold nanoparticles by vapor deposition: A given amount of gold metal was placed in a ceramic boat in a vapor deposition chamber. An equimolar amount of the appropriate CB was also placed in a shallow bed in the appropriate position of the vapor deposition chamber. The chamber was sealed and a vacuum of 10^{-7} Torr was reached. At this pressure, the gold crucible was heated to a temperature of 1200 °C. Gold sublimed on the CB sample opposite. For CB[5] and CB[6], the final sample appeared as a metallic mirror covering the white powder. In contrast, for CB[7], the solid became slightly pink and no mirror was formed. After vapor deposition, the CB samples were characterized by chemical analysis and TEM.

Preparation of Au@CB[7]BH$_4$: $HAuCl_4$ (0.672 mg) (10^{-4} M) was added at room temperature to a stirred solution of CB[7] (2.32 mg) (10^{-4} M) in a 1:1 mixture of water/ethanol (20 mL), and the solution allowed to mix for 15 min. Then, a 0.1 M solution of $NaBH_4$ (50 μL) in ethanol was added. The solution became immediately colored, which indicated the reduction of Au^{III} to form gold nanoparticles. TEM studies were performed by diluting this suspension about 1000 times with toluene and sonicating the diluted mixture before depositing one drop of solution onto a carbon/copper grid. The solvent was allowed to evaporate at ambient temperature. Identical experimental procedures were followed for CB[5] and CB[6], but in these cases the colloids were not stable upon reduction with $NaBH_4$ and spontaneously separated from the liquid phase upon standing.

The gold content of the Au@CB[7] samples was determined by quantitative atomic absorption spectroscopy by using standards that were calibrated by dissolving the solid at 60 °C in a 1:1 HNO_3/HCl mixture. UV-visible spectra of the Au@CB[7] samples were recorded in solution by using a Shimadzu PC4140 spectrophotometer before treating the ethanol/water mixture with $NaNO_3$ to precipitate Au@CB[7].

Particle size was estimated by TEM by using a 100 kV Philips microscope. A drop of a suspension that contained gold nanoparticles encapsulated in CB was placed on a conductive graphitized grid.

Extraction with TOABr: An aqueous solution (3 mL) of gold nanoparticles prepared in the presence of CB[5], CB[6], or CB[7] (1 mg) was stirred with TOABr (3 mg) in toluene (3 mL) for 10 min at room temperature. After this time, the aqueous phase was collected and UV/Vis spectra of these solutions were recorded. In many cases, the intensity of the surface plasmon band was significantly reduced at the same time as the toluene phase became intensely colored. However, for Au@CB[7]BH$_4$ the organic phase was practically colorless and the UV/Vis spectrum of the aqueous solution remained constant after treatment.

Treatment of gold nanoparticles/CB solutions with CN$^-$: An aqueous solution (3 mL) of gold nanoparticles (1 mg) prepared in the absence or in the presence of CB[5], CB[6], or CB[7] (1 mg) was stirred at room temperature for 15 min in the presence of equivalent amounts of tetrabutylammonium cyanide (Au/CN$^-$ molar ratio equal to 1). After this time, the solutions were studied by UV/Vis spectroscopy, which revealed the disappearance of the surface plasmon band in many cases because the gold nanoparticles had dissolved. In contrast, for Au@CB[7]BH$_4$, the intensity of the UV/Vis absorption band experienced a small decrease of about 20 %.

Shape-selective interaction of Au@CB[7]BH$_4$ with amines: An aqueous solution (3 mL) of Au@CB[7]BH$_4$ (1 mg) was stirred at room temperature with equimolar amounts of the appropriate amine that had been previously dissolved in water (volume amine/volume water = 0.01). After 10 min, stirring was stopped and UV/Vis spectra of the solutions were recorded. The amines that were used in this study were methylamine, aniline, triphenylamine, and ethylendiamine. Control experiments with an aqueous solution of colloidal gold, which had been prepared according to the Turkevich procedure, in the absence of CB[7] show that all of the amines were able to interact with the nanoparticles to give the complete disappearance of the surface plasmon band.

Preparation of Au/CDs: Gold nanoparticles were incorporated into α, β, and γ-cyclodextrin by vapor deposition and also by $NaBH_4$ reduction by following analogous procedures to those described above. The samples were studied by TEM, which indicated large particle sizes. When these samples were suspended in water, phase separation of gold occurred in 3 h, which indicated that no permanent encapsulation had occurred.

Acknowledgements

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[1] G. Lemière, V. Gandon, N. Agenet, J.-P. Goddard, A. de Kozak, C. Aubert, L. Fensterbank, M. Malacria, *Angew. Chem.* **2006**, *118*, 7758; *Angew. Chem. Int. Ed.* **2006**, *45*, 7596.
[2] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* **1987**, 405.
[3] M. Haruta, M. Date, *Appl. Catal. A* **2001**, *222*, 427.
[4] M. Haruta, *Stud. Surf. Sci. Catal.* **2003**, *145*, 31.
[5] M.-C. Daniel, D. Astruc, *Chem. Rev.* **2004**, *104*, 293.
[6] S. Carrettin, J. Guzman, A. Corma, *Angew. Chem.* **2005**, *117*, 2282; *Angew. Chem. Int. Ed.* **2005**, *44*, 2242.
[7] A. Corma, P. Serna, *Science* **2006**, *313*, 332.
[8] L. Prati, M. Rossi, *J. Catal.* **1998**, *176*, 552.
[9] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely, G. A. Attard, G. J. Hutchings, *Top. Catal.* **2004**, *27*, 131.
[10] D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362.
[11] A. Wolf, F. Schuth, *Appl. Catal. A* **2002**, *226*, 1.
[12] B. J. Hornstein, R. G. Finke, *Chem. Mater.* **2003**, *15*, 899.
[13] D. Astruc, F. Lu, J. R. Aranzaes, *Angew. Chem.* **2005**, *117*, 8062; *Angew. Chem. Int. Ed.* **2005**, *44*, 7852.
[14] S. K. Ghosh, S. Nath, S. Kundu, K. Esumi, T. Pal, *J. Phys. Chem. B* **2004**, *108*, 13963.
[15] S. Praharaj, S. K. Ghosh, S. Nath, S. Kundu, S. Panigrahi, S. Basu, T. Pal, *J. Phys. Chem. B* **2005**, *109*, 13166.
[16] G. Budroni, A. Corma, *Angew. Chem.* **2006**, *118*, 3406; *Angew. Chem. Int. Ed.* **2006**, *45*, 3328.
[17] J.-P. Sylvestre, A. V. Kabashin, E. Sacher, M. Meunier, J. H. T. Luong, *J. Am. Chem. Soc.* **2004**, *126*, 7176.
[18] K. Kim, N. Selvapalam, D. H. Oh, *J. Incl. Phenomena Macrocycl. Chem.* **2004**, *50*, 31.
[19] W. L. Mock, *Compr. Supramol. Chem.* **1996**, *2*, 477.
[20] P. Cintas, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *17*, 205.
[21] R. Hoffmann, W. Knoche, C. Fenn, H.-J. Buschmann, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 1507.
[22] D. Whang, J. Heo, J. H. Park, K. Kim, *Angew. Chem.* **1998**, *110*, 83; *Angew. Chem. Int. Ed.* **1998**, *37*, 78.
[23] Y.-M. Jeon, J. Kim, D. Whang, K. Kim, *J. Am. Chem. Soc.* **1996**, *118*, 9790.
[24] W. Ong, A. E. Kaifer, *J. Org. Chem.* **2004**, *69*, 1383.
[25] K. Moon, A. E. Kaifer, *Org. Lett.* **2004**, *6*, 185.
[26] W. Ong, A. E. Kaifer, *Angew. Chem.* **2003**, *115*, 2214; *Angew. Chem. Int. Ed.* **2003**, *42*, 2164.
[27] A. Abad, C. Almela, A. Corma, H. Garcia, *Tetrahedron* **2006**, *62*, 6666.
[28] A. Abad, P. Concepción, A. Corma, H. García, *Angew. Chem.* **2005**, *117*, 4134; *Angew. Chem. Int. Ed.* **2005**, *44*, 4066.
[29] J. Lagona, P. Mukhopadhyay, S. Chakrabarti, L. Isaacs, *Angew. Chem.* **2005**, *117*, 4922; *Angew. Chem. Int. Ed.* **2005**, *44*, 4844.

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