Au–silica nanoparticles by "reverse" synthesis of cores in hollow silica shells†

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Core–silica shell nanoparticles were prepared in a "reverse" manner by nucleation and growth of Au cores within hollow silica nanospheres.

Recently, interest in nanomaterials has been growing tremendously due to their attractive and unique physical and chemical size-dependent properties.[1] Metal nanoparticles, and gold in particular, have attracted great attention since ancient times.[2] This is due to their promising new applications in fields such as materials science, medicine, catalysis, and fluorescence-spectral engineering based on surface-enhancement effects.[3]

The synthesis of such materials by wet chemical methods is based on the reduction of an inorganic or organo-metallic precursor in the presence of a stabilizing agent.[2,4] The surface of nanoscaled materials is very reactive, and needs to be protected by surface ligands to avoid irreversible growth and agglomeration. The choice of such ligands is critical for the monodispersity and the quality of the resulting particles. Different compounds such as surfactants or polymers were used for this purpose. Confinement within nano-reactors such as micelles and dendrimers was utilised to stabilise metal nanoparticles as well.[5] A further method is template synthesis, within porous host materials such as alumina and mesoporous silica to confine nanoparticles and nanowires as guests.[6]

An alternative and advantageous route to stabilise and functionalise nanoparticles colloidally is to encapsulate them with silica shells. Silica is an inert, robust and optically transparent material. The silica shells not only enhance the colloidal stability, but also control the distance between core particles within assemblies by the thickness of the shell. Furthermore, this shell is hydrophilic, biocompatible and easy to functionalise with several groups using different silane coupling agents. These unique characteristics and the possibility of bio-conjugation made silica coating an attractive route for bio-analytical and medical applications of metal nanoparticles. Extensive studies have been performed on the homogeneous coating of metal nanoparticles with silica shells. Typically, ligand-stabilised nanoparticles were covered with a silica shell of varying thickness subsequently. Two main synthetic pathways were developed. The first one is based on the hydrolysis–condensation[7] of a silica precursor onto the particle in alcoholic medium (Stöber method).[8] The second is based on the microemulsion method,[9] leading to a complete shell with tunable thickness. Liz-Marzán, Mulvaney, and co-workers have extensively studied metal–silica core–shell particles prepared by a liquid phase procedure in which the use of a silane coupling agent was necessary to provide the surface with silanol anchor groups.[7] Other authors have demonstrated that the coating of materials such as gold or silver with silica shells can be accomplished without using silane coupling agents. Xia and co-workers, for instance, prepared silica-coated gold nanospheres and silver nanowires by hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in ethanol.[10] Graf *et al.* used poly(vinylpyrrolidone) as a stabiliser to transfer gold nanoparticles into ethanol and perform a direct coating with TEOS.[11]

In this communication, we present the first synthesis of silica coated gold particles ($Au@SiO_2$) by means of hollow silica particles used as nano-reactors. In recent years, such hollow materials have attracted a lot of interest due to their low density, low toxicity, large surface area, high chemical and thermal stability, surface permeability, and the consequent possible applications in drug release[12] and catalysis.[13] However, to the best of our knowledge, they have not been used as reactors for nanoparticle synthesis so far.

In the present work, the metal particles were grown *in situ*, in the internal cavity of the previously prepared hollow silica particles. The latter were synthesised from silica coated CdSe–ZnS nanocomposites as published earlier.[9] The etching of the core material was possible in acidic or alkaline conditions,[14] due to the porosity of the silica shell.[12] This strategy was exploited to transfer a gold precursor and a reducing compound into the silica's empty cavity, giving rise to the $Au@SiO_2$ nanocomposites. Firstly, we let the metal precursor ($HAuCl_4$) diffuse into the holes, and then we added an excess amount of $NaBH_4$ as reducing agent. The latter could be diffused into the cavity of the silica spheres, which were filled with Au^{3+} cations and reduced. The metal nanoparticle formation took place by nucleation and growth of Au(0) atoms. The silica shell avoided further growth of the nanoparticles, acting as a template (as confinement factor)[5] and finally stabilised them. The final product is a gold nanometric particle surrounded by a silica shell. The suggested chemical process is depicted in Scheme 1.
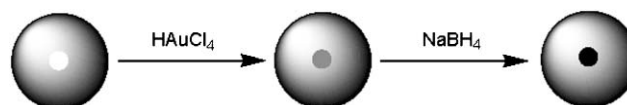
Scheme 1 A suggested chemical process that leads to the formation of $Au@SiO_2$ from hollow silica nanoparticles.

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The yielded nanocomposites were characterised by transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDAX) and UV–vis spectroscopy. The synthesis was quite reproducible. Some gold particle aggregates which eventually formed outside the SiO_2 shells were removed by further washing and precipitation.

It is interesting to notice the importance of the silica pore size for the success of such a reaction. Indeed, using a bigger molecule as reducing agent (e.g. sodium citrate), we obtained large gold clusters outside the shell (cf. supporting information). This result suggests that the dimensions of the existing pores were too small for such a compound to enter the cavity. The reaction could then only take place in the solution outside the silica particles, containing $HAuCl_4$ in excess, giving rise to big particles mildly stabilised by citrate.

TEM (Zeiss LEO 912 Omega operating at 120 kV) was used to investigate the size and the structure of the pristine hollow empty silica particles and the final nanocomposites. For the measurements, drops of nanoparticle solution were dispersed onto a carbon-coated copper grid. The core–shell structure of the hollow (Fig. 1a) as well of the $Au@SiO_2$ nanoparticles (Fig. 1b) is revealed because of the different electron penetrability of the core and shell material. Size distribution measurements performed randomly on TEM micrographs showed for the gold nanoparticles an average diameter of 10 nm, and for the silica shell an average thickness of 40 nm (cf. supporting information).

EDAX measurements (by EDX Oxford) confirmed the presence of Si and O in the hollow particles and in the nanocomposites, and moreover Au in the final nanocomposite materials in agreement with the formation of $Au@SiO_2$ (Fig. 2) (Cu, C, and Ti are introduced from the TEM grid and the sample holder in the TEM apparatus). Chemical elements related to the original CdSe–ZnS quantum dot cores were not detected.

The UV–vis analysis of the silica encapsulated gold particles presented a quite broad absorption peak with a λ_{max} situated at 550 nm (Fig. 3). The latter was clearly attributed to the plasmon band of Au(0). The position and the width of the signal were in agreement with the TEM data, which showed the size dispersion of the core gold nanoparticles around the average value of 10 nm.

The ensemble of measurements here reported allowed the identification of the particles synthesised inside the hollow silica as gold nanoparticles. Such a method is reproducible and can be applied for the preparation of other silica encapsulated metal particles by only changing the precursors. For instance, by using $AgNO_3$ it was possible to synthesise $Ag@SiO_2$ (figures not shown).
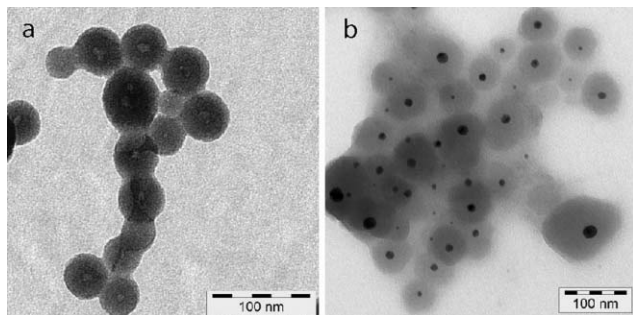

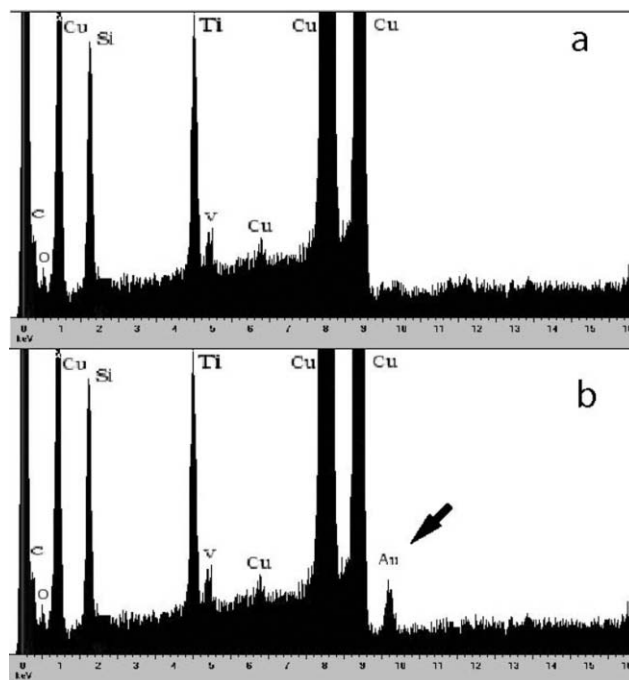**Fig. 1** TEM micrographs of hollow silica nanoparticles (a) and the $Au@SiO_2$ derived nanocomposites (b).

Fig. 2 EDAX spectra of hollow silica nanoparticles (a) and the $Au@SiO_2$ derived nanocomposites (b).
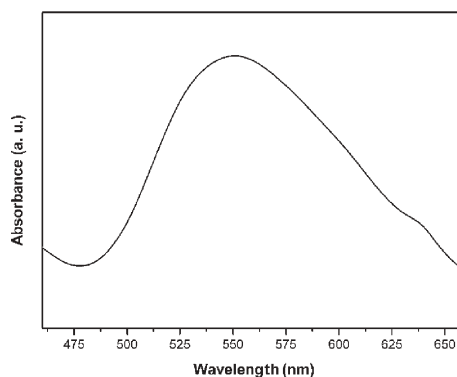

Fig. 3 UV–vis spectrum of the $Au@SiO_2$ nanocomposites.

In conclusion, a novel and original use of hollow silica particles is described. It consists of growing monodisperse gold nanoparticles into preformed empty silica shells, giving rise to $Au@SiO_2$ nanocomposites. The method can be easily transferred to other materials to obtain a variety of core–silica nanoparticles with spherical shape. Their size can be controlled by tailoring the hole size in the silica reactors. The silica shell increases the mechanical and colloidal stability, enables transfer into polar solvents and allows an easy functionalisation, widening the potential applications of such nanocomposite materials.

Notes and references

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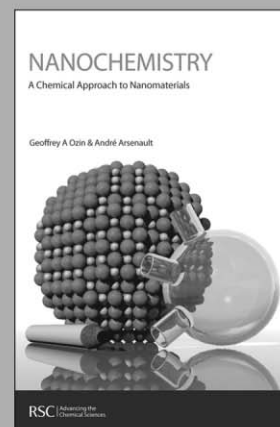14 M. Darbandi, R. Thomann and T. Nann, *Chem. Mater.*, 2007, **19**, 1700.