# A silica-based magnetic platform decorated with mixed ligand gold nanoparticles: A recyclable catalyst for esterification reactions

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A novel and convenient synthetic strategy for the preparation of magnetically responsive silica nanospheres decorated with mixed ligand protected gold nanoparticles is described. Gold nanoparticles are attached to the silica surface via stable amide bond formation. The hierarchical nanospheres show promising results as a reusable and efficient catalyst for esterification reactions and they can be recovered through a simple magnetic separation.

The combination of different materials in a nanoparticle construct to create novel and multifunctional composite systems has attracted much attention due to their huge potential in various fields of application such as diagnostics and therapy, electronics and catalysis.[1-6] Recently, our group showed that gold nanoparticles (AuNPs) protected by a monolayer composed of one hydrophobic ligand and one hydrophilic ligand containing terminal sulfonic acid head groups had potential as catalysts in esterification reactions.[7] These mixed ligand coated AuNPs are only mildly dispersible in the reaction medium, so they can be recovered from the solution by centrifugation. However, this is an expensive process that becomes rather cumbersome if all particles from the reaction solution have to be removed.

Here, we present an elegant approach to recover the catalytic gold nanoparticles from the solution with a simple magnet and within few seconds. Starting from a core@shell structure composed of superparamagnetic $\gamma$-Fe$_2$O$_3$ (maghemite) nanoparticles coated with SiO$_2$ and taking advantage of the chemical versatility of the silica materials,[8-10] we surface-functionalized them with amine to anchor the catalytically active mixed ligand AuNPs. We present the synthesis of these Fe$_2$O$_3$@SiO$_2$@Au hierarchical nanospheres and verify that the AuNPs bonded to the silica retain their catalytic activity. While the silica layer confers water dispersibility to the nanospheres, the magnetic core allows us to attract and remove them from the reaction medium by a magnet assisting the reusability of the material. This multifunctional composite emerges as an ideal combination of silica, iron oxide and gold to obtain a recyclable and efficient catalyst for the esterification of carboxylic acids.

In this study, AuNPs coated with 3-mercaptopropane-1-sulfonic acid (MPSA) and octanethiol (OT) mixed ligands are used as this combination was proven the most effective catalyst for esterification reactions.[7,11] MPSA:OT covered AuNPs are synthesized using a modified version of one-phase Brust-Schiffrin method.[12] First, 0.9 mmol of HAuCl$_4$ is dissolved in 150 mL of ethanol in a clean round-bottom flask. In a separate vial, 0.50 mmol of 3-mercapto-1-propanesulfonic acid sodium salt (MPSA) and 0.25 mmol of 1-octanethiol (OT) is mixed in 10 mL of methanol and added to the stirring gold solution. After 10 min stirring at room temperature, 150 mL of NaBH$_4$ (378.1 mg) is added dropwise to the reaction flask. The reaction is stirred for 2 h more before placing it at 4 °C overnight in order to precipitate the particles. The supernatant is removed, and the particles are cleaned of impurities through centrifugation in acetone, ethanol and methanol. Then, the pellet is dried under vacuum overnight.

TGA is used to quantify the percentage of organic material on the MPSA:OT covered AuNPs. Fig. 1 shows a representative TGA plot. The mass loss below 200 °C is due to solvent evaporation and corresponds to a weight loss below 1.0 %. The two main stages of weight loss in the temperature ranges of 200-400 °C and 400-650 °C can be attributed to mostly the decomposition of OT (7.5 %) and MPSA (4.7 %), respectively. The estimated mass percentage of total ligand shell is found

~ 12 %. A TEM image of MPSA:OT protected AuNPs is included in the inset of Fig. 1 showing their spherical shape and a mean size of 3 ± 0.8 nm. The MPSA:OT ligand molar ratio on the surface of AuNPs is determined by [1]H Nuclear magnetic resonance (^{1}H NMR) after etching the gold core with iodine solution. The peak at 2.20 ppm corresponds to β-$CH_2$ neighbouring to the sulfonate on the 3-mercapto-1-propanesulfonate (MPSA) ligand, whereas the -$CH_3$ peak of the 1-octanethiol (OT) ligand appears at 0.92 ppm (ESI†, Fig. S1). The ^{1}H NMR spectra of the particles before the etching process shows those particles are free of impurities (data not shown). Based on the calculations using their peak ratio, the ratio of MPSA:OT on the surface of the particles is determined. Although the nominal molar ratio of MPSA:OT ligands is 2:1, the experimentally obtained result showing the global ligand composition of the sample is found to be 8:1. From the results acquired by TGA, TEM and ^{1}H NMR, the ligand density of MPSA:OT protected AuNPs is found to be 4.8 ligand molecules/nm$^2$.
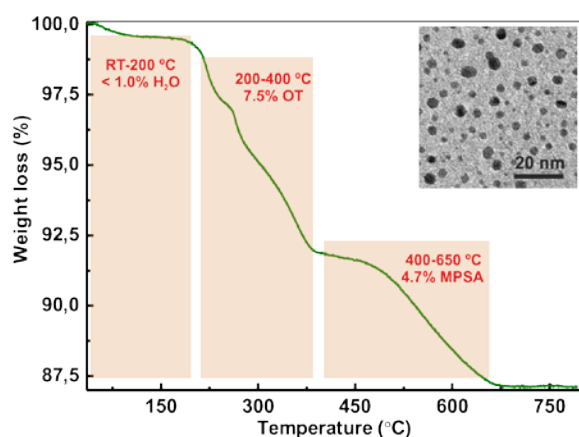


**Fig. 1** TGA curve of MPSA:OT covered AuNPs. Inset shows a TEM image of MPSA:OT covered AuNPs.

Once the MPSA:OT protected AuNPs are synthesized, a partial ligand exchange reaction is performed between the MPSA/OT ligands and N-Hydroxysuccinimidyl 11-mercaptoundecanoate (ProChimia Surfaces) using a modified version of a previously reported method by us.[13] The concentration of N-Hydroxysuccinimidyl 11-mercaptoundecanoate is adjusted in such a way that it displaces a few ligands from the surface.[14] 10 mg of MPSA:OT protected AuNPs is dissolved in 2.0 mL of MQ water. In another separate vial, 5 mg of N-Hydroxysuccinimidyl 11-mercaptoundecanoate dissolved in 0.5 mL of Dimethylformamide is added to the AuNPs solution. After 30 min of stirring, particles are cleaned with SephadexTM LH-20 column (GE Healthcare) and washed with water. Fig. 2a shows the schematic representation for the partial ligand functionalization of MPSA:OT covered AuNPs.
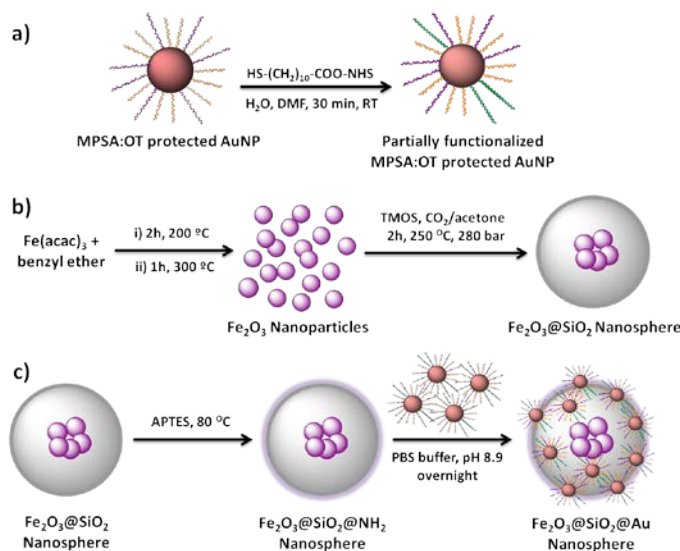
**Fig. 2** Schematic illustration of: (a) the partial ligand exchange of MPSA:OT covered AuNPs, (b) the synthesis of Fe$_2$O$_3$@SiO$_2$ and (c) Fe$_2$O$_3$@SiO$_2$@Au hierarchical nanospheres.

To prepare the core@shell nanospheres, the superparamagnetic maghemite (γ-Fe$_2$O$_3$) nanoparticles composing the cores are first synthesized by thermal decomposition of iron acetylacetonate (Fe(acac)$_3$) in benzyl ether using oleic acid and oleylamine as capping ligands.[14,15] The as-obtained nanoparticles are uniform and spherical in shape with a mean diameter of 5.0 ± 1 nm (ESI†, Fig. S2a). The magnetic nanoparticles are then encapsulated by a supercritical assisted sol-gel reaction previously reported by us.[16,17] Tetramethylortosilicate (TMOS) is used as silicon precursor while no catalyst is needed for the formation of silica. The process is schematized in Fig. 2b. Resulting core@shell nanospheres (180 ± 20 nm in diameter) are displayed in Fig. S2b (ESI†). The mass portion of Fe$_2$O$_3$ with respect to the total mass is 9.2 % by ICP-MS.[18] The magnetic properties of the core@shell material are studied. The saturation magnetization value at 300 K is 5.4 emu/g of Fe$_2$O$_3$@SiO$_2$ (ESI†, Fig. S3a). This value converts to 59 emu/g when it is referred to the mass of Fe$_2$O$_3$ and it is comparable to other reported data.[19] The absence of coercivity and remanence at room temperature indicates the superparamagnetic character of the composite nanospheres, which behave as ferrimagnets at 5 K, as observed from the hysteresis loop in the inset of Fig. S3a (ESI†). Zero field cooled-field cooled magnetization curve (ZFC-FC; ESI†, Fig. S3b) highlights the narrow size distribution of the magnetic clusters and confirms the superparamagnetism of the nanospheres with blocking temperature (TB) = 61 K. The strong magnetic response of the material enables its easy recovery from the reaction medium by using an external magnet.

The Fe$_2$O$_3$@SiO$_2$ nanospheres are then functionalized with 3-(aminopropyl)triethoxysilane (APTES), a modification of a reported synthesis by us is used.[7] 200 mg of Fe$_2$O$_3$@SiO$_2$ nanospheres is dispersed in 350 mL of ethanol for 20 min *via* ultrasonication, and then 2 mL of APTES is added to the reaction mixture. The reaction is allowed to proceed at 80 ºC for 5 h. The amino modified Fe$_2$O$_3$@SiO$_2$ nanospheres are washed three times with ethanol, and then dried under vacuum for 24 h. Finally, the functionalization of the Fe$_2$O$_3$@SiO$_2$@Au nanospheres, with N-hydroxysuccinimide ester functional group allows MPSA:OT protected AuNPs to react with –NH$_2$ groups on the surface of Fe$_2$O$_3$@SiO$_2$ nanospheres to form stable amide bonds in basic aqueous media. First, 50 mg of Fe$_2$O$_3$@SiO$_2$@NH$_2$ spheres is dissolved in 38.5 mL of water and then 5 mL of 10x PBS buffer (pH 8.9, Ambion) is added to the reaction medium. After 10 min of sonication, 8.5 mg of MPSA:OT coated AuNPs in 6.5 mL of water is added and stirred overnight at room temperature at dark. The resulting hierarchical nanospheres are then cleaned five times with water *via* magnetic decantation. The synthesis of the Fe$_2$O$_3$@SiO$_2$@Au spheres (hereafter, hierarchical nanospheres) is schematically represented in Fig. 2c.

The as-prepared hierarchical nanospheres are visualized using TEM, as shown in Fig. 3. Clearly, the silica surface is uniformly covered with MPSA:OT protected AuNPs. It should be noted that AuNPs are successfully attached to the Fe$_2$O$_3$@SiO$_2$ nanospheres only when the functionalization with N-Hydroxysuccinimidyl 11-mercaptoundecanoate is performed; a control experiment led to silica nanospheres almost free of MPSA:OT covered AuNPs (There are a few

particles adsorbed to the silica surface due to non-specific adsorption.) (ESI†, Fig. S4). The efficiency of the coupling reaction is remarkable given that the N-Hydroxysuccinimidyl 11-mercaptoundecanoate ligand is added on MPSA:OT covered AuNPs only in a low fraction, indeed its signal could not be detected in ^{1}H NMR even after decomposition of the gold core when the same amount of AuNPs to determine MPSA:OT ligand ratio is used in the etching process.
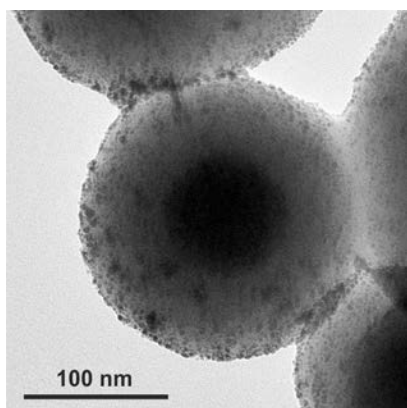


**Fig. 3** TEM images of hierarchical $Fe_2O_3$@$SiO_2$@Au nanospheres.

To test the catalytic efficiency of hierarchical nanospheres acetylation of benzyl alcohol (BzOH) is chosen as a test reaction (ESI†) since the product benzyl acetate (BzAc) is a widely used compound in the industry as a solvent, odorant, plasticizer, and also as a precursor for many agrochemicals, pharmaceuticals, and further fine chemicals.[1] Prior to the reaction, the terminal sulfonate head groups of the ligand on the monolayer of AuNPs are acidified. The acidification process of sulfonate groups is adapted from the literature (ESI†).[1,2] Without this step, no catalytic efficiency is observed (data not shown). Sulphuric acid does not cleave the amide bonds,[20] therefore the attachment of MPSA:OT covered AuNPs to the silica surface is stable under the acidification process.
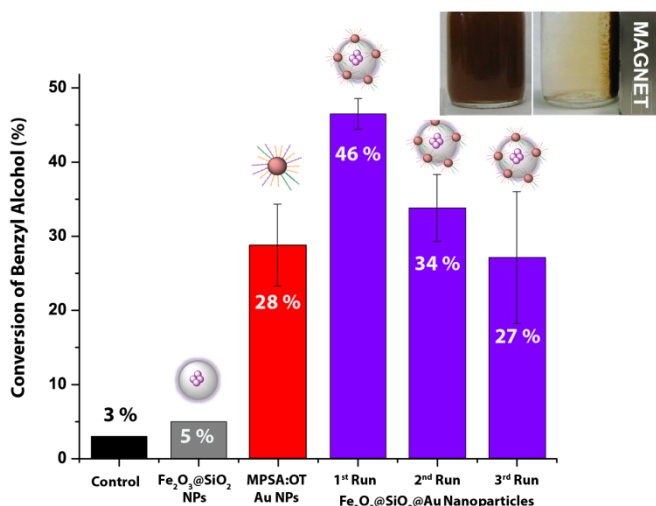


**Fig. 4** Efficiency and reusability of MPSA:OT protected AuNPs, $Fe_2O_3$@$SiO_2$ nanospheres and hierarchical $Fe_2O_3$@$SiO_2$@Au nanospheres as catalysts for the acetylation reaction of benzyl alcohol. Inset displays photographs of the aqueous dispersion of $Fe_2O_3$@$SiO_2$ nanospheres without and with a ~ 0.5 T magnet. The conversion efficiencies of the hierarchical nanospheres and MPSA:OT covered AuNPs are averages of three independent measurements (i.e. three independently synthesized hierarchical nanospheres). All conversions were calculated starting from the same amount of Au NPs, the increase in efficiency from MPSA:OT Au NPs (28%) to the 1st run of $Fe_2O_3$@$SiO_2$@Au spheres is most

probably due to the fact that the MPSA:OT Au NPs are not colloidally stable in the reaction mixture while the $Fe_2O_3@SiO_2@Au$ spheres are (ESI†, Fig. S11).

The catalytic test reaction is conducted in a 10 mL round-bottom flask fitted with a reflux condenser. Efficiencies are evaluated after the reaction of 270 mg (2.5 mmol) of BzOH (Sigma Aldrich, anhydrous), 300 mg (2.5 mmol) of acetic acid (AcOH) (Sigma Aldrich, %99.99 purity) and 40 mg of the hierarchical nanospheres at 100 $^o$C for 3 h. To investigate the activities of MPSA:OT covered AuNPs and $Fe_2O_3@SiO_2$ nanospheres, 5 mg and 40 mg of particles are used, respectively, under the same conditions. After separation of the particles from the reaction medium ($Fe_2O_3@SiO_2$ and hierarchical nanospheres are recovered via external magnet while MPSA:OT covered AuNPs are separated by centrifugation) the products are analysed by means of $^1$H NMR. The products are kept at -4 $^O$C fridge prior to analysis to be assessed simultaneously. The recovered hierarchical nanospheres are then washed with water, and poured in the acidification reaction medium again to be used in another subsequent reaction under similar conditions.

Conversion ratios of BzOH to the product BzAc are calculated as percentages in order to evaluate the catalytic efficacy of hierarchical nanospheres. The results are presented in Fig. 4. The contro experiment, which is performed without addition of any nanoparticles, gives less than 3 % conversion of BzOH to BzAc (ESI†, Fig. S5). $Fe_2O_3@SiO_2$ nanospheres show also similar results to the control experiment in terms of conversion efficiency (5 %) as expected since Brønsted acidity of surface hydroxyl groups of the nanospheres is not strong enough to act as a source for the protons to be transferred in an acid catalysis system (ESI†, Fig. S6).

The hierarchical nanospheres (46 %) show higher efficiency than MPSA:OT covered AuNPs (28 %) as it can be observed in Fig. 4 and in ESI† (Fig. S7 and Fig. S8). All conversion efficiencies were achieved by using the same quantity of MPSA:OT covered AuNPs in the reaction medium, as determined by optical absorption (ESI†). Two reasons may explain the superior activity of the hierarchical nanospheres over MPSA:OT covered AuNPs. First, MPSA:OT coated AuNPs are not dispersible in the reaction medium, whilst the hierarchical nanospheres are very well dispersed and act as both a homogeneous and heterogeneous catalyst (ESI†, Fig. S11). Since the hierarchical nanospheres are homogeneously dissolved in the reaction medium, MPSA ligands located at the periphery of the self-assembled monolayer (SAM) behave as if molecularly dissolved. Second, since MPSA:OT covered AuNPs are attached to the silica surface forming a uniform layer homogeneously distributed (without creating aggregates), interactions of the sulfonate head groups with the substrate were promoted in higher amount in the case of hierarchical nanospheres when compared with MPSA:OT protected AuNPs.

In order to examine the reusability of the synthesized hierarchical nanospheres, those particles undergo two more cycles. Fig. 4 shows that hierarchical nanospheres maintain their ability to catalyse the reaction with high efficiency compared to the control experiment after several uses (34 %, 27 %) (Fig. S9 and Fig. S10). However, there is a decrease in the activity of hierarchical nanospheres after each run. The third run exhibits even less catalytic activity compared to MPSA:OT covered AuNPs. In order to understand the reason behind this decrease, TEM sample of hierarchical nanospheres is prepared from third acidification reaction prior to the cleaning step (magnetic decantation). Free MPSA:OT covered AuNPs identified on the TEM images suggest that this loss can be attributed to the decrease in the number of MPSA:OT covered AuNPs on the surface of hierarchical nanospheres after each run. On the other hand, there is not any pronounced morphological change of hierarchical nanospheres (ESI†, Fig. S12). We suppose that the detachment of the MPSA:OT covered AuNPs from silica surface might be caused by desorption of the thiol group of anchoring ligand, N-Hydroxysuccinimidyl 11-mercaptoundecanoate from gold surface.

## Conclusions

In summary, we present a novel approach of synthesizing well-defined $Fe_2O_3@SiO_2@Au$ nanospheres. These hierarchical nanospheres are highly promising catalytic agents for esterification reactions since they can be recovered and reused with the help of an external magnet and they hold the characteristics of both homogenous and heterogeneous catalysts. They showed a pronounced effect on the conversion of BzOH to BzAc compared to the MPSA:OT covered AuNPs. Our studies to improve the catalytic efficiency of these nanospheres still are in progress.

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