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Phosphinine stabilised gold nanoparticles; synthesis and immobilisation on mesoporous materials†

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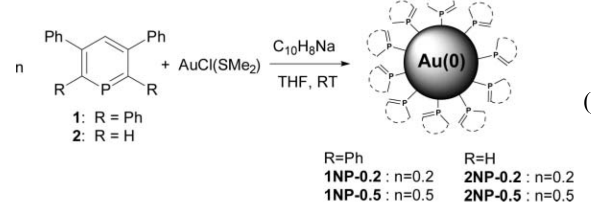
The first synthesis of gold nanoparticles stabilised by a sub-stoichiometric amount of sp^2 phosphorus containing ligands was performed, as well as their immobilisation on mesostructured silica and titania hosts.

Noble metal nanoparticles have attracted much attention recently for their potential applications in electronics,[1] catalysis,[2,3] biochemistry[4] and non-linear optics.[5] Classical tertiary phosphines have been, alongside thiols or amines, frequently employed as ligands for the synthesis and stabilisation of size-controlled nanoparticles (NPs) especially in the case of gold derivatives.[6] Surprisingly, despite their pronounced π-accepting capacity[7] which makes them very attractive ligands for the stabilisation of zerovalent and reduced transition metal centres,[8] molecules featuring sp^2-hybridised phosphorus atoms such as phosphinines have never been investigated in this area. For example, some years ago we showed that, contrary to most usual P, N, S and O ligands, phosphinines could be efficiently employed for the stabilisation of monomeric Au(0) complexes.[9]

Phosphinines **1**[10] and **2**† were chosen as starting precursors. Classical syntheses of phosphine stabilised gold NPs usually proceed *via* reduction of $HAuCl_4$ in aqueous or biphasic media with a large excess of reducing agent ($NaBH_4$ in most cases).[11] Here, the reduction was carried out using sodium naphthalenide and the $[AuCl(SMe_2)]$ complex as a source of gold. The reduction process takes place smoothly at room temperature in THF by adding dropwise a solution of $C_{10}H_8Na$ to a mixture of the complex and *n* molar equivalents of phosphinine **1** or **2** ($n = 0.2$, 0.5). The resulting dark blue/purple solution was stirred at room temperature and after evaporation of the solvent the blue/purple solid obtained was washed several times with THF and hexanes to remove both naphthalene and salts. The solid could then be redispersed in THF for storage (eqn. (1)).



(1)

Figs. 1(a) and (b) show transmission electron microscopy (TEM) images of Au NPs **1NP-0.2**, **1NP-0.5**.‡ A narrow size distribution is observed in the case of $n = 0.5$. The mean size of the particles is 8.3 nm ± 2.0. For $n = 0.2$, the NPs are more polydisperse and even polymorph. The mean size of the particles, 20.1 nm ± 7.5, is much larger than in the case of $n = 0.5$. Some of these NPs exhibit angles and facets, features that have already been observed before alongside polydispersity.[12,13] The sub-stoichiometric amount of ligand and the rate of the reduction process are probably responsible for these features. High resolution TEM was also performed on the NPs with $n = 0.5$ (Fig. 2). This picture shows the reticular planes inside the nanoparticle, which account for the crystallinity of the nano-objects, as checked by large angle X-ray diffraction. Indeed, the NPs adopt a cubic *Fm*3*m* crystal system.†

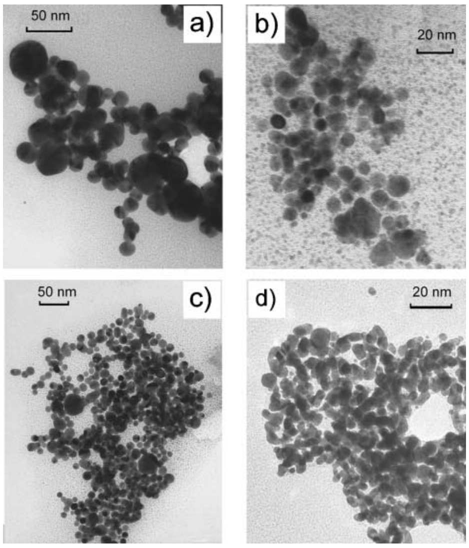


Fig. 1 Representative transmission electron microscopy pictures of gold nanoparticles for (a) **1NP-0.2**, (b) **1NP-0.5**, (c) **2NP-0.2**, (d) **2NP-0.5**.

The evidence for the formation of Au NPs was also provided by UV–visible spectroscopy. A very large surface plasmon band centred on ~580 nm was observed.† Values tabulated in the literature for similar sized NPs with other ligands (phosphine,[11] thiol,[14] amine[15]) account for a more energetic plasmon band, around 520 nm. This low energy shift can have many causes: particle shape, medium dielectric constant, temperature *etc.* It can also be related to the core charge of the nanoparticle, an electron deficiency being associated with a red-shift.[6,16] The strong π-accepting ability of phosphinine ligands, which partly deprives

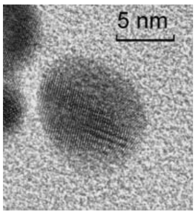


Fig. 2 High resolution transmission electron microscopy pictures of gold nanoparticles **1NP-0.5**.

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† Electronic supplementary information (ESI) available: experimental section, UV–vis, TEM, IR, XRD, TGA and BET. See http://www.rsc.org/suppdata/cc/b4/b412553c/

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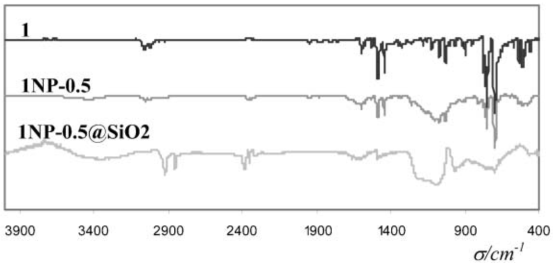

Fig. 3 IR spectra of phosphinine **1**, the corresponding gold nanoparticles **1NP-0.5** and the silica immobilised nanoparticles **1NP-0.5@SiO$_2$** (as the signal is very weak, the spectrum of silica was subtracted).

the particle of its electron density, can explain this experimental result.

The presence of the phosphinine on the surface was evidenced by several experiments. The thermo-gravimetric analysis† of **1NP-0.5**‡ revealed a loss of mass of 45.6%, which confirms that the ligand is still present on the surface after several washings. This weight loss corresponds to a Au–phosphinine ratio of 2.3, close to the initial one (2). This also indicates that only a small amount (15 mol%) of the phosphinine was washed away. To the best of our knowledge this $C_{10}H_8Na$-based reduction process has never been employed for the synthesis of Au NPs. Interestingly, as phosphinines are well adapted to the coordination of Au(0), working with a sub-stoichiometric amount of ligand is suitable for Au NP formation contrary to the usual approaches involving classical tertiary phosphines. The IR spectra of both **1** and **1NP-0.5** (Fig. 3) confirmed that the ligand is grafted on the particles. The most characteristic peaks of **1** (two strong absorptions at 700 and 750 cm^{-1} corresponding to out of plane vibrations of the aromatic C–H bonds, an absorption at 760 cm^{-1} ascribed to the P–C bond and a broad band around 1450 cm^{-1} characteristic of aromatic C=C vibrations) are clearly observed in the spectrum of **1NP-0.5**.

Experiments were also carried out with phosphinine **2**. This ligand was chosen because phenyl groups in the α-position in **1** were thought to induce an important steric hindrance upon complexation onto the gold surface. The TEM pictures (Figs. 1(c) and (d)) showed for both ratios a smaller average particle size, 5.7 nm ± 1.3 for $n = 0.5$ and 12.7 nm ± 3.7. for $n = 0.2$. This data confirms the assumption that the presence of bulkier groups in the α-position hinders the binding of **1** to the particles; phosphinine **2** therefore is a better ligand for the synthesis of NPs than **1**.

Those particles seemed to be a good starting point for immobilisation studies. Indeed, finding a method for immobilisation of preformed metallic NPs that would preserve the particles' shape, size and coordination is a challenging topic for catalytic applications.[2] In that respect, mesoporous materials are interesting as they are accessible through numerous versatile methods and feature a wide range of pore sizes and organisations.[17] Besides, it is now well established that the nature of the support strongly influences catalytic performances.[18]

The most convenient process to elaborate a material with a high loading in gold, a controlled structure and a suitable porosity is the evaporation induced self assembly (EISA).[19] In order to test the stability of our phosphinine-based Au NPs toward such techniques, **1NP-0.5** (15 mg) was added (3 wt%) to a standard precursor sol using cetyltrimethylammonium bromide (CTAB) as the templating agent ($SiOEt_4$–EtOH–H_2O–HCl–CTAB $= 1 : 30 : 40 : 0.045 : 0.2$). The aerosol was then generated using a commercial atomiser and air as an atomisation gas. The resulting powder, **1NP-0.5@SiO$_2$**, has a strong purple colouration. The TEM micrographs of **1NP-0.5@SiO$_2$** (Fig. 4) clearly evidenced the incorporation of gold nanoparticles into the mesoporous material. Importantly, no apparent modification of the shape and size of the NPs was noted. The powder has a very large specific surface (1050 m^2 g^{-1}) and a narrow pore size distribution (28 Å ± 1).† These results indicate that the entrapped NPs should be accessible to substrates.

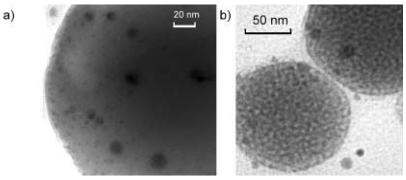

Fig. 4 TEM images of nanoparticles included into a silica matrix (a) or a titania matrix (b) (note that due to the opacity of titania, the contrast is lower than with the silica matrix).

Moreover IR measurements showed that the phosphinine ligand is still present on the particle surface. The spectrum obtained by subtraction of the IR spectrum of **SiO$_2$** to the spectrum of **1NP-0.5@SiO$_2$** is presented in Fig. 3. Weak absorption bands characteristic for the phosphinine ligand are observed, indicating that the bonding of the ligand to the NPs is strong enough to prevent the phosphinine from leaching. The procedure followed for **1NP-0.5@SiO$_2$** was repeated for immobilisation on titania. For the blue powder then obtained (**1NP-0.5@TiO$_2$**), DRX analyses are in good agreement with standard TiO_2 aerosols and TEM images are comparable to those of **1NP-0.5@SiO$_2$** (Fig. 4). The material specific surface is large (576 m^2 g^{-1}) and average pore size is slightly smaller than for 1NP-0.5@SiO$_2$ (26 Å ± 1).†

In conclusion, we have demonstrated that phosphinines efficiently stabilise Au NPs. The structural diversity of these sp^2-hybridised phosphorus ligands, the availability of numerous functionalised structures (heteroditopic, multidentate, oligomeric ligands *etc.*) combined with their modulable π-accepting properties should find interesting applications.

Notes and references

‡ The Au NPs are labeled **XNP-*n*** (X being the ligand **1** or **2** and *n* the number of molar equivalents of phosphinine).

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