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Gold nanoparticles were highly dispersed in polysilsesquioxane hollow spheres in which cyanopropyl groups were distributed homogeneously, showing high catalytic performance in the reduction of 4-nitrophenol. The reaction was performed in an environmentally friendly aqueous system.
Controlled synthesis of novel cyanopropyl polysilsesquioxane hollow spheres loaded with highly dispersed Au nanoparticles for catalytic applications†

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The design and synthesis of novel cyanopropyl polysilsesquioxane hollow spheres lead to production of a highly active and stable catalyst in the reduction of 4-nitrophenol catalyzed by Au nanoparticles.

Hollow spheres with porous structure on the shell have attracted tremendous attention due to their unusual chemical/physical properties and potential applications as drug carriers, catalyst supports, reaction containers and so on.1–4 Hollow spheres can be fabricated through Kirkendall effect, chemical etching, emulsion templating or hard templating processes.5–9 In a hard-template method, a shell was usually coated on a sacrificial template, which could be removed to leave behind a hollow spherical shell. Compared to other methods, the hard template process is more efficient to control the spherical morphology, shell thickness and surface composition of the shell. In particular, hollow spheres with functional moieties on the surface can enhance the performance of the materials, for example, precisely modified hollow spheres have been used as drug carriers,10 nanovalves,11 optical coatings,12 as well as catalyst supports.13

Supported metal catalysts have attracted great interest for their applications in chemical synthesis, environmental control and energy processing.14,15 However, catalyst performance and stability have been restricted due to the agglomeration among tiny metal particles. To overcome this limitation, metal affinity groups, such as –NH2,16 –SiH,17 –SH18 groups, have been post-grafted onto the catalyst supports to stabilize and disperse metal nanoparticles.19 Unfortunately, these post-treatment processes are complicated and limited to offer well dispersed functional groups on the matrix. Up to now, directly fabricating a suitable catalyst support with metal-affinity groups grown homogeneously on the surface still remains a major challenge.20

Herein, we report a new catalyst support, cyanopropyl polysilsesquioxane (CPSQ) hollow sphere, whose surface is initially and homogeneously covered by cyanopropyl groups. Polysilsesquioxane (PSQ) is a kind of molecular level organic–inorganic hybrid materials, containing silicon-based frameworks (offering the materials stability) and outsurface organic moieties (offering the materials functional sites).21 Recently, we have developed a method to synthesize polysilsesquioxane hollow spheres via a hydrolysis–polycondensation process by using polystyrene (PS) latex as a hard template.22,23 In the present work, cyanopropyl polysilsesquioxane hollow spheres were fabricated for the first time, which initially combined pores on the shell and cyanopropyl groups evenly distributed throughout the shell of the hollow spheres. The pores make it possible for a gold precursor to diffuse through the shell, and the cyanopropyl groups are used to stabilize Au nanoparticles due to the high affinity between CN and Au.24 Au/CPSQ hybrid nanocomposite hollow spheres were fabricated and used as catalysts for reduction of 4-nitrophenol. To the best of our knowledge, this is the first report that highly dispersed Au nanoparticles could be loaded onto polysilsesquioxane hollow spheres for catalytic applications.

Scheme 1 illustrates the process of fabricating Au/CPSQ hybrid nanocomposite hollow spheres (see experimental section in ESI†). In the first step, polystyrene beads were prepared by soap-free emulsion polymerization. Then, CPSQ hollow spheres were formed by polycondensation of hydrolyzed cyanopropyltriethoxysilane on the PS template, which could be dissolved synchronously in the aqueous ammonia solution.22 Finally, Au/CPSQ hybrid nanocomposites were fabricated and used as catalysts for reduction of 4-nitrophenol. The results are in Scheme 1.
prepared through an impregnation-reduction process by using HAuCl₄ as metal precursor, NaBH₄ as reduction agent and cyanopropyl groups on the surface of the support as stabilizing agents.²⁵

Fig. 1 displays the TEM images of as-prepared CPSQ hollow spheres and Au-loaded CPSQ hollow spheres. It is clear that CPSQ hollow spheres have a particle size of approximately 250 nm, with the shell thickness of about 50 nm. The particle size and shell thickness can be precisely controlled by adjusting precursor concentrations (Fig. S1 in ESI†). From the HRTEM image (Fig. 1F), dark spherical spots can be clearly observed indicating that Au nanoparticles (2–5 nm) were well dispersed throughout the hollow spheres. SEM images in Fig. 2 show that the metal-loaded hybrid nanocomposites preserved the uniform size and shape of the as-prepared CPSQ hollow spheres. As shown in the energy-disperse X-ray (EDX) pattern and elemental mapping, the weak but evenly distributed signals from Au further confirmed the well dispersion of gold nanoparticles in the sample. This well dispersion of Au was suggested to be related to the even distribution of cyanopropyl groups on the support.²⁰

CN groups were reported to play an important role in stabilizing and dispersing Au nanoparticles in catalyst supports due to their high affinity for gold.²⁶ As confirmed by the ²⁹Si NMR spectrum (Fig. 3A), these cyanopropyl groups were well preserved in the course of preparation without Si-C cleavage on the framework, since there are no peaks that are assigned to Q¹ [Si(OSi)₅(OH)₄] species appearing between −90 and −120 ppm,²⁷ while intense and less intense peaks are observed at −68.7 ppm and −59.2 ppm that could be assigned to the T³ [RSi(OSi)₃] and T² [RSi(OSi)₂OH] species, respectively. The typical XPS survey spectra (Fig. 3B) of the hybrid nanocomposites further confirmed the presence of Au and N (the mole ratio of Au to N is estimated as ca. 0.025). The asymmetric nature of Au 4f suggests multiple species of gold in the spheres (inset of Fig. 3B).²⁸ As shown in the XRD pattern (Fig. 3C), the broadened diffraction peak at 2θ = 38° can be assigned to the tiny gold particles grown on the shell,²⁹ which agrees well with the TEM result. In FT-IR spectra, a sharp band at 2247.6 cm⁻¹ for the CN group stretch and a weak peak at 1185.9 cm⁻¹ for the (CH₂)₃CN stretch are found for both samples with and without Au (Fig. 3D). TGA analysis also confirmed that a large number of organic groups exist in the CPSQ materials (Fig. S2, ESI†). Our preliminary experiments showed that other PSQ hollow spheres like methyl-functional PSQ hollow spheres or CPSQ solid spheres without hollow structure exhibit uneven distribution of gold nanoparticles in such support materials (Fig. S3 and S4, ESI†).

To investigate the catalyst performance of Au/CPSQ hybrid nanocomposite hollow spheres (1.53 wt% Au, determined by ICP analysis), the catalytic reduction of 4-nitrophenol by sodium borohydride was carried out. Without using a catalyst, no conversion of 4-nitrophenol occurred. However, when Au/CPSQ nanocomposites were used as catalysts, the absorption intensity of 4-nitrophenol at 400 nm decreased successively with time, accompanied by the simultaneous appearance of a new peak at 300 nm (Fig. 4). The UV-Vis spectra also show an isosbestic point (315 nm), indicating that the catalytic reduction of 4-nitrophenol gives 4-aminophenol only without byproduct formation.³⁰ The complete conversion of 4-nitrophenol can be also confirmed by the clear color change of the solution from originally bright
yellow to colorless (inset of Fig. 4). To study the recyclability of the Au/CPSQ hybrid nanocomposites, the same catalyst was used to perform the same reduction reaction for the next run. After each use, the catalyst was centrifugated, washed and dried for the next cycle of catalysis. The catalyst exhibits high activity as the conversion just slightly decreased in the same reaction time (60 min) after running for 5 cycles (inset table of Fig. 4). 94.5 wt% of the original Au remained after recycling 5 times. Such results indicate that the presence of CPSQ support was sufficient to stabilize the catalytic nanoparticles by preventing their aggregation, producing a good catalyst with high activity and stability.

In summary, a new structured catalyst support, cyanopropyl polysilsesquioxane hollow spheres, was prepared for the first time and applied as support for highly dispersed gold nanoparticles. The Au/CPSQ hybrid nanocomposites exhibit high activity and reusability in the catalytic reduction of 4-nitrophenol. We believe that the current cyanopropyl polysilsesquioxane materials would find more catalytic applications after being loaded with other types of metals.

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Notes and references