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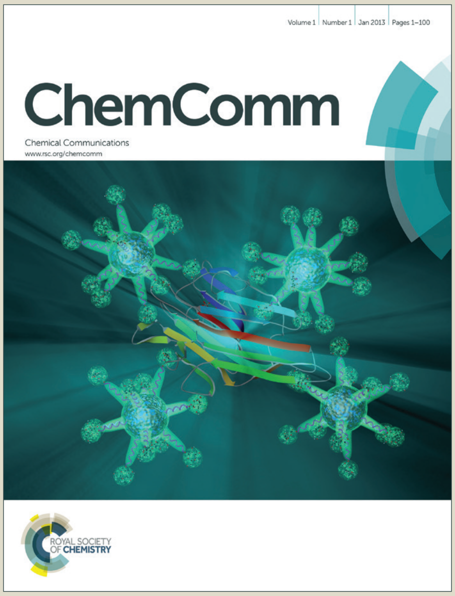

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Designing yolk/shell type porous organic network using phenyl modified template

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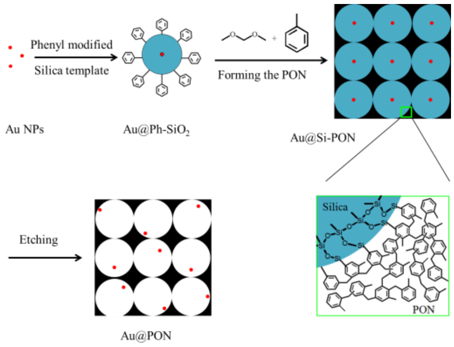
A new strategy was developed to introduce gold nanoparticles into the yolk/shell type porous organic networks under the assistance of phenyl modified SiO_2-based template. The obtained material showed good properties such as thermal-stability and anti-aggregation, and can be used as an efficient nanoreactor for the catalytic decomposition of cyclohexyl hydroperoxide.

Porous organic network (PON), formed by the polymerization of organic building blocks, has attracted increasing research interest for their porous structure, low density and easy functionalization.[1] Compared with the traditional inorganic porous materials, such as zeolites, activated carbon, SiO_2, the particular organic nature of the PON together with the diverse structure enable it to show promising application performance especially involving with organic substrate.[2] All these predominance made it good candidate as catalysts.[3] For instance, Cooper's group reported the synthesis of bipyridine-ligated complex-functionalized conjugated microporous polymers as an efficient heterogeneous catalyst for reductive amination.[4] Wang *et al.* used imine COFs to support palladium complexes which showed excellent performance in Suzuki coupling reactions.[5] In addition, a bottom-up strategy was developed by the same group to fabricate Tröger's base-functionalised organic nanoporous polymer for catalytic application.[3e] Thomas *et al.* immobilized palladium nanocrystals onto the surface of covalent triazine frameworks and used them in catalytic alcohol oxidation reactions.[6] Generally, three ways were used to introduce active site into PONs: (a) employing homogeneous catalysts as polymer building blocks[7], (b) post-grafting active sites to PONs[8] and (c) encapsulating well-defined metal nanoparticles in their pores[9]. However, to develop new ways to introduce catalytic active sites into PONs is still a challenging work.

Confining metal nanoparticles in the hollow spheres to make yolk/shell structure is an effective way to introduce stable active sites.[10] This kind of structure can not only avoid aggregation to protect metal or metal-oxides but also supply a nanospace as nanoreactor which can be used in shape selective catalysis, cascade reactions, *etc*.[11] To prepare the yolk/shell structure, silica confining metal nanoparticles was usually used as a sacrificial template.[12] Recently, a kind of hyper-crosslinked microporous network capsules and hollow conjugated microporous network using SiO_2 template have been reported individually.[13] However, due to the hydrophobic nature of the PONs and hydrophilic nature of silica, it is difficult to direct combine them together.[14]

Herein, we promoted a new strategy to introduce catalytic site into PONs through making PONs with yolk/shell structures. In our previous work, surface organic modification method was developed to modify the template surface hydrophilicity/hydrophobicity with different organic groups.[15] Using similar strategy, a kind of core-shell structured phenyl-modified Au@SiO_2 was designed as the reactive template. The introduction of phenyl groups facilitated the growth of PON on the template *via* F-C reaction. After the removing of SiO_2, the novel yolk/shell type PON confining gold nanoparticles was successfully obtained. To the best of our knowledge, this is the first example of introducing catalytic sites into PON with yolk/shell structure.

The synthesis of yolk/shell type PON was started with the fabrication of phenyl modified SiO_2 template (Scheme 1). Firstly, Au nanoparticles (NPs) with average diameter about 13 nm were synthesized according to the previous report (Fig. S1).[16] The UV-Vis absorption peak of Au NPs appears at 528 nm (Fig. S7), which was assigned to a Plasmon resonance band of spherical Au NPs.[17] Then, Au NPs were covered with phenyl modified silica shells by co-condensation of tetraethyl orthosilicate and phenyltriethoxysilane to form the mono-dispersed core-shell Au@Ph-SiO_2 with diameter of 120 nm (Fig. S20). One gold core was observed at the centre of sphere (Fig. 1a). The phenyl groups were successfully immobilized in the shell as characterized by Fourier transform infrared spectroscopy (FT-IR) (Fig. S6) and ^{29}Si cross polarization/magic-angle spinning nuclear magnetic resonance (^{29}Si CP/MAS NMR) (Fig. S19). The typical band of phenyl groups at 1600, 1450, 738 and 698 cm^{-1} appeared in FT-IR spectrum. And in the ^{29}Si CP/MAS NMR spectrum, the peaks at about -100 and -110 ppm were assigned to $HOSi(OSi)_3$ (Q^3 signal) and $(OSi)_4$ (Q^4 signal) species, respectively. In addition, the appearance of organosilane signals at about -65 ppm (T^3 = $PhSi(OSi)_3$) is the direct evidence of fully cross-linked organosiloxane species in agreement with the FT-IR results.[18] The introduction of benzene groups made the surface of the Au@Ph-SiO_2 fluffy (Fig. S5). Due to the coating silica shells, Plasmon resonance band of gold nanoparticles in Au@Ph-SiO_2 shifted from 528 to 536 nm (Fig. S7).[19] The wide-angle X-ray diffraction (WAXRD) pattern shows five diffraction peaks at 2θ = 38.2, 44.5, 64.7, 77.6 and 81.8°, which were assigned to (111), (200), (220), (311) and (222) reflections of the cubic (fcc) gold lattice, respectively, indicating the presence of crystalline gold in the core-shell structure (Fig. S8).[20]



Scheme 1 Procedure of preparation of yolk/shell type PON

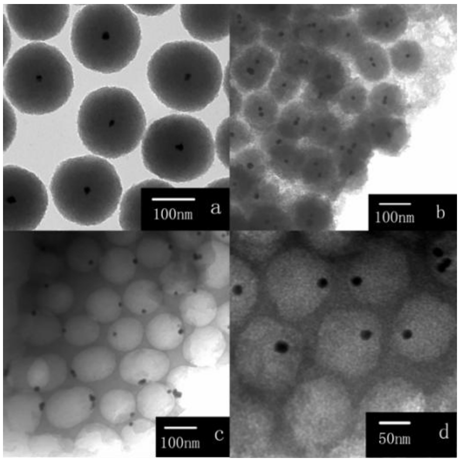


Fig. 1 TEM images of a) Au@Ph-SiO$_2$; b) Au@Si-PON; c and d) Au@PON

Afterwards, the PONs were knitting on the surface of silica template (Au@Si-PON) with the assistance of phenyl groups. The knitting process was realized by dispersing the template into 1,2-dichloroethane solution of toluene and formaldehyde dimethyl acetal (FDA), followed by adding FeCl$_3$ as catalyst. The phenyl groups on the template surface will guide FDA and toluene directly knit on the surface of template. As a result, the template and PON were tightly combined (Fig. 1b). The ^{13}C cross polarization/magic-angle spinning nuclear magnetic resonance (^{13}C CP/MAS NMR) clearly showed the resonance peaks near 137 ppm due to substituted aromatic carbon, and the resonance peak near 36 ppm due to carbon in methylene linker (Fig. 3 and S22).[21] The network based on toluene showed resonance peak at 22 ppm which can be assigned to methyl carbon connected to the benzene ring.[21] The porous properties of the samples were analysed by nitrogen adsorption/desorption analysis (Table S1). The BET surface area of Au@Si-PON reaches 1240 m^2/g. As shown in Fig. 2ia, the adsorption isotherms indicated a steep nitrogen gas uptake at lower relative pressure ($P/P_0 < 0.001$), reflecting abundant micropore structure.[21] The isotherm showed a slight hysteresis loop implying a spot of mesopore, as the pore size distribution showed in Fig. 2iia.

Finally, the silica was etched away with aqueous HF. Transmission electron microscope (TEM) images show that the obtained Au@PON materials possess yolk/shell type morphology with gold nanoparticles inside the cavities (Fig. 1c, 1d and S23). Compared with the composite Au@Si-PON，the missing band at 1150 cm^{-1} in Au@PON in FT-IR shows the silica template was completed etched away (Fig. S10).[22] The similar ^{13}C CP/MAS NMR spectra before and after silica removing indicated PON structure was retained in the etching process. The gold cores are no longer at the centre of the cavities indicating they are free to move. The size distribution of the cavities is similar to that of Au@Ph-SiO$_2$ spheres (Fig. S21). No particles grow up during the preparation process (Fig. S4). Reflections of the cubic (fcc) gold lattice are also observed in the WAXRD pattern, the same as Au@Ph-SiO$_2$ (Fig. S9). The BET surface areas of Au@PON still retained 980 m^2/g, and at lower relative pressure ($P/P_0 < 0.001$) the steep nitrogen gas uptake was also retained, meaning the microporous structure still remained. The high surface areas paved way to the catalytic process.

To illustrate the importance of introduction of benzene groups, Au@SiO$_2$ template without phenyl groups was synthesized (Fig. S5a). PON failed to grow on the surface of this template which dispersed loosely on the PON surface (Fig. S18a). No hollow structure was observed after etching process and gold particles were dispersed on the PON randomly (Au/PON) (Fig. S18b). This phenomenon clearly shows the necessity to introduce phenyl group on the template surface. PONs prepared by F-C reactions between FDA and phenyl monomers was made of hydrophobic phenyl groups and methylene groups.[3a, 23] Due to the plenty of Si-OH on the surface of SiO$_2$ template, it is difficult to direct coating the hydrophobic PON onto the hydrophilic template. After modified the template with phenyl groups, on the one hand it will change the template surface more hydrophobic, facilitating the adsorption of the organic molecules; on the other hand benzene groups on the surface will react with the monomer thus guiding the network to knit on the template surface.

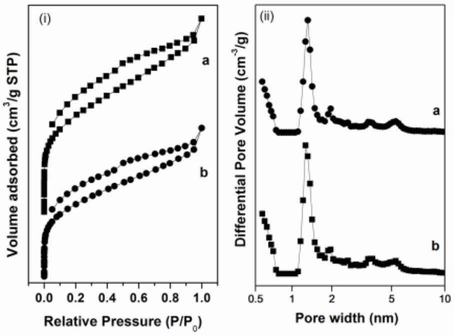


Fig. 2 N$_2$ adsorption/desorption isotherms at 77 K (i) and pore size distributions calculated using NLDFT methods (ii); a) Au@Si-PON; b) Au@PON

Yolk/shell or rattle-type nanoreactors containing a movable core and rigid outer shell are promising in catalysis in virtue of protecting the core nanoparticle from growing up. To demonstrate the high temperature-resistant property of Au@PON, the two samples Au/PON and Au@PON were treated under N$_2$ atmosphere at 473 K for 2 h. The outside deposited sample of Au/PON had suffered from serious sintering of the gold nanoparticles. Very bulky gold particles appeared, and the average diameter increased to about 20 nm (Fig. S14). Meanwhile, due to the separate confinement in the cavities of PON shells, Au NPs in Au@PON were stable and no sintering occurred (Fig. S13). In addition, Thermogravimetric (TG) curves showed that the PONs were stable up to 573 K (Fig. S17).

Liquid-phase autoxidation of cyclohexane is an important industrial process, with producing cyclohexanone and cyclohexanol (K/A oil) about 6×10^6 t/year.[24] In order to maximize the yield of K/A oil, the industrial process is usually divided into two steps: the first step is cyclohexane oxidation in absence of catalysts at high temperature (160 ℃) with low conversion (3.5–4.5%) to maximize the selectivity of cyclohexyl hydroperoxide (CHHP) (60–70%); the second step is the catalytic decomposition of CHHP to K/A oil using NaOH aqueous containing Co^{2+} as the catalyst.[25] Considering environmental pollution, great effort has been made to develop high active catalysts for the decomposition of CHHP without base.[26] Here, we found the Au@PON was effective, stable and recyclable in the decomposition of CHHP without base. The conversion was only 15% in the absence of catalyst. When Au@PON was employed, 90% conversion of CHHP and 86% selectivity for K–A oil were obtained (Fig. 4). This means Au@PON are active for the decomposition of CHHP. Furthermore, this material is stable and could be reused at least three times without significant loss of activity. The yolk/shell structure is still retained and the Au core shows no obvious aggregation (Fig. S15). The XRD pattern of the catalyst indicated no obvious difference of the Au core after reaction (Fig. S16).

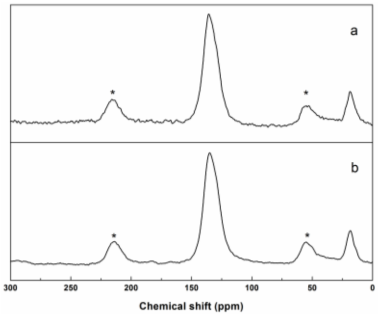


Fig. 3 ^{13}C CP/MAS NMR at the spinning rate of 8 Kz of a) Au@Si-PON; b) Au@PON; * Spinning sidebands

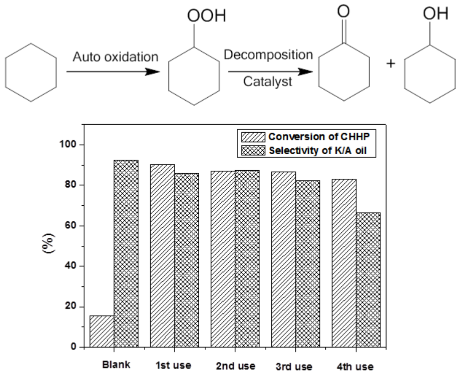


Fig. 4 Catalytic decomposition of CHHP and the reusability of the catalyst

In conclusion, a new strategy was developed to introduce gold nanoparticles as the catalytic active site into the PON with yolk/shell structure. The modified strategy of the reactive template is crucial for the formation of the yolk/shell structure. The gold nanoparticles are trapped separately in the cavities and show high thermal stability *via* the protection of the PON shells. This yolk/shell Au@PON has been proved to be an effective catalyst for the decomposition of CHHP. Good catalytic activity is expected to be obtained for the other kind of catalytic reaction involving organic molecules. The corresponding research work is underway.

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Notes and references

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