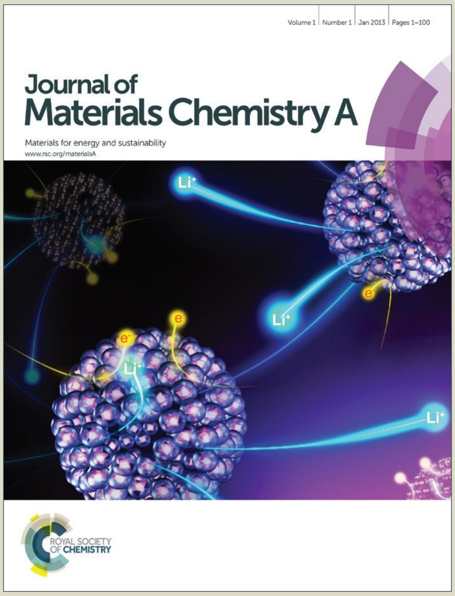
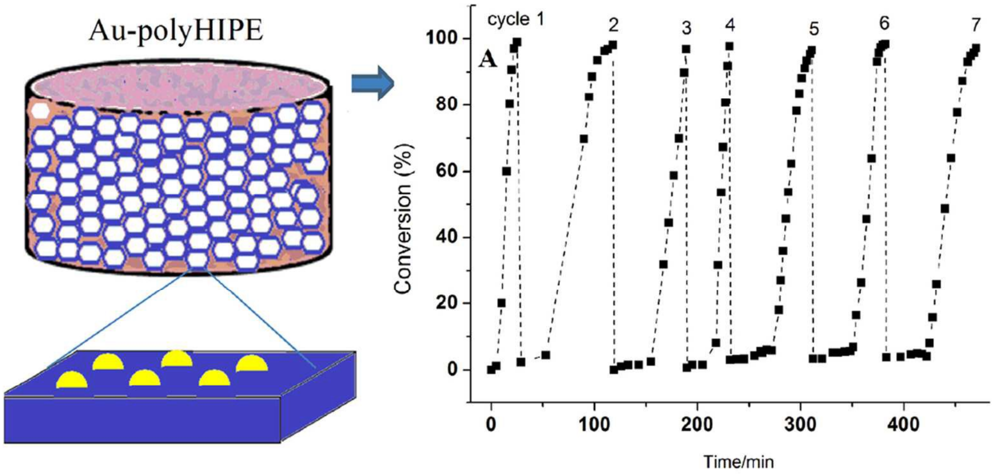
Journal of
Materials Chemistry A

Accepted Manuscript





gold nanoparticles can be organized onto a macroscopic surface in a one-pot process, leading to well recyclable catalyst
94x45mm (300 x 300 DPI)

Journal of Materials Chemistry A RSCPublishing

ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

One-Pot to Porous Monolith-Supported Gold Nanoparticles as a Well Recyclable Catalyst

Yonglian Ye,[a] Ming Jin[a] and Decheng Wan*[a]

Gold nanoparticles (AuNPs) are excellent catalysts but the recycle remains a central concern. Support of AuNPs on a porous monolith is one popular strategy but usually suffers from multistep and inefficient preparation. Here we show a one-pot strategy to well recyclable AuNPs supported on a porous monolith. It is known that polymerization of the oil phase of a high internal phase emulsion (HIPE) stabilized by surfactants can lead to a macroscopic and porous monolith (polyHIPE). If the surfactant is replaced with a dendritic amphiphile (DA) of PEI@PS (hyperbranched polyethylenimine (PEI) functionalized with polystyrene (PS) and dodecyls), and the water phase is charged with chloroauric acid, one-pot fabrication of AuNP-decorated polyHIPE (Au-DA-polyHIPE) is feasible. Alternatively, if Au-DA (AuNP stabilized with PEI@PS) is used in the place of the surfactants, Au-DA-polyHIPE can be similarly obtained. The Au-DA-polyHIPE samples are of open-cell and porous structure, and can well catalyze the reduction of 4-nitrophenol. The catalytic materials are well recyclable with no decreased activity at least within 6 cycles, where the multivalent and multi-ligand PEI should be responsible for the stability.

Introduction

The recycle of noble metal catalyst remains a central concern for several reasons: (1) most metal catalysts are expensive; (2) it favors cost-effective production, environment protection and sustainable development; (3) it favors quality products, especially where pharmaceuticals involve. Noble metal nanoparticles represent a family of exciting catalysts arising from their size-dependent property[1-4] but are usually poorly recyclable. For a high activity of conventional nanoscale AuNPs, the surface should be of large area and be active; while for good stability and well recyclable AuNPs, the surface should be sufficiently passivized. In recent decades, with the advent of the large-scale, cost-effective production of hyperbranched polymers (dendritic polymers), preparation of nanoscale, quality, stable and well dispersible metal catalysts has become possible. Unlike a small surfactant and linear polymer, dendritic polymers can act as multi-ligand stabilizers, size-controlling templates and in some cases simultaneously as a steric stabilizer, which are favorable to produce a stable while active gold nanocomposite.[5-11] However, gold nanocomposites are usually of very small sizes and poorly recyclable. Ying et al.[3] claimed in a review that "The challenge in the future of nanocatalyst research lies in the rational design and development of multifunctional, robust, and recyclable nanocomposite catalysts…..". Support of metal catalysts on magnetic materials[12-17] or inorganic frameworks[17, 18] is favorable to recycle. Recently, macroscopic and porous polymeric matrixes are becoming popular supports of metal nanoparticles.[19-29] For example, Backov et al.[24] successfully immobilized catalytic palladium nanoparticles onto a porous polymeric material via a 5-step procedure, and the resulting catalyst appears well recyclable. Zhang et al.[29] successfully prepared very large porous beads (diameters at millimeter scale), with AuNPs embedded on the surface as recyclable catalyst. However, a straightforward way to supported metal nanoparticles is still rarely reported.

Polymerization of a high internal phase emulsion (HIPE) is a well-known and convenient way to prepare a highly porous material usually with interconnected pores throughout the structure (termed polyHIPE).[30, 31] In a conventional process of polyHIPE, small surfactants are used as stabilizers, which undergo self-assembly along the water-in-oil (W/O) interface to stabilize the HIPE systems until polyHIPEs are formed. But in such a case, the surfactants only loosely adhere to the interface and are labile to running off, thus can poorly act as functional sites. One strategy is washing away the surfactants and chemically introducing new covalent functional groups onto the matrix, but such a strategy is less popular for the usually low efficiency of a heterogeneous reaction. Recently, it was found that some amphiphilic block copolymers can replace the surfactants, where the latter tends to irreversibly adhere to the interface and directly act as a functional surface.[32] Some inorganic particles,[33-35] polymers or polymeric gels[36-38] can also mediate the synthesis of a polyHIPE for their usually quasi-irreversible adhesion[39] to the interface. The ready availability of porous polyHIPE renders it one important candidate support of metal nanoparticles. Regardless of this fact, most routes to supported metal nanoparticles suffer from several drawbacks: (1) multi-step and less efficient immobilization of metal nanoparticles on a porous solid due to the heterogeneous reactions, and the solid-supported catalysts are usually less well controlled during synthesis and the resulting materials are less efficiently characterized; (2) metal leakage and contamination of the product due to poor stabilizing ability of the support; (3) aggregation or ripening of the metal nanoparticles, which leads to deterioration of the catalytic property. Many dendritic amphiphiles can act as multi-ligand stabilizer of AuNPs[5-10] while rarely inhibit their catalytic property, and are rather conveniently available. In view that dendritic amphiphiles are versatile building blocks of a variety of interesting nanostructures for their amphiphilic property and the unique topology,[40, 41] they should be possible to replace the small surfactants in a HIPE system. In fact, it is very recently reported by us that dendritic amphiphiles alone could directly leads to a functional polyHIPE.[42] If a AuNP-bearing dendritic amphiphile can be used as a stabilizer of a HIPE system, then 3D AuNPs-decorated polyHIPE will be one-pot available. Here we show the first example that AuNPs-bearing dendritic amphiphile can be used as a stabilizer of a HIPE system for one-pot preparation of Au-DA-polyHIPE. Alternatively, Au-DA-polyHIPE can also be prepared by just charging chloroauric acid in a dendritic amphiphiles-mediated HIPE process. The resulting Au-DA-polyHIPE can be used as a well recyclable catalyst.

Experimental Section

Materials

Toluene, 2, 2-azobisisobutyronitrile (AIBN) and chloroauric acid ($HAuCl_4$, 99%) were purchased from SCRC (China). Styrene (St, 99%) and divinyl benzene (DVB, 80%) were acquired from Aladdin and purified by distillation under vacuum to eliminate the inhibitor. AIBN was recrystallized with ethanol. Phosphate buffered water (pH = 7.4, 0.01 M) was used as the disperse phase. The Teflon filter-bag with hydrophilic pores (~ 45 μm) and Teflon sewing thread were purchased from China Micron Filter Expert and Tianshun Polymeric Materials (China), respectively. Branched polyethylenimine (PEI, $M_n = 1 \times 10^4$, $M_w/M_n = 2.5$, degree of branch = 60%) was purchased from Aldrich.

Preparation of dendritic amphiphiles

DA1 and DA2 (Table 1) were synthesized as previously reported.[42, 43] DA3 was synthesized as follows: DA2 (5 g, with 1.2 mmol residual amino protons) and glycidyloxydodecane[44] (0.58 g, 2.4 mmol) in chloroform (20 mL) was prepared and stirred at room temperature for 2 d. The solution was subjected to dialysis against fresh chloroform for 2 d (dialyzing tube: spectro/por, MWCO: 8000-14000) before evaporation of the solvent to yield a solid (5.2 g). ^{1}H NMR ($CDCl_3$, δ/ppm): 6.8-7.4 (22.0 H), 6.2-6.8 (14.2 H), 1.1-2.4 (43.0 H), 2.4-4.5 (10.7 H), 0.85 (3.8 H).

Table 1. Structures of several dendritic amphiphiles (DA)

DA	Structure[a]	M_n (cald.)
DA1	PEI@PS21-31	81300
DA2	PEI@PS520-16	875280
DA3	PEI@PS520-16-(C12)-162	914484

[a] Nomenclature: e.g. PEI@PS520-16-(C12)-162 means for one PEI, 16 polystyrene (PS) chains (with a polymerization degree of 520) and 162 dodecyl (C12) groups were attached to.

Preparation of AuNPs stabilized by a dendritic amphiphile

Typically (for a molar ratio of N/Au = 16), to a solution of DA3 (0.1 g, 0.026 mmol N) in chloroform (5 mL), $HAuCl_4$ in water (1.6×10^{-6} mol in 9.7 μL water) was added under stirring. The stirring was kept for 24 h, followed by drying over sodium sulfate and evaporation of the chloroform to yield a brown powder, denoted as Au-DA3.

Preparation of Au-DA-polyHIPE, route a

Typically, to an oil phase (2 mL) composed of St (0.96 mL), DVB (0.24 mL), toluene (0.78 mL), AIBN (11.6 mg) and DA3 (0.2 g), buffered water (8 mL) containing $HAuCl_4$ (6 μg, 1.6×10^{-6} mol) was added dropwise under vigorous stirring. The resulting emulsion was subjected to heating at 70 °C for 2d without stirring, followed by washing in sequence with deionized water and ethanol before drying in vacuum.

Preparation of Au-DA-polyHIPE, route b

Typically, to an oil phase (2 mL) composed of St (0.96 mL), DVB (0.24 mL), toluene (0.78 mL), AIBN (11.6 mg) and Au-DA3 (0.2 g), buffered water (8 mL) was added dropwise under vigorous stirring. The following workup was similarly to route a.

Catalytic reduction of 4-nitrophenol

Typically, to an aqueous solution (20 mL) containing 4-nitrophenol (0.06 mM) and $NaBH_4$ (0.5 g), Au-DA-polyHIPE (0.1 g, containing 8.9×10^{-6} mol Au atoms), cutting into pieces and packed in a hydrophilic Teflon filter-bag, was added. The reduction in the aqueous system was under gentle stirring and was monitored with a UV/vis spectrometer at a regular time interval. The bag was fished out, sucked with filter paper and dropped in another recycle reaction.

Characterization

UV/vis spectra were recorded on a Mapada UV-6300 spectrophotometer (Shanghai Mapada Instruments Co., Ltd.). Transmission electronic micrograph (TEM) was recorded on an H-800 Omega microscopy operating at an acceleration voltage of 200 kV on a carbon-coated copper grid. Samples were prepared by applying a drop of the dispersion in chloroform to a carbon-coated copper grid and the solvent was evaporated. In the case of polyHIPE, it was grounded and dispersed in ethanol before measurement. Thermogravimetry analysis (TGA) was performed using a Netzsch STA 449 C thermogravimetric analyzer with air purging and a heating rate of 10 °C/min over the temperature range of ca. ambient to 1000 °C. Scanning electron micrographs (SEM) were recorded on a FEI's QUANTA250FEG microscopy by placing a sample on an aluminum stub with an adhesive carbon pad. PolyHIPE samples without gold species were coated with gold; otherwise they were coated with platinum (approximately 15 nm) using a Q150R ES (Quorum) sputter coater. The samples were measured at an accelerating voltage of 10 kV and spot size of 2.0 nm. Energy dispersive x-ray spectroscopy (EDX) was measured along with the SEM. The porosity and surface area of polyHIPE was measured with a mercury intrusion porosimetry (MIP) of Pore Master 60-GT (Quantachrome Corp). ^{1}H NMR spectra were recorded on Bruker (400 MHz) with TMS as a reference. Element analysis was conducted on a VarioEL III analyzer (elementar Analysensysteme GmbH). The X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of $4^{\circ}\mathrm{min}^{-1}$ in the 2θ range of 20–80° using a Rigaku D/max2550VB3+/PC X-ray diffractometer with Cu Kα radiation (λ = 1.54178Å).

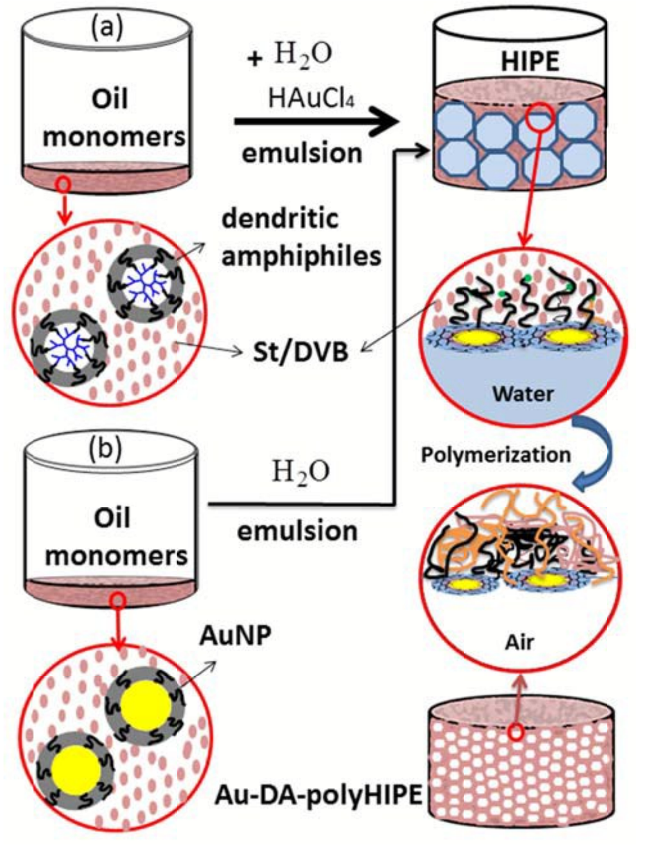


Fig. 1. Schematic presentation of two routes for dendritic amphiphiles mediated synthesis of Au-DA-polyHIPE.

Results and discussion

One-pot Preparation of 3D AuNP-Decorated PolyHIPE (Au-DA-polyHIPE)

The strategy of DA mediated synthesis of Au-DA-polyHIPE is outlined in Fig. 1, where two routes are available. A typical recipe for route a is shown in Table 2, where DA3 (Fig. 2) is used as a stabilizer, the volume ratio of W/O is 80/20, and the molar ratio of N/Au = 16. It is found a stable HIPE is available, and polymerization of the HIPE system directly leads to Au-DA-polyHIPE. The formation of crystalline AuNP is supported by XRD detection (Fig. s1, ESI) of the grounded sample. It is known that tertiary amino groups can spontaneously reduce gold ions into AuNPS,[45, 46] so the formation of AuNPs should be due to the PEI in DA3. TGA analysis (Fig. s2, ESI) shows the incombustible part (elemental Au) makes up 1.76 wt.% of the polyHIPE, agreeing with that of 1.87 wt.% of gold species in the feed. SEM measurement (Fig. 3a) shows clear and typically porous structure of polyHIPE. The interconnected pore structure is supported by MIP measurement (Fig. s3, ESI), where the surface area is 16.3 m^{2}g^{-1}. Alternatively, the Au-DA-polyHIPE is immersed into fluorescein sodium-contaminated water for 2 d, and a cutting slice shows that the inside polyHIPE is colored as well as the surface, supporting the open-cell structure. SEM micrograph also shows clear open-cell structure (Fig. s4, ESI).

Table 2. A typical recipe for preparation of Au-DA-polyHIPE (route a).

Organic phase (2 mL)	St	0.96 mL
	DVB	0.24 mL
	Toluene	0.78 mL
	DA3	0.20 g
	AIBN	11.6 mg
Aqueous phase (8mL)	H_2O	8.0 mL
	$HAuCl_4$	0.006 mg

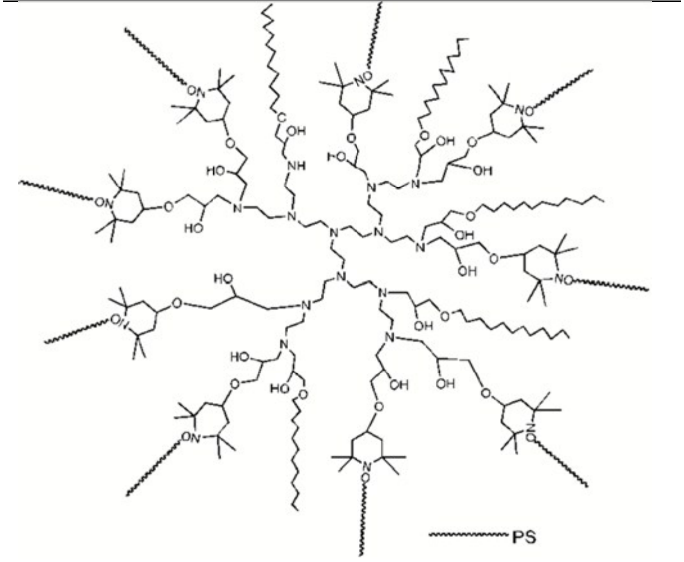


Fig. 2. Chemical structure of DA3.

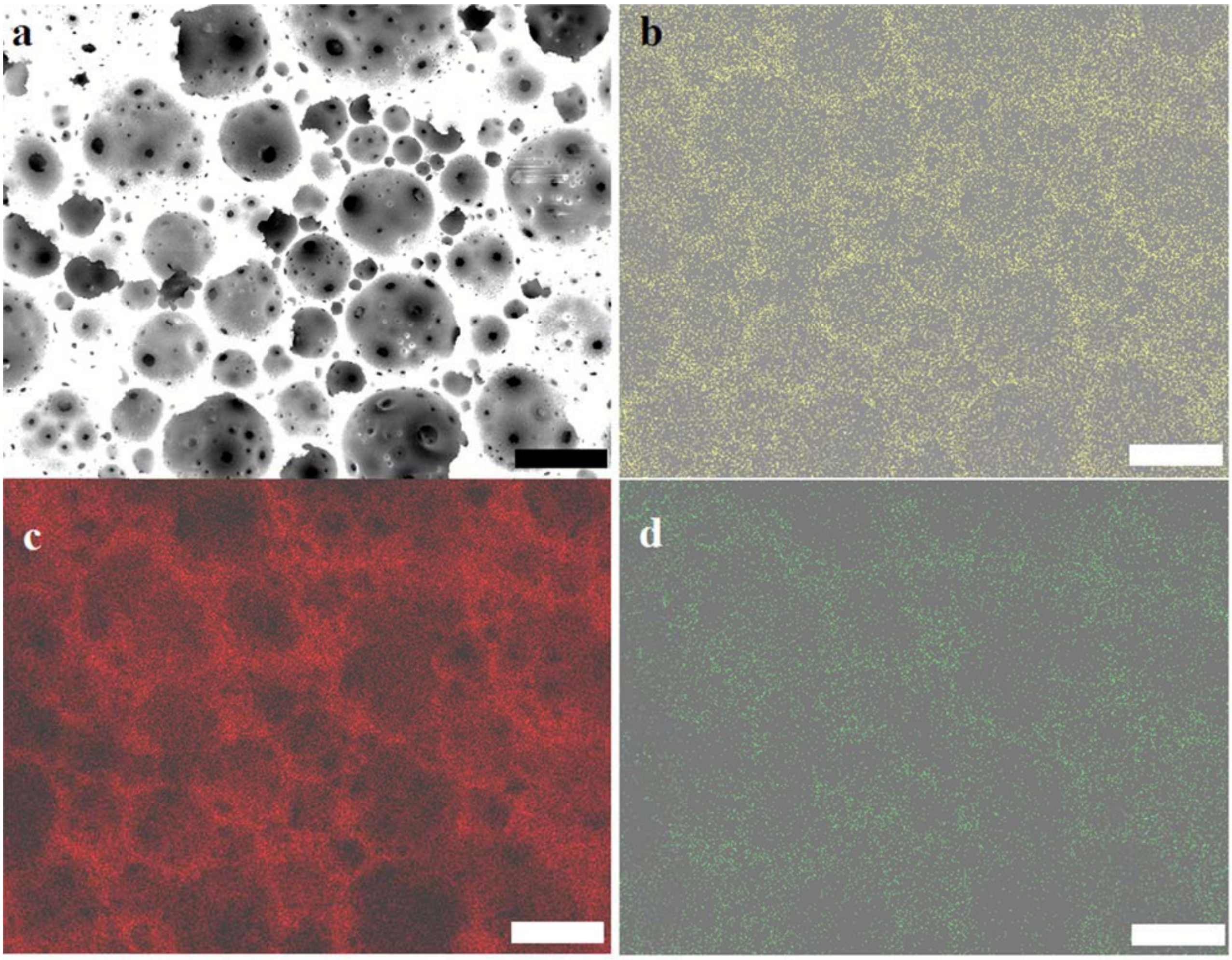
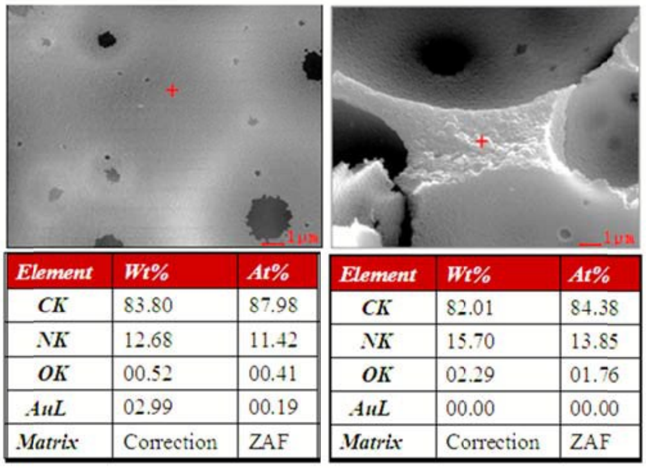


Fig. 3. SEM of a debris of Au-DA-polyHIPE (a) and the corresponding EDX micrographs of element Au (b), carbon (c) and nitrogen (d) on the surface layer. The detection depth of EDX is 2 μm and the scale bar is 20 μm.

EDX elemental analysis shows signals of element Au, C and N (Fig. s5, ESI). As shown in Fig. 3b and 3d, the signals of element gold and nitrogen are found rather "homogeneously" distributed on the surface layer, and correspond well with the SEM morphology (Fig. 3a), suggesting that these elements are mainly distributed along the surface. While the signal of carbon (Fig. 3c) appears to be abundant in the framework but less on the thin walls. The EDX spectra show stronger signals of gold and nitrogen at the crossover areas than those at the walls. Noticing that the thinnest part of the Au-DA-polyHIPE is usually less than 1 μm (Fig. s4, ESI) while the detection depth is 2 μm, such a phenomenon is understandable. In further test, several point analyses by EDX are carried out and one of them is shown in Fig. 4. It is found that gold species is detectable at the matrix surface, but hardly in the inner part of the matrix. However, the nitrogen element is detectable both at the surface and at the inside part (Fig. 4). This fact implies that DA3 (see recipe in Table 2) is in excess that some DA3 localize inside the continuous oil phase besides assembly along the interface.



Element	Wt%	At%
CK	83.80	87.98
NK	12.68	11.42
OK	00.52	00.41
AuL	02.99	00.19
Matrix	Correction	ZAF

Element	Wt%	At%
CK	82.01	84.38
NK	15.70	13.85
OK	02.29	01.76
AuL	00.00	00.00
Matrix	Correction	ZAF

Fig. 4. EDX point analysis (d = 2 μm) of a local surface (Left) and the interior (Right) of porous Au-DA-polyHIPE.

To further learn the formation mechanism of AuNP and the localization detail of gold species, a control experiment is carried out with a recipe similar to that shown in Table 2 except that the amount of water is reduced to 10 μL instead of 8 mL and the monomers and toluene are replaced with chloroform at equal volume. A brownish red color soon appears in the system without heating. TEM (Fig. s6a, ESI) clearly shows that the in-situ produced AuNPs localize along the W/O interface like a ring. After drying over sodium sulfate, a UV/vis measurement shows typical absorbance of AuNP (Fig. s7, ESI), and TEM shows that most rings disappear and discrete AuNPs are observed (Fig. s6b, ESI). It is concluded from these facts that the DA3 molecules localize along the W/O surface and sequesters the gold species, followed by spontaneous reduction of the gold species.

Au-DA-polyHIPE can be alternatively prepared using Au-DA3 as a stabilizer (route b in Fig. 1). The recipe is similar to that shown in Table 2 except that DA3 and the chloroauric acid are replaced with Au-DA3, and the corresponding HIPE is also found very stable and the resulting Au-DA-polyHIPE is also obtained as an open-cell structure (Fig. s8, ESI). Spot detection with EDX shows Au species mainly distributed on the surface but is occasionally detectable inside the matrix (micrograph not shown). In view that many metal nanocomposites are now available and a large fraction of them is still of amphiphilic nature, our method appears promising as a general route to recyclable catalyst.

Catalytic performance and recyclable property of Au-DA-polyHIPE.

The catalytic performance of Au-DA-polyHIPE is tested for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP), a well-known test reaction to evaluate catalytic metal nanoparticles.[47-49] Typically, when 4-NP (0.6 mmol) in water (20 mL) is mixed with $NaBH_4$ (1125 eq. of 4-NP) under stirring, a strong absorbance at 400 nm appears (due to formation of anionic 4-NP) and the absorbance decreases very slowly with time. However, upon addition of Au-DA-polyHIPE (Au species is 0.74 eq. of 4-NP) packed in a Teflon filter bag (with 0.45 um hydrophilic pores), the reduction of 4-NP proceeds quickly after an induction period, as shown in Fig. 5A. Regarding the mechanism, it is generally believed that both reactants are adsorbed by the AuNPs (Langmuir–Hinshelwood model), then reduction reaction proceeds and followed by desorption of the reduced product.[47, 50] In case the $NaBH_4$ is in large excess, the kinetics can be simplified to a pseudo-first-order reaction:

$$\ln(C_t/C_0) = \ln(A_t/A_0) = -k_{app}\,t \quad (1)$$

where C_t and C_0 represent the conversion at t moment and initial moment, and A_t and A_0 represent the absorbance at t moment and initial moment, and k_{app} represents the apparent rate constant. As shown in Fig. 5, the reduction kinetics complies with this model and the rate constant is 6.3×10^{-3} s^{-1} for the first cycle.

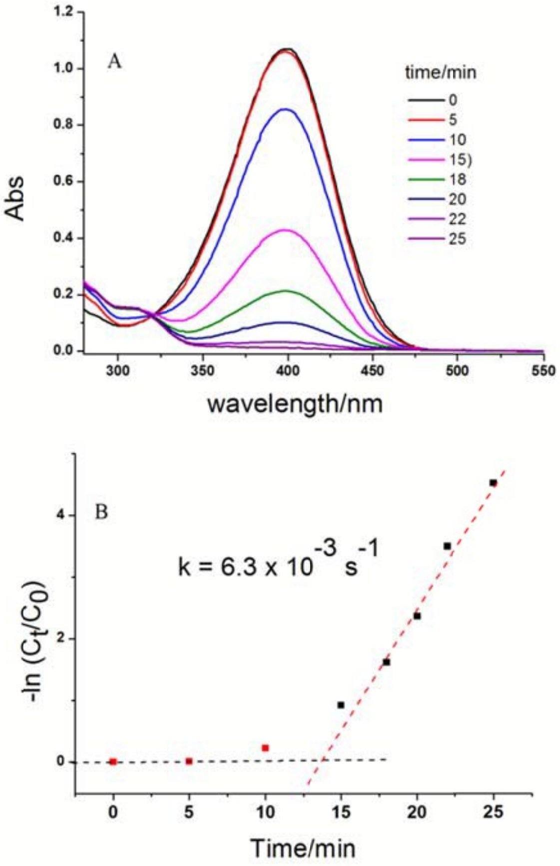


Fig. 5. UV/vis spectra during reduction of 4-NP (A) and kinetic analysis of the reaction (B). Conditions: 4-NP (0.06 mM), NaBH4 (1125 eq.) and Au-DA-polyHIPE (0.74 eq. of Au atoms with respect to 4-NP).

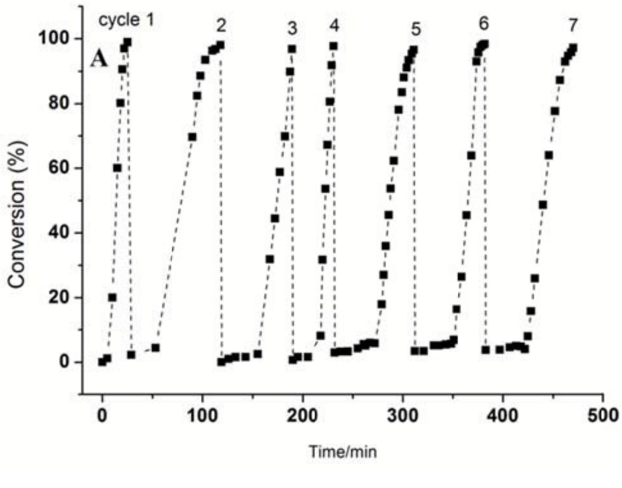


Fig. 6. Repeated use of Au-DA-polyHIPE (stabilized with DA3) on reduction of 4-NP. See Fig. 5 for reaction conditions.

The Au-DA-polyHIPE can be well recycled, and in each time over 99% conversion of 4-NP to 4-AP is found, as shown in Fig. 6, but in each cycle there is an induction period at random lengths (5-50 minute). TEM detection (Fig. 7) shows little size change of the immobilized AuNPs within 6 cycles, also supporting that the catalyst is robust and well recyclable.

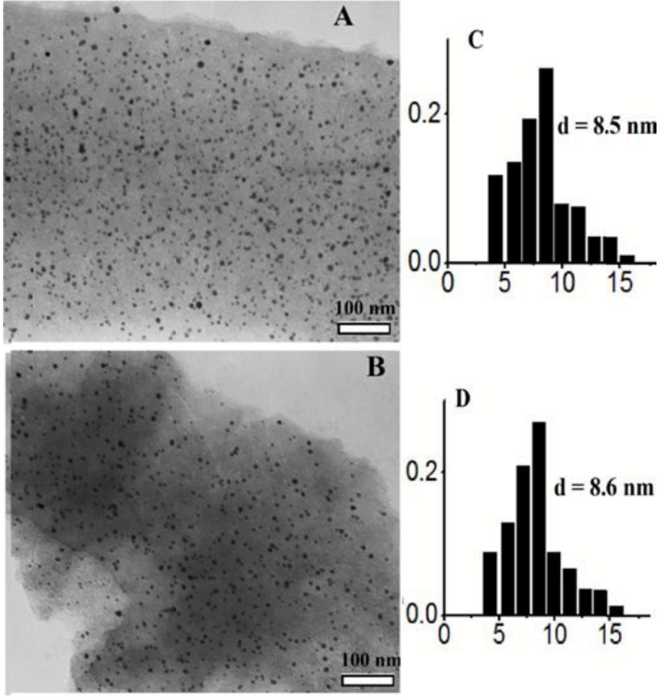


Fig. 7. TEM (A, B) and histograms (C, D) of a grounded Au-DA-polyHIPE debris before (A, C) and after (B, D) 6 cycles as catalyst for reduction of 4-NP.

It is found that DA1 and DA2 can similarly lead to Au-DA-polyHIPE and the catalytic property is also tested. As shown in Table 3, the decreased dosage of gold in preparation of Au-DA-polyHIPE leads to smaller size, while the resulting catalytic material shows higher turnover frequency (TOF) values (calculated by TOF = [4-NP]/[Au] × (conversion/t)). This is understandable because smaller AuNPs have relatively higher surface area. Noticing the macroscopic size, the low TOF is acceptable. In the case of Au-DA1-polyHIPE, the conversion of 4-NP is no longer around 99-100%, but falls to 92-95% with recycles (Fig. 8). In this aspect, DA3 seems to be superior. The reason is not understood yet.

Table 3. Au-DA-polyHIPE mediated reduction of 4-NP.

Dendritic amphiphile	N: Au (molar ratio)	Size of AuNP (nm)	TOF (h^{-1})^a
DA3	16：1	8.5 ± 1.8	0.72
DA2	100：1	6.8 ± 1.6	10.59
DA1	200：1	4.0 ± 1.5	13.51

[a] average values on 3 cycles.

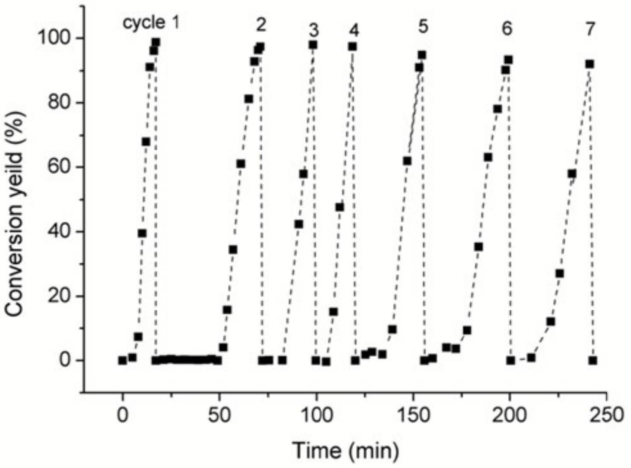


Fig. 8. Repeated use of Au-DA-polyHIPE (stabilized with DA1) on reduction of 4-NP. See the experimental section for reaction conditions.

Conclusions

With a dendritic amphiphile as a stabilizer, two routes for one-pot production of 3D AuNP-decorated porous polyHIPE (Au-DA-polyHIPE) are realized. EDX detection shows that the AuNPs are mainly distributed on the surface layer of the resulting polyHIPE. The Au-DA-polyHIPE is of large surface area and of open-cell structure and can well catalyze the reduction of 4-NP, and can act as a readily and well recyclable catalyst due to the macroscopic size and stability. TEM detects no considerable ripening of the immobilized nanoscale AuNPs at least within 6 cycles. This is the first example of one-pot production of nanoscale, robust and well recyclable AuNP on a macroscopic support of polyHIPE. The extraordinary stability of Au-DA-polyHIPE should be related with the multivalent and multi-ligand property of the dendritic amphiphiles. Noticing that many metal nanocomposites are of certain amphiphilicity, and the only requirement of our strategy is an appropriate amphiphilicity, our method provides a convenient route to organize well-designed nanoparticles into a macroscopic material with a nanoengineered surface.

Acknowledgements

Financial Support from NSFC (51273149) of China is gratefully acknowledged.

Notes and references

[a] Institute of Functional Polymers, School of Materials Science and Engineering, Tongji University. 4800 Cao-an Road, Shanghai 201804, PR China.

Electronic Supplementary Information (ESI) available: XRD, TGA, MIP, SEM, EDX spectral and UV/vis spectral characterization of the materials. See DOI: 10.1039/b000000x/

1 M. C. Daniel, D. Astruc, *Chem. Rev.,* 2004, **104**, 293.

2 A. Roucoux, J. Schulz, H. Patin, *Chem. Rev*., 2002, **102**, 3757.

3 L. L. Chng, N. Erathodiyil, J. Y. Ying, *Acc. Chem. Res.*, 2013, **46**, 1825.

4 H. W. Hu, J. H. Xin, H. Hu, X. W. Wang, D. G. Miao, Y. Liu, *J. Mater. Chem. A*, 2015, **DOI:** 10.1039/C5TA00753D.

5 R. M. Crooks, M. Q. Zhao, L. Sun, V. Chechik, *Acc. Chem. Res.*, 2001, **34**, 181.

6 K. Hayakawa, T. Yoshimura, K. Esumi, *Langmuir*, 2003, **19**, 5517.

7 X. Z. Hu, L. Zhou, C. Gao, *Colloid Polym Sci*, 2011, **289**, 1299.

8 X. Y. Liu, F. Cheng, Y. Liu, H. J. Liu, Y. Chen, *J Mater Chem,* 2010, **20**, 360.

9 L. Zhou, C. Gao, X. Z. Hu, W. J. Xu, *Chem. Mater.*, 2011, **23**, 1461**.**

10 M. L. Wang, T. T. Jiang, Y. Lu, H. J. Liu, Y. Chen, *J. Mater. Chem. A*, 2013, **1**, 5923.

11 D. C. Wan, H. T. Pu, *Mater. Lett*., 2007, **61**, 3404.

12 L. Zhou, C. Gao, W. J. Xu, *Langmuir*, 2010, **26**, 11217.

13 F.-H. Lin, R.-A. Doong, *J. Phys. Chem. C*, 2011, **115**, 6591.

14 S. Ko, J. Jang, *Angew. Chem., Int. Ed*., 2006, **45**, 7564.

15 V. Polshettiwar, R. S. Varma, *Chem.-Eur. J*. 2009, **15**, 1582.

16 X. D. Le, Z. P. Dong, Y. S. Liu, Z. C. Jin, T.-D. Huy, *J. Mater. Chem. A*, 2014, **2**, 19696.

17 A. Corma, H. Garcia, *Chem. Soc. Rev.,* 2008, **37**, 2096.

18 K. Mori, T. Hara, T. Mizugaki, K. Ebitani, *J. Am. Chem. Soc*., 2004, **126**, 10657.

19 S. J. Pierre, J. C. Thies, A. Dureault, N. R. Cameron, J. C. M. van Hest, N. Carette, T. Michon, R. Weberskirch, *Adv. Mater*., 2006, **18**, 1822.

20 Y. Zhang, L. Zhao, P. K. Patra, J. Y. Ying, *Adv. Synth. Catal*., 2008, **350**, 662.

21 Y. Liu, Y. Fan, Y. Yuan, Y. Chen, F. Cheng, S.-C. Jiang, *J. Mater. Chem*., 2012, **22**, 21173.

22 X. Fang H. Ma, S. L. Xiao, M. W. Shen, R. Guo, X. Y. Cao, X. Y. Shi, *J. Mater. Chem.,* 2011, **21**, 4493.

23 Y. C. Liu, M. L. Li, G. F. Chen. *J. Mater. Chem. A*, 2013, **1**, 930.

24 A. Desforges, R. Backov, H. Deleuze, O. Mondain-Monval, *Adv. Funct. Mater*., 2005, **15**, 1689.

25 S. Ungureanu, H. Deleuze, C. Sanchez, M. I. Popa, R. Backov, *Chem. Mater*., 2008, **20**, 6494.

26 A. Desforges, H. Deleuze, O. Mondain-Monval, R. Backov, *Ind. Eng. Chem. Res.,* 2005, **44,** 8521.

27 N. Brun, P. Hesemann, G. Laurent, C. Sanchez, M. Birot, H. Deleuze, R. Backov, New J. Chem., 2013, **37**, 157.

28 P. Krajnc, J. F. Brown, N. R. Cameron, *Org. Lett.*, 2002, **4**, 2497.

29 H. F. Zhang, I. Hussain, M. Brust, A. I. Cooper, *Adv. Mater.* 2004, **16**, 27.

30 H. Bartl, W. V. Bonin, *Makromol. Chem.,*1962*,* **57**, 74.

31 H. F. Zhang, A. I. Cooper, *Soft Matter.* 2005, **1**, 107.

32 P. Viswanathan, D. W. Johnson, C. Hurley, N. R. Cameron, G. Battaglia, *Macromolecules,* 2014, **47**, 7091.

33 B. P. Binks, *Adv. Mater.* 2002**,** **14**, 1824.

34 M. S. Silverstein, *Prog. Polym. Sci.,* 2014, **39**, 199.

35 N. Brun, S. Ungureanu, H. Deleuze, R. Backov, *Chem. Soc. Rev.,* 2011, **40**, 771.

36 S. Zhang, Y. Zhu, Y. Hua, C. Jegat, J. Chen, M. Taha, *Polymer*, 2011, **52**, 4881.

37 W. Li, Y. Yu, M. Lamson, M. S. Silverstein, R. D. Tilton, ,Matyjaszewski, *Macromolecules,* 2012*,* **45**, 9419.

38 P. J. Colver, S. A. F. Bon, *Chem. Mater.,* 2007*,* **19**, 1537.

39 P. Pieranski, *Phys. Rev. Lett.* 1980*,* **45**, 569.

40 Y. F. Zhou, W. Huang, J. Y. Liu, X. Y. Zhu, D. Y. Yan, *Adv. Mater.*, 2010, **22**, 4567.

41 Y. F. Zhou, D. Y. Yan, Chem. Commun., 2009, 1172.

42 Y. L. Ye, D. C. Wan, J. Du, M. Jin, H. T. Pu. *J. Mater. Chem. A.*, 2015, **3**, 6297.

43 D. C. Wan, J. J. Yuan, H. T. Pu, *Macromolecules,* 2009*,* **42**, 1533.

44 D. C. Wan, H. T. Pu, X. Y. Cai, *Macromolecules*, 2008, **41**, 7787.

45 P. L. Kuo, C. C. Chen, M. W. Jao, *J Phys Chem B*, 2005, **109**, 9445.

46 P. R. Selvakannan, P. S. Kumar, A. S. More, R. D. Shingte, P. P. Wadgaonkar, M. Sastry, *Adv. Mater.*, 2004, **16**, 966.

47 S. Wunder, Y. Lu, M. Albrecht, M. Ballauff, *ACS Catal*., 2011, **1**, 908.

48 N. Pradhan, A. Pal, T. Pal, *Colloids Surf., A*, 2002, **196**, 247.

49 K. Esumi, K. Miyamoto, T. Yoshimura, *J. Colloid Interface Sci.*, 2002, **254**, 402.

50 Y. Mei, G. Sharma, Y. Lu , M. Ballauff, *Langmuir,* 2005, **21**, 12229.