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Responsive hybrid nanosheets of hyperbranched poly(ether amine) as a 2D-platform for metal nanoparticles†

Cite this: *Chem. Commun.*, 2013, **49**, 603

Received 20th October 2012, Accepted 21st November 2012

DOI: 10.1039/c2cc37645h

www.rsc.org/chemcomm

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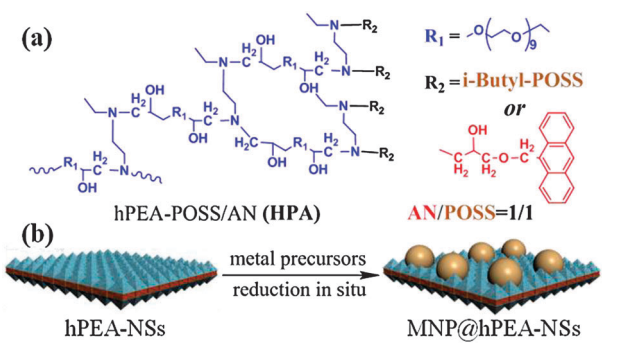
Hybrid nanosheets of hyperbranched poly(ether amine) are demonstrated as a novel 2D-platform for metal nanoparticles, which makes metal nanoparticles transfer reversibly between oil and water phases.

Metal nanoparticles (MNPs) are some of the most extensively studied nanomaterials, have many unique optical, chemical, electrical, and catalytic properties, and have attracted an enormous amount of interest for catalytic, biological, and chemical sensing applications.[1–5] Usually, these metal nanoparticles are decorated on platforms such as microspheres, vesicles, nanowires, nanotubes, nanosheets, and microgels to increase their stability, amphiphilicity, and stimuli-response.[6–10] Of these platforms, nanosheets are attractive because of their large specific surface area and load efficiency. Nanosheets as platforms can lead to two-dimensional arrays of the decorated MNPs. As prepared by oxidative exfoliation of graphite, graphene oxide (GO) and reduced graphene oxide (RGO) nanosheets modified with functional molecules are widely used as novel platforms for MNPs with varying sizes, shapes, compositions, and surface properties.[11,12] These GO or RGO nanosheets can enhance the performance of the decorated MNPs in some aspects such as stability, electric, and in catalysis, but cannot improve their dispersion in various solvents. However, other organic nanosheets are less widely reported as platforms for MNPs, which might be due to difficulties in preparation of functional organic nanosheets.

In this communication, we demonstrate hybrid nanosheets of hyperbranched poly(ether amine) (hPEA) as a novel 2D-platform for gold and silver nanoparticles. Recently, hybrid hPEA nanosheets (hPEA-NSs) with edge lengths of 1–2 μm and ultrathin thicknesses of 4–5 nm have been developed by our group through self-assembly of hyperbranched poly(ether amine) ended with polyhedral oligomeric silsesquioxane (POSS) and anthracene (AN).[13] hPEA-NSs possess a sandwich-like structure, which is comprised of the hydrophilic outer layer of hPEA and the hydrophobic crosslinked inner layer of POSS and AN moieties. Due to their multi-stimuli response, amphiphilicity, and special sandwich-like structure, hPEA-NSs are expected to be novel potential platforms for MNPs, which may control the dispersion of MNPs in both water and oil phases. The whole strategy to decorate MNPs on hPEA-NSs is illustrated in Scheme 1. MNPs are generated on hPEA-NSs through *in situ* reduction. The obtained hybrid nanomaterials (MNP@hPEA-NSs) are amphiphilic and multi-responsive in aqueous solution. Furthermore, MNP@hPEA-NSs can transfer between water and toluene phases reversibly, controlled by temperature, ionic strength and pH.

Firstly, gold nanoparticles (AuNPs) were fabricated on the hPEA-NSs. As shown in Scheme 1, the precursor of Au was adsorbed on the surfaces of the hPEA-NSs through the well-known complexation between metal atoms and amino groups in the hydrophilic hPEA outer layer of hPEA-NSs. Meanwhile, the Au precursor was further reduced *in situ* into nanoparticles by amino groups in the hPEA-NSs, and no other reductive agent (for example, $NaBH_4$) is needed. The formation of AuNPs on hPEA-NSs by reduction *in situ* was traced using UV-vis spectroscopy (Fig. S1a, ESI†). The aqueous solution turns wine-red, and



Scheme 1 (a) Structure of POSS/AN ended hyperbranched poly(ether amine) which can self-assemble into hybrid nanosheets. (b) The proposed mechanism of metal nanoparticle decoration on hPEA-NSs.

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† Electronic supplementary information (ESI) available: Detailed experimental procedures; UV-vis spectra, AFM, DLS analysis of MNP@hPEA-NSs; photographs of AuNP@hPEA-NSs after a month and AuNP@hPEA-AN particles without POSS moieties. See DOI: 10.1039/c2cc37645h

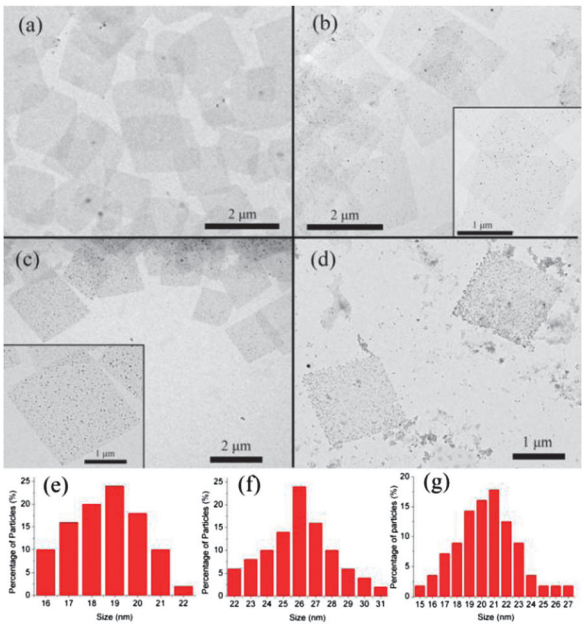

Fig. 1 TEM images of hPEA-NSs (a), AuNP@hPEA-NSs with a proportion of $HAuCl_4$ and nanosheets (w/w) 1 : 12 (b) and 1 : 6 (c), and AgNP@hPEA-NSs with a proportion of $AgNO_3$ and nanosheets (w/w) 1 : 6 (d), respectively. (e)–(f) Size distribution histograms of the metal nanoparticles on the nanosheets in the TEM images in (b)–(d), respectively. 50 nanoparticles were counted for the distribution.

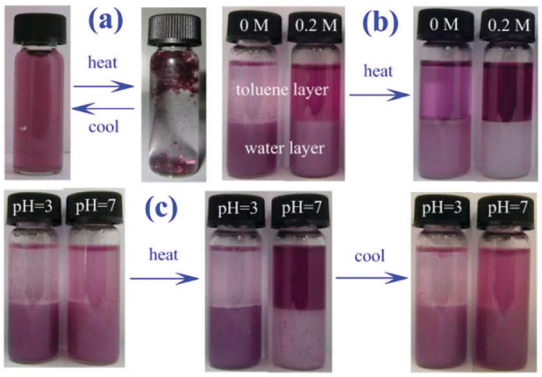

Fig. 2 (a) Photographs of AuNP@hPEA-NSs aqueous solution (pH = 7.0) at 25 °C and 75 °C. (b) Photographs of AuNP@hPEA-NSs (pH = 5.0) transferring from water to toluene phase upon heating from 25 °C to 75 °C; left: without NaCl, right: with 0.2 M NaCl. (c) Photographs of AuNP@hPEA-NSs transferring from water to toluene phase and returning to the water phase upon heating from 25 °C to 75 °C and then cooling to 25 °C, respectively; left: pH = 3.0, right: pH = 7.0. All the photographs were taken after the solution was shaken for a while and equilibrated for 10 min. The AuNP@hPEA-NSs concentration in water is 500 mg L^{-1}.

the gradual increase of the characteristic plasmonic band absorption at around 530 nm suggests the formation of AuNPs. Moreover, the *in situ* reduction was also carried out at 60 °C. The characteristic plasmonic absorption increased faster when the solution was equilibrated at 60 °C, indicating the formation rate of AuNPs is faster at the higher temperature (Fig. S1b and S1c, ESI†).

The morphology of AuNPs on the hybrid hPEA-NSs (AuNP@hPEA-NSs) was observed using transmission electron microscopy (TEM) (Fig. 1a–c). As shown in Fig. 1b and c, hPEA-NSs are covered by the uniform-sized AuNPs. Meanwhile, no AuNPs appear in the background of the TEM image, indicating that AuNPs are completely fixed on the surfaces of the hybrid nanosheets. Moreover, the diameters and densities of the AuNPs decorated on the nanosheets can be tunable with the amount of $HAuCl_4$ in the feed. With an increase of the $HAuCl_4$ in the feed from 1/12 to 1/6, the size of the AuNPs becomes larger from 18.6 ± 1.6 nm to 26.1 ± 2.5 nm in diameter (Fig. 1e and f). At the same time, the density of the AuNPs decorated on the nanosheets also increases. The decoration of AuNPs was also confirmed from an atom force microscopy (AFM) image (Fig. S2, ESI†). Similarly, we also used hPEA-NSs as platforms for the reduction of silver nanoparticles (AgNPs) through the same method (Fig. 1d), and the average diameter of the AgNPs on the nanosheets was 19.9 ± 3.6 nm determined from their TEM image (Fig. 1g). The decoration of MNPs on hPEA-NSs was further supported by the change of fluorescence of hPEA-NSs aqueous solution (Fig. S3 and S4, ESI†).

Due to the hydrophilic hPEA outer layer of the hybrid nanosheet, the obtained AuNP@hPEA-NSs are very stable in aqueous solution, and no obvious precipitation or aggregation occurred when the solution was kept at room temperature for one month (Fig. S5, ESI†). With an increase in temperature, hydrogen bonds between water molecules and the hydrophilic chains of hPEA are destroyed, resulting in the reduced hydrophilicity of the outer layers, consequently leading to the aggregation of the hybrid nanosheets. As shown in Fig. 2a, after heating to the high temperature (75 °C), AuNPs aggregate with hPEA-NSs. This phenomenon is consistent with the dynamic light scattering (DLS) results (Fig. S6b, ESI†). The *Z*-average diameter of AuNP@hPEA-NSs at pH = 7 remains almost unchanged at low temperature, while with the increase of the temperature to 55 °C, the *Z*-average diameter will increase up to more than 5 μm. The complete aggregation of AuNPs with hPEA-NSs indicates that all AuNPs are fixed on the surface of hPEA-NSs, which is also in good agreement with the TEM results. The aggregation of AuNP@hPEA-NSs can be further proven by surface plasmon resonance (SPR) of the AuNPs (Fig. S7, ESI†); with an increase of the temperature to 65 °C, the SPR of AuNPs exhibits an obvious red shift from 540 to 548 nm, which is as a result of the aggregation of AuNPs.[14,15] It should be noted that this process is reversible, and AuNP@hPEA-NSs could be dispersed in water again when shaken slightly at room temperature.

Motivated by the responsive behaviour of AuNP@hPEA-NSs in aqueous solution, we investigated their phase transfer between water and oil media, which is expected to be controlled by environmental stimuli. The study of the transfer behaviours of MNPs at fluid–fluid interfaces is very important in many traditional processes such as industrial catalysis, food formulation, crude oil extraction, and mineral flotation.[16] Most of the transfers across the oil–water interface are achieved by coating MNPs with stimuli-responsive polymer brushes,[15–17] while decoration of MNPs on responsive platforms to make MNPs transfer with the platforms is rarely reported. To test the phase transfer of hPEA-NSs, toluene was added above the aqueous solution of AuNP@hPEA-NSs. With the addition of NaCl in the

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water phase, the toluene layer became purple, indicating that AuNP@hPEA-NSs transfer into the toluene layer with larger ionic strength in the water phase (Fig. 2b). This might be attributed to the salting-out effect.[18] The presence of NaCl leads to the partial dehydration of the PEO chains, resulting in a less hydrophilic outer layer of the hPEA-NSs, and consequently water-to-oil transfer of the AuNP@hPEA-NSs. Moreover, the phase transfer of AuNP@hPEA-NSs from water to toluene can be triggered by the environmental temperature and pH. When the temperature increases to 75 °C, AuNP@hPEA-NSs transfer into the toluene layer, and the water layer turns colorless with 0.2 M NaCl (Fig. 2b). These phenomena can be further confirmed by DLS results (Fig. S6a, ESI†); the *Z*-average diameter of the nanosheets becomes larger at a higher ionic strength, and increases with the temperature. After heating to 75 °C, the toluene layer becomes wine-red when the pH of the aqueous solution is 7.0, while the toluene layer stays almost colorless when the pH is 3.0 (Fig. 2c), indicating that the phase transfer can be controlled by pH. This phenomenon is ascribed to the protonation of the amino groups at lower pH, resulting in more hydrophilic nanosheets. This can also be confirmed by the DLS results, and the *Z*-average diameter of the nanosheets keeps almost unchanged at pH = 3 even on heating to 85 °C (Fig. S6b, ESI†). When the temperature decreases to the room temperature, AuNP@hPEA-NSs can transfer back to the water phase from toluene (Fig. 2c), indicating that the phase transfer of AuNP@hPEA-NSs between toluene and water is reversible.

Generally, two-step processes are dominant in the phase transfer of nanoparticles across the oil–water interface: nanoparticle attachment onto the interface from a liquid phase and detachment from the interface to the other liquid phase.[17] As reported, the size of nanoparticles is one of key factors in the phase transfer, and nanoparticles above 50 nm could not cross the oil–water interface but attached at the interface due to the high attachment energy there.[16,17] It is surprising that AuNP@hPEA-NSs with hydrodynamic volumes of more than 500 nm can cross the oil–water interface reversibly. In contrast, AuNPs were also decorated on the hPEA nanospheres with a size of 80 nm in diameter.[13] AuNPs decorated on the hPEA nanospheres cannot transfer to the toluene phase and only aggregate at the toluene–water interface when heated to 75 °C (Fig. S8, ESI†). We proposed that the ultra-thin thickness of hPEA-NSs might decrease the attachment energy when AuNP@hPEA-NSs cross the oil–water interface, leading to the reversible phase transfer. The phase transfer performance gives metal nanoparticles potential in catalytic applications. AgNP@hPEA-NSs could be used as a catalyst to reduce *p*-nitrophenol (Nip) in the presence of $NaBH_4$ as reductant (Fig. S9, ESI†).

In summary, we have demonstrated that hybrid nanosheets of hyperbranched poly(ether amine) (hPEA-NSs) can be used as a novel 2D-platform for metal nanoparticles. Noble metal nanoparticles such as Au and Ag can be fixed on hPEA-NSs to generate MNP@hPEA-NSs by *in situ* reduction, and the size and density of the metal nanoparticles decorated on the nanosheets can be controlled by the proportion of the nanosheets and metal precursors. The obtained AuNP@hPEA-NSs are responsive to temperature, pH, and ionic strength. Especially, AuNP@hPEA-NSs can transfer reversibly between toluene and water phases under the control of temperature, pH, and ionic strength. To the best of our knowledge, AuNP@hPEA-NSs are the first example in which a nanosheet platform can lead to the reversible phase transfer of MNPs decorated on it. AuNP@hPEA-NSs are believed to provide an important alternative for the controlled phase transfer of MNPs between oil and water phases, which will find potential in industrial applications.

We thank the National Nature Science Foundation of China (21174085, 21274088), Science and Technology and Education Commission of Shanghai Municipal Government (11QA1403100, 12ZZ020), and Shanghai Leading Academic Discipline Project (B202) for their financial support. X. Jiang is supported by the SMC Project of Shanghai Jiao Tong University.

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