A synthetic strategy for carbon nanospheres impregnated with highly monodispersed metal nanoparticles

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N-doped mesoporous carbon nanospheres (N-MCN@M) impregnated with uniformly dispersed noble-metal (Au, Pt, Rh, Ru, Ag, Pd and Ir) nanoparticles are rationally designed and synthesized for hydrogenation reactions. This facile and generally applicable synthetic strategy ensured confinement of the noble-metal nanoparticles within different carbon morphologies, including mesoporous spheres, hollow particles and core–shell particles. High loading of the noble-metal nanoparticles from 8 to 44% was accomplished by tuning the initial concentration of metal salts. Even at very high loadings (> 40 wt%), a homogeneous dispersion of uniform metal nanoparticles throughout the carbon nanostructures was achieved. The proposed synthesis is also well suited for the fabrication of carbon spheres loaded with bimetallic nanoparticles (AuPt, AuRh and PtRh). Examination of these metal-loaded carbon particles as catalysts for the hydrogenation of benzaldehyde gave 100% selectivity toward carbonyl group at room and higher reaction temperatures. The outstanding performance of Au nanoparticles gave an unprecedented turnover frequency 2–4 times greater than those of Pt nanoparticles with the same size, loading and support.

INTRODUCTION

Metallic and bimetallic nanoparticles with controlled shape, size and composition have attracted considerable attention because of their excellent catalytic performance in refining petroleum compounds, organic transformations, hydrogen production and many other important chemical reactions.1–4 Among them, gold nanoparticles are powerful catalysts for aerobic oxidative processes, but considered as unfavorable for hydrogenations because of their low hydrogenation rates. Agglomeration of gold and other metal nanoparticles under conventional reaction conditions (for example, high temperature, high pressure, strong acidic or basic conditions) is recognized as one of the major limitations in catalysis.5 Therefore, supported metal nanoparticles were developed to improve the stability and catalytic performance.6–9 Until now, various methods including impregnation, ion exchange, deposition–precipitation and atomic layer deposition have been used to control metal-support interactions, and to optimize catalytic activity.10 Most of these methods suffer from involved procedures that result in relatively low loading of metal nanoparticles (< 20%). Therefore, there is a strong demand for a new synthetic strategy that allows high loadings of various metal nanoparticles, uniformly dispersed and spatially separated on solid supports.

To date, various supports such as polymers,11 oxides12–14 (for example, SiO2, Al2O3, TiO2 and CeO2), metal organic frameworks15 and carbon materials16–19 have been employed for loading metal nanoparticles. Among them, carbon nanospheres have been considered as an ideal platform because of their good thermal stability under inert atmosphere, intrinsic hydrophobic nature, presence of vast functional groups facilitating metal loading, and spherical morphology ensuring fast mass transfer and minimal viscous effects.20–22 Several attempts have been reported to decorate nanoporous carbonaceous spheres with metal nanoparticles. The most popular method is to reduce metal ions on the as-prepared carbon nanoparticles via thermal or chemical reduction. For example, Schüth and co-workers tested a method involving thermal reduction of metal ions confined in carbon nanopores to obtain noble-metal nanoparticles encapsulated in hollow carbon nanospheres.23–25 However, no matter
how the as-synthesized metal nanocrystals were prepared, by surfac-
tant-assisted, microemulsion or polyl reaction methods, the ligands stabilizing the as-synthesized metal nanocrystals weakened the interactions between metal active sites and reactants, resulting in a decreased catalytic activity. Furthermore, because of the lack of suitable functional groups in the inert pre-synthesized carbon spheres, the post-synthetically loaded metal nanoparticles were non-uniform and randomly distributed onto the carbon spheres. Therefore, the development of a general and facile method for loading high amounts of small and uniform metal nanocrystals that are homogeneously distributed on the surface of carbon spheres has so far been elusive.

Here, we report a general coordination chemistry-based method for the in situ confinement of various metal nanocrystals such as Au, Pt, Rh, Ru, Ag, Pd, Ir and their bimetallic alloy counterparts into carbon spheres.

MATERIALS AND METHODS

Chemicals: Hexadecyltrimethylammonium bromide (99%), Pluronic F127, tetraethylorthosilicate (99%), resorcinol (99%), 3-aminophenol (98%), ammonium hydroxide solution (25%), formaldehyde aqueous solution (37%) and all metal salts (K2PtCl6, AuCl3, RhCl3, RuCl3, AgNO3, PdNO3, and IrCl3) were purchased from Sigma-Aldrich company (Castle Hill, NSW, Australia). Water was purified by a Milli Q system and had an electrical resistance of 18 MΩ cm. Chemicals: Hexadecyltrimethylammonium bromide (99%), Pluronic F127, tetraethylorthosilicate (99%), resorcinol (99%), 3-aminophenol (98%), ammonium hydroxide solution (25%), formaldehyde aqueous solution (37%) and all metal salts (K2PtCl6, AuCl3, RhCl3, RuCl3, AgNO3, PdNO3, and IrCl3) were purchased from Sigma-Aldrich company (Castle Hill, NSW, Australia). Water was purified by a Milli Q system and had an electrical resistance of 18 MΩ cm.

First, metal 1-APFs@silica core–shell nanospheres were dispersed in 0.2 M HCl methanol solution at 60 °C during 6 h; this process was repeated twice to remove the remaining surfactant. Then, 40 mg of the surfactant-free metal 1-APFs@silica core–shell nanospheres was dispersed in the mixture of 25 ml of water, 8.2 ml of ethanol, 15 mg of hexadecyltrimethylammonium bromide and 169 µl of ammonium solution. After 30 min, 50 mg of aminophenol and 70 µl of formaldehyde were added respectively before leaving reaction for another 24 h. Finally, the mixture was transferred to autoclave for hydrothermal treatment at 100 °C for another 24 h. The resulting metal 1-APFs@silica@APFs sample was obtained by washing with water and ethanol for three times. To prepare metal 1-APFs@silica@M2-APF nanoparticles, the above metal 1-APFs@silica@M2-APF nanospheres were centrifuged and dried in a vacuum desiccator for 10 h. These metal 1-APFs@silica@M2-APF nanoparticles were dispersed in metal 2 salt aqueous solution (10 mls) for another 12 h. Next, these metal 1-APFs@silica@M2-APF nanospheres were centrifuged and dried in a vacuum desiccator for 10 h. Then, the obtained N-MCN@M1@N-MCN@M2 yolk–shell nanospheres (route C) were obtained after removal of silica with HF solution (see Supplementary Table S1).

Characterization

Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100F microscope (JEOL, Tokyo, Japan) operated at 200 kV. The samples for TEM measurement were suspended in ethanol and supported onto a holey carbon film on a Cu grid. Scanning electron microscopy was taken with a JEM-7800F field emission electron microscope. The N2 sorption experiments were performed at −196 °C on a Micromeritics Tristar 3000 (Atlanta, GA, USA) system with micropore analysis. Before the measurement, the samples were out-gassed at 120 °C for at least 6 h. The Brunauer-Emmett-Teller specific surface areas were calculated using adsorption data at a relative pressure range of P/P0 = 0.05–0.25. The total pore volumes were estimated from the amount of nitrogen adsorbed at a relative pressure (P/P0) of 0.99.

Hydrogenation evaluation

The catalysts were pretreated under H2 with a flow rate of 40–50 ml min−1 for 1 h at 400 °C. Hydrogenation of benzaldehyde was carried out in an aqueous phase in a stainless-steel autoclave with a magnetic stirrer. The autoclave was filled with the reaction mixture consisting of a substrate (0.05 M benzaldehyde), water (6 ml) and catalyst (4–30 mg, corresponding to 1.7 mg of metal, and the molar ratio of 35), unless specified otherwise. The autoclave was pressurized with hydrogen (0.3 MPa) and heated to the required reaction temperature (room temperature or 80 °C).

RESULTS

The fabrication of metal nanoparticle-loaded carbon nanospheres

As illustrated in Figure 1, first, the mesoporous APF polymer resin nanoparticles with uniformly distributed amino groups were prepared via a dual surfactant templating method according to our previous report. Second, nitrogen-doped mesoporous carbon nanospheres decorated with monodispersed metal nanocrystals (N-MCN@M) were formed via coordination-type interactions between metal ions and amine groups, followed by thermal reduction of metal ions to form...
the metal nanoparticles (Figure 1, route A). The cross-section TEM images in Figure 1A(a–d) show monodispersed metal nanoparticles (Au, Pt, Rh and Ru) onto N-MCNs. We believe that the pore channels in mesoporous APFs resin spheres have a dominant role as nano-containers to control the growth of metal nanocrystals during thermal reduction. This resulted in very small and uniform metal nanoparticle sizes even after high temperature carbonization. For N-MCN@Au, the mean Au particle size was estimated to be 6.1 ± 3.0 nm. In the case of N-MCNs decorated with other metal nanoparticles, the mean particle size of Pt, Rh and Ru was estimated to be 2.5 ± 1.5, 2.2 ± 0.8 and 2.5 ± 1.0 nm, respectively. The distribution of homogeneous metal nanoparticles was confirmed by the energy-dispersive X-ray spectroscopy spectra (Supplementary Figure S1). The formation of metal nanoparticles was further confirmed by the XRD patterns. In the case of Au nanoparticles, which possessed larger sizes than the other metals because of faster nucleation of Au, the XRD patterns exhibited distinct reflections at 2θ of 44, 52 and 76° attributed to the 111, 200 and 220 peaks of the face-centred cubic (fcc) Au nanocrystals (Supplementary Figure S2). The lattice distance corresponding to (111) diffraction peak was 2.35 Å, which is in a good agreement with the Au lattice fringe estimated by analysis of the high resolution transmission electron microscopy (HRTEM) images (Supplementary Figure S3). The Au particle size estimated from the (111) peak using the Scherer formula was around 6.1 nm, which also agrees well with the particle size observed by TEM (6.0 nm). The XPS spectra and electron energy loss spectroscopy mapping data show that the metal decorated N-MCNs consisted of carbon, nitrogen, oxygen and metal species corresponding to the Au, Pt, Rh and Ru metal ions used in the synthesis (Supplementary Figures S4 and S5). To demonstrate the generality of the synthetic method, Supplementary Figure S6 shows the TEM, XPS and XRD characterization results for N-MCN decorated with Ag, Pd and Ir nanoparticles. The dominant interaction between carbon precursor and metals is coordination, in which aminophenol can provide amine functional groups for coordination of metal ions. Moreover, the thermal reduction process involving consumption of carbon and reduction of metal in nanoparticles is favorable for formation of uniformly dispersed metal nanoparticles embedded in carbon spheres.30,31 It is believed that the concave curvature on the carbon sphere surface, which was generated during the thermal reduction process, allows for homogeneous formation of metal nanoparticles in the N-doped carbon spheres.

We further demonstrate that metal nanoparticles can be confined in the interior of N-doped hollow mesoporous carbon nanospheres to form the rattle-type nanoparticles with metal cores and hollow N-doped carbon shells (N-HMCN@M) (Figure 1, route B, and Supplementary Figure S7). Because the noble-metal nanoparticles were obtained by thermal reduction of coordinated metal ions, this synthesis route can be easily applicable to other metal species such as Au, Pt, Rh and Ru (Figure 1B(a–d)). The entrapped metal ions inside carbon spheres can be reduced to metal nanoparticles at high temperature and confined in these spheres (Supplementary Figure S8). The shell thickness of the metal confined N-HMCNs was assessed to be around 25 nm; and the mean particle sizes of Au, Pt, Rh and Ru were estimated to be 5.4, 2.0, 1.8 and 2.2 nm, respectively (Figure 1B(a–d) and Supplementary Figure S8). The shells of these nanoparticles were mesoporous as evidenced by the type IV shape of adsorption-desorption isotherms having a H4 hysteresis loop.

The layer-by-layer method was used to selectively deposit bimetallic nanoparticles on the yolks and shells of N-doped yolk–shell carbon nanoparticles (N-MCN@HMCN) (Figure 1, route C). TEM images Figure 1C(a–c) indicate that the metal catalyst nanoparticles were uniformly distributed in/on the mesoporous carbon cores and microporous shells. The scanning electron microscopy images (Supplementary Figure S9) show broken yolk–shell spheres.
having mesoporous carbon cores decorated with metal nanoparticles. N2 adsorption isotherms with H4 hysteresis loop and the shape being a combination of types I and IV (Supplementary Figure S10a), and the corresponding pore size distributions (Supplementary Figure S10b) indicate that each yolk–shell structure consists of an empty space between the microporous carbon core and mesoporous carbon shell. The aforementioned three different synthesis routes were used to design and synthesize a series of catalysts with different metal nanoparticles, morphologies and structures as confirmed by their detailed characterization.

Varying the loading of metal nanoparticles

Furthermore, the loading of metal nanoparticles can be conveniently controlled by tuning the initial concentration of the metal salts used. The TG profiles shown in Figure 2A indicate that the Pt loading can be tailored from 9.7 to 26.7% in the N-MCN@Pt samples, while the loading of Au nanoparticles can be altered from 8 to 44% in the N-MCN@Au samples. Interestingly, the carbon spheres with high loading of Pt nanoparticles showed better catalytic oxidation performance as evidenced by lower carbon oxidation temperature (that is, 220 instead of 340 °C). The TEM images of N-MCN@Pt (Figure 2B) indicate that the amount of metal nanoparticles in each carbon nanosphere increases with increasing concentration of metal salt. Surprisingly, even at the metal loading as high as 44% these metal nanoparticles are still uniformly dispersed and spatially separated on the carbon support (Figure 2B and Supplementary Figures S11–S15). As shown in Supplementary Figure S13, the Pt nanoparticle size increased gradually from 1.5 to 2.4 nm with increasing Pt loading from 12.4 to 26.7 wt%, whereas the Au nanoparticle size does not change with increasing Au loading from 13.5 to 43.6 wt%. In addition, the mesoporous structure of carbon spheres was quite well preserved at the concentration of metal salt smaller than 10 mM (Supplementary Figure S16). Figure 2C shows the relationship between the metal particle size and the corresponding metal loading in the N-MCN@Pt and N-MCN@Au samples. As can be seen, the size of Pt particles tends to increase with increasing metal loading; however, the size of Au particles is independent of the loading of Au. A possible explanation is the presence of –NH2 groups in mesoporous APFs resin spheres, which interact strongly with Au species and limit the growth of Au nanoparticles in the pore channels.

Catalytic performance

Catalytic performance of these catalysts was evaluated for hydrogenation of benzaldehyde in water using a high-pressure reactor. Benzaldehyde is a renewable chemical compound of bio-oil obtained by partial pyrolysis of biomass.32,33 The catalytic hydrogenation of benzaldehyde is a model reaction for hydrogenation of aromatic aldehydes leading to alcohol (benzyl alcohol) or hydrocarbons.

Figure 2 (A) The TG profiles of (a) N-MCN@Pt and (b) N-MCN@Au nanospheres calcined in air. (B) TEM images of (a) N-MCN@Pt with different loadings of Pt nanoparticles (wt%) (a1) 12.4%, (a2) 17.3% and (a3) 26.7%; (b) N-MCN@Au with different loadings of Au nanoparticles (wt%) (b1) 13.5%, (b2) 26.9% and (b3) 43.6%. (C) The average size of metal nanoparticles vs loading (wt%) of these nanoparticles in (a) N-MCN@Pt and (b) N-MCN@Au spheres.
Metal nanoparticles loaded carbon spheres as nanoreactors

DISCUSSION

By increasing the reaction temperature, one can enhance the hydrogenation rate for both Pt and Au catalysts as confirmed by the enlarged TOF values at 80 °C in comparison with those at room temperature (Supplementary Table S2). However, at higher temperature the catalytic activity of Pt and Au is opposite to that observed at room temperature; the TOF values 102–478 h\(^{-1}\) for Pt catalysts are much higher than those obtained for Au catalysts (45–79 h\(^{-1}\)). Up to 80 °C (Supplementary Figure S23), the conversion of benzaldehyde was greater than 70% in just 5 min and reached 100% in 60 min over N-MCN@Pt 9.6% and N-MCN@Pt 26.7%; these values are much higher than those obtained on Au catalysts. The size of metal nanoparticles has a significant effect on their catalytic activity;\(^{37}\) metal catalysts with small particle sizes usually show better catalytic activity.\(^{38}\) However, if the particle size is too small, then the catalytic activity can be also reduced.\(^{39}\) According to our results, N-MCN@Pt 26.7% particles with sizes of 2.3 nm showed higher activity toward hydrogenation of benzaldehyde and higher selectivity to toluene (TOF: 478 h\(^{-1}\); selectivity: 91%) in comparison with N-MCN@Pt 9.6% with a particle size of 1.7 nm (TOF: 396 h\(^{-1}\); selectivity: 87%). Similarly, Prashar et al.\(^{37}\) reported that Pt/SiO\(_2\) with relatively larger Pt particles with sizes of 8 nm displayed better catalytic performance (selectivity: 79% at 75% conversion) toward hydrogenation of cinnamaldehyde to cinnamyl than Pt/SiO\(_2\) with a mean Pt size of 1.8 nm (selectivity: 57% at 75% conversion). Also, another report\(^{34–36}\) demonstrated that Au/TiO\(_2\) with a mean Au particle size of 5.3 nm exhibited higher activity (513 μmol g\(^{-1}\) Au s\(^{-1}\)) than that of an analogous catalyst with a mean Au size of 2.0 nm (400 μmol g\(^{-1}\) Au s\(^{-1}\)) during catalytic hydrogenation of acrolein to allyl alcohol. In this research, N-MCN@Au catalysts with 8.0 and 26.8% of Au and similar mean Au particle sizes of 6 nm preformed slightly different (TOF: 52 and 45 h\(^{-1}\), respectively), which may cause some difference in the internal diffusion of reactant/product inside both catalysts. Namely, the higher pore volume (0.26 cm\(^3\) g\(^{-1}\)) of the N-MCN@Au 8.0% catalyst may offer better internal diffusion as compared with N-MCN@Au 26.8% (0.17 cm\(^3\) g\(^{-1}\)). The different performance of Pt and Au catalysts at different temperatures may be influenced by the ad/desorption rates on the surface. The Pt sites could strongly adsorb reactants and products, which reduce the desorption rate of the catalytic cycle on the Pt surface and produce a relatively low TOF.\(^{38,40}\) An increase in the reaction temperature would promote a faster ad/desorption of products on/from the Pt surface. Generally, H\(_2\) dissociation is considered as a key step in hydrogenation reactions. The desorption activation energy for H\(_2\) over Au(111) is estimated to be ~28 kJ mol\(^{-1}\) (0.29 eV), while over Pt(111) is about 0.74–0.87 eV.\(^{40}\) A low desorption activation energy of Au(111) suggests a weak

![Figure 3](image-url)

Figure 3 (a–c) HRSEM images, (d–f) high resolution transmission electron microscopy images, (g–i) EDS spectra and (j) N\(_2\) adsorption desorption isotherms of (a, d and g), N-MCN@AuPt, (b, e and h), N-MCN@AuRh, (c, f and i) and N-MCN@PtRh, respectively.
interaction between atomic H and the Au(111) surface. Therefore, more active species are possible on the gold surface because single H atoms interact very weakly with Au as compared to other metallic surfaces.

The strongly enhanced reaction activity/conversion on the prepared catalysts at 80 °C (for example, in the case of N-MCN@Pt 26.7%; TOF is 40 times greater than that at room temperature) does not change the chemoselectivity of hydrogenation. Even for prolonged reaction times after 100% benzaldehyde conversion there was no evidence for hydrogenation of aromatic rings or loss of C=O (benzene production was not detected) at 80 °C. Hydrogenation of benzaldehyde generated only two products, benzyl alcohol and toluene as shown in Supplementary Figure S23. The possibility of reusing the catalysts was also tested as shown in Supplementary Figures S24 and S25; the conversion of benzaldehyde on all the regenerated N-doped carbon supported Au and Pt catalysts was compared with that on the fresh catalysts with 100% selectivity toward carbonyl group. In addition, no leaching and sintering were detected on the catalysts used via hot filtration test (Supplementary Figure S26) and TEM imaging analysis (Supplementary Figure S27), respectively. Thus, the catalysts with monodispersed metal nanoparticles are super-highly chemoselective for hydrogenation reactions.

In conclusion, a general strategy was developed for the synthesis of versatile carbon nanospheres impregnated with highly monodispersed metal nanoparticles. The morphology and porosity of carbon spheres as well as the loading of metal nanoparticles can be well controlled. For the first time, we demonstrated that carbon spheres could be impregnated with uniformly dispersed Au and Pt nanoparticles at loadings as high as 44 wt%. A morphology-dependent catalysis on Au nanoparticles was found for hydrogenation of benzaldehyde at room temperature, which is reflected by the highest activity (TOF 2–4 times higher than that on the Pt particles with the same size and metal loading) and selectivity (100% to toluene). It is expected that the carbon spheres loaded with the aforementioned metal nanoparticles and other transition metal nanoparticles will provide an ideal platform for understanding the relation between structure and catalytic activity.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

ACKNOWLEDGEMENTS
This work was financially supported by the Australian Research Council (ARC) through Discovery Project program (DP1094070) and Linkage Project program (LP150101158). JL gratefully acknowledges the support of UQ Foundation Research Excellence Award, France-Australia Science Innovation Collaboration (FASIC) program Early Career Fellowships and Curtin University Pro Vice-Chancellor Awards for Research Excellence. JH acknowledges the MCR Scheme and the Cluster Scheme at the Faculty of Engineering & IT, the University of Sydney. JL and MM designed the research, TYY synthesized the metal nanoparticle-loaded carbonaceous nanospheres. HJL and JH performed the hydrogenation experiments. TYY, JH and JL co-wrote the manuscript with input from JFL, MJ and MM.
Supplementary Information accompanies the paper on the NPG Asia Materials website (http://www.nature.com/am)