COMMUNICATION

Gold nanoparticles encapsulated in porous carbon†

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Gold nanoparticles encapsulated in porous carbon spheres with high surface areas (~ 800 m^2 g^{-1}) have been synthesized by ultrasonic spray pyrolysis (USP). The porous carbon-encapsulated gold nanoparticles exhibit excellent catalytic activity toward the reductions of both hydrophilic and hydrophobic nitroaromatics.
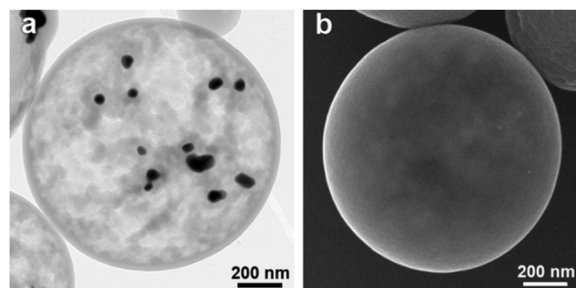
Gold was considered catalytically inactive until 1987, when Haruta and co-workers found that gold nanoclusters supported by metal oxides showed high activity toward CO oxidation even below room temperature.[1] Since then, there has been intense interest in the use of Au nanoparticles (NPs) to catalyse a variety of reactions, including low temperature oxidation of CO,[2–4] selective oxidation of alcohols,[5] epoxidation of alkenes[6] and reduction of nitroaromatic compounds.[7–9] Due to their high surface energy, however, Au NPs readily sinter, resulting in a substantial decrease in catalytic activity.[10,11] To solve this problem, encapsulated structures have been developed using various porous supports, including metal oxides,[12–17] silica,[8,18,19] dendrimers,[20,21] organic polymers,[9,22,23] and porous carbon,[24,25] which have improved the catalytic activity and stability of Au NPs. Encapsulated Au NPs are currently prepared using deposition–precipitation[7] or the coating of support materials on Au NPs followed by further chemical etching to introduce porosity into the supports.[8,9,12,23,24] These preparation methods are usually cumbersome, require multiple steps, and use sacrificial templates or toxic etching reagents. Improvements are therefore still needed in both the synthetic methodology and the production of porous encapsulating supports.

Ultrasonic spray pyrolysis (USP) is a continuous and one-step aerosol process for the production of various micro and nano-structured materials,[26–32] including quantum dots,[33] metal oxides,[34] metal sulphides,[35] and novel morphologies of high surface area carbons.[36,37] We describe here the first preparation of porous carbon-encapsulated Au nanoparticles using USP (abbreviated USP Au/C) and report on their excellent catalytic activity for the reduction of both hydrophilic and hydrophobic nitroaromatics.

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† Electronic supplementary information (ESI) available: Experimental details, characterization, tables for the comparison of USP Au/C with control catalysts, more SEM and TEM images, carbon support pore-size distribution, FTIR, XPS, control UV spectra, UV spectra and kinetics for the reduction of nitrobenzene. See DOI: 10.1039/c2cc34616h

The preparation of porous carbon-encapsulated metal nano-particles using USP is illustrated in Fig. S1 (see ESI†). Ultrasound (1.7 MHz, 6 W cm^{-2}) is applied to generate an aerosol of precursor solution (0.005 M HAuCl$_4$, 0.5 M sucrose and 1 M NaNO$_3$) which is swept through a heated zone (*e.g.*, 700 °C) by an inert gas (Ar) with a residence time of 10 s. The temperature is set high enough to decompose HAuCl$_4$ into gold and sucrose into carbon in the presence of NaNO$_3$ as catalyst and pore formation agent.[37] The resulting USP Au/C catalyst contains 3.3 wt% Au.

TEM and SEM micrographs (Fig. 1 and Fig. S2, ESI†) show that Au NPs are encapsulated in carbon microspheres, and that a furnace temperature of 700 °C gives the most highly dispersed Au NPs. XRD (Fig. 2) confirms the crystallinity of the Au NPs in an amorphous carbon matrix. The surface areas of the carbon supports are 770 m^2 g^{-1}, 40 m^2 g^{-1}, and 10 m^2 g^{-1} for the products produced using furnace temperatures of 700 °C, 600 °C, 500 °C, respectively; at 800 °C, sintering of the Au NP occurs. The optimum reaction temperature in terms of porosity of support and minimal sintering is therefore 700 °C.
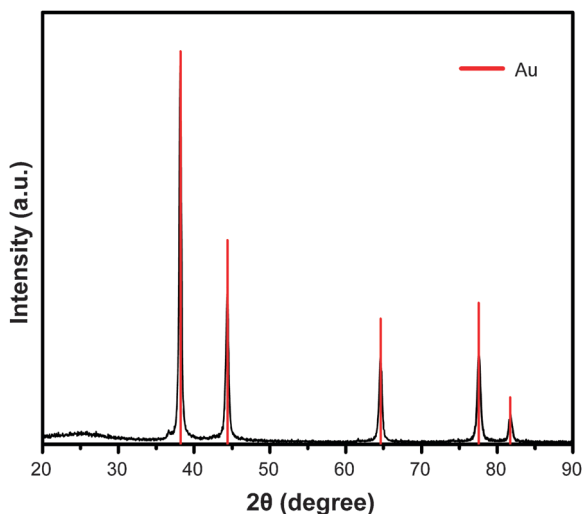
The average crystallite size of the Au NPs in carbon spheres synthesized at 700 °C, calculated by the Debye–Scherrer equation, is 31 nm, which is slightly smaller than that measured directly from TEM images (33 nm) (Fig. S3, ESI†). This demonstrates that Au NPs are mostly single crystallites with minimal polycrystalline domains. The pore-size distribution of USP Au/C shows it to be a mesoporous material with most pores smaller than 10 nm (Fig. S4, ESI†). The pore volume calculated from pore-size distribution results (Fig. S4, ESI†) is 0.4 cm^3 g^{-1} for USP Au/C synthesized at 700 °C. The density of porous carbon is thereby estimated to be 1.1 g cm^{-3} (*i.e.*, roughly half the density of graphite). The volume occupied by Au with 3.3 wt% loading can then be calculated to be $\sim 0.19\%$. That is to say,

Fig. 1 (a) TEM and (b) SEM images of USP Au/C microspheres synthesized at 700 °C.
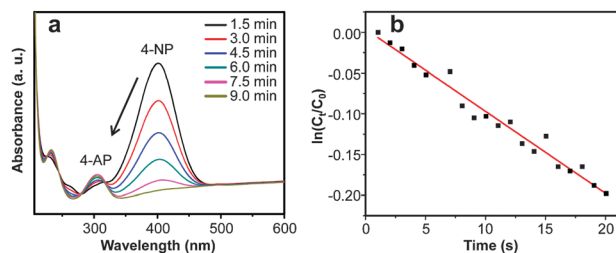
Fig. 2 XRD pattern (black) of USP Au/C synthesized at 700 °C compared with the standard Au XRD PDF # 00-004-0784 (red).

only a negligible amount of the total pore volume is occupied by the gold nanoparticles: *i.e.*, no clogging of the catalyst pore structure occurs.

FTIR spectrum shows the presence of aromatic structures as well as polar surface functionality (*e.g.*, hydroxyl and carboxylic acid groups) on the USP Au/C microspheres (Fig. S5a, ESI†). Consistent with the FTIR data, the C 1s and O 1s peaks in XPS spectra indicate the presence of surface carboxylic acid and ester functionalities (Fig. S6, ESI†).

The catalytic activity of USP Au/C was evaluated using a standard benchmark reaction:[7] the reduction of 4-nitrophenol (4-NP) by NaBH₄. NaBH₄ does not reduce 4-NP in the absence of USP Au/C particles or in the presence of USP C without Au (Fig. S7, ESI†). After the addition of 0.2 mL of an aqueous suspension of USP Au/C (1 mg mL⁻¹), the yellow colour of the reaction mixture gradually diminished. As shown in the UV-Vis spectra, the 4-NP absorption peak at 400 nm decreases and a new peak due to the formation of 4-aminophenol (4-AP) at 300 nm appears (Fig. 3a). The isosbestic points at 317, 280, 244 and 225 nm demonstrate that 4-AP is the only significant product of the catalytic reduction of 4-NP.

Since the concentration of NaBH₄ was much higher than that of 4-NP ($C_{NaBH4}/C_{4-NP} = 1200$), pseudo-first-order kinetics were used to calculate the rate constant. A linear relationship between $\ln(C_t/C_0)$ and the reaction time was found which fit

the first-order reaction kinetics (Fig. 3b). The apparent rate constant k_{app} was calculated to be 1.0×10^{-2} s⁻¹. In terms of the catalyst mass, the rate constant per g of gold is 1.5×10^3 s⁻¹ g⁻¹ (3.0×10^5 s per mol of gold). It was found that the apparent rate constant k_{app} was proportional to the surface area of Au NPs in the reaction system:[39]

$$-\frac{dc_t}{dt} = k_{app}c_t = k'Sc_t \qquad (1)$$

where c_t is the concentration of 4-NP at time t, and k' is the rate constant normalized to the surface area S of Au NPs. k' is calculated to be 9.1×10^{-3} s⁻¹ cm⁻² (or 6.3×10^6 s per mol of surface gold atoms), which is the most active yet reported (Table 1).

During the catalytic reaction, 4-NP first diffuses into the carbon support and absorbs on the surface of the Au NPs where the catalytic reaction occurs, followed by the desorption of 4-AP and then diffusion out of the carbon support.[39] Therefore, the high catalytic activity of this USP Au/C catalyst is likely due to the increased accessibility of the gold catalyst; with low porosity carbons (formed at 500 or 600 °C), the catalytic reaction is negligible (*i.e.*, ≪1% as fast). Increased Au loadings in the final catalyst can be achieved by increasing the concentrations of HAuCl₄ in aqueous precursor solutions. The higher loadings, however, also intrinsically increase the Au nanoparticle sizes within the catalysts. The k'_{gold} (the rate constant per g Au) are comparable for lower Au concentrations (5 mM and 20 mM), but decreases (as expected) at higher Au concentration (50 mM) where sintering and larger Au nanoparticles are formed (Fig. S8 and Table S1, ESI†). For comparison, a conventional wet impregnation method was used to make Au-loaded on activated carbon (referred to as Au/AC) with the same Au loading (3.3 wt%) as USP Au/C. Compared to USP method, the conventional wet impregnation method gives larger Au particle size (Fig. S9, ESI†) and lower surface area (340 m² g⁻¹) of Au/AC, which decreases the catalytic activity by a factor of four (Table S2, ESI†).

In previous studies, induction times of up to several minutes were observed before the catalytic reduction of nitrophenol occurs;[39–41] it was speculated that these induction times may be related to an activation or restructuring of the metal surface by nitrophenol. For USP Au/C, however, we do *not* observe any induction period and the reaction occurs immediately upon addition of the catalyst (Fig. 3b), which indicates that no activation step is needed for the Au NPs in our catalysts to achieve high catalytic activity.

Importantly, our USP Au/C catalyst exhibits good catalytic activity for *both* hydrophilic and hydrophobic reactants (Table 2), making it a catalyst with broader potential applications. Prior Au catalysts are generally effective for the reduction of hydrophilic nitroaromatics only.[7,8,12,18,38] Only one study, using Au NP embedded in a block copolymer, reported the ability to reduce a *hydrophobic* nitroaromatic (nitrobenzene), but that catalyst was unable to reduce hydrophilic substrates.[22] We examined the catalytic activity of USP Au/C for reductions of a series of nitroaromatic compounds with different hydrophobicities; log *P* in Table 2 is the log of the Hansch coefficient of hydrophobicity (*i.e.*, the octanol/water partition coefficient).[42] USP Au/C catalysed reductions of 2,4-dinitrophenol,

Fig. 3 (a) Time-dependent UV-Vis absorption spectra over the full time of reduction of 4-nitrophenol with NaBH₄ catalysed by USP Au/C synthesized at 700 °C. (b) Plot of $\ln(C_t/C_0)$ *versus* reaction time for initial rate studies. C_t/C_0 is calculated based on the absorbance of 4-NP at 400 nm.

Table 1 Comparison of the catalytic activities of composite gold catalysts for the reduction of 4-nitrophenol

Catalyst	Reference	Structure	Surface area ($m^2\ g^{-1}$)	Au NP diameter (nm)	k_{app} (s^{-1})	k'_{gold}[a] ($s^{-1}\ g^{-1}$)	$k'_{surface\ gold}$[b] ($s^{-1}\ cm^{-2}$)	$k''_{surface\ gold}$[b] ($s^{-1}\ mol^{-1}$)
USP Au/C	This work	Encapsulated	770	33	1.0×10^{-2}	1.5×10^3	9.1×10^{-3}	6.3×10^6
Au@SiO$_2$	8	Core–shell	Not reported	43	3.9×10^{-3}	1.2×10	9.4×10^{-5}	6.5×10^4
Au@ZrO$_2$	12	Ball-in-ball	222	6.3	5.2×10^{-3}	1.1×10^3	1.2×10^{-3}	8.1×10^5
Au–Fe$_3$O$_4$	38	Dumbbell	7.5	5.0	1.1×10^{-2}	2.8×10	2.5×10^{-5}	1.7×10^4
Fe$_3$O$_4$@SiO$_2$–Au@mSiO$_2$	7	Core–shell	236	12	5.8×10^{-3}	8.8×10	1.9×10^{-4}	1.3×10^5

[a] k'_{gold} is the rate constant per gram of gold used. [b] $k'_{surface\ gold}$ is the rate constant per gold cm^2 and $k''_{surface\ gold}$ is per mol of surface gold atoms, using a mean atomic radius for gold of 135 pm.

Table 2 Partition coefficients and rate constants of catalysed reductions of chosen nitroaromatic compounds

Substrate	log P	k (s^{-1})
4-Nitrophenol	1.61	1.0×10^{-2}
2,4-Dinitrophenol	1.74	1.7×10^{-2}
2-Methyl-4-nitrophenol	2.01	1.3×10^{-2}
2,6-Dimethyl-4-nitrophenol	2.35	1.2×10^{-2}
Nitrobenzene	1.92	8.9×10^{-3}

2-methyl-4-nitrophenol, 2,6-dimethyl-4-nitrophenol, and nitrobenzene were carried out at similar conditions as those for 4-nitrophenol (Fig. S10, ESI†). Our USP Au/C shows high catalytic activity for all reactants, and similar rate constants were obtained for the reductions of nitrophenols regardless of their hydrophobicity (Table 2). This indicates that compounds with different hydrophobicities can readily diffuse into the carbon support and access the surface of Au NPs. The catalytic activity of our material for both hydrophobic and hydrophilic nitro-aromatics is mostly due to the amphiphilicity of our carbon support, as indicated by the FTIR analysis (Fig. S5, ESI†), which showed both hydrophobic structures as well as hydrophilic functional groups in the carbon.

In conclusion, gold nanoparticles encapsulated in porous carbon spheres were synthesized using a simple one-step, template-free ultrasonic spray pyrolytic method. The rate constant in terms of surface Au atoms for the reduction of 4-nitrophenol is about ten times higher than the best prior literature report. The USP Au/C also exhibits high catalytic activity for the reduction of more hydrophobic substrates (*e.g.*, nitrobenzene). The high catalytic activity of USP Au/C for the reduction of both hydrophilic and hydrophobic nitroaromatic compounds is due to the high porosity and amphiphilicity of the carbon support.

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