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Water-soluble Au–CeO$_2$ hybrid nanosheets with high catalytic activity and recyclability†

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Received 9th April 2012, Accepted 23rd April 2012
DOI: 10.1039/c2dt30766a

A facile one-pot aqueous method has been fabricated for synthesis of Au–CeO$_2$ hybrid nanosheets. l-Lysine molecules are employed as the junctor to connect the two components of Au and CeO$_2$ nanoparticles. The obtained catalysts exhibited high catalytic activity, stability, and recyclability for the reduction reaction of p-nitrophenol into p-aminophenol by NaBH$_4$.

In the past decades, Au supported on CeO$_2$ nanoparticles (NPs) have been paid much attention due to their greatly improved catalytic performance.1–3 The obtained hybrids have been widely used as efficient conversion catalysts and three-way catalysts, whose catalytic properties are strongly dependent on their size, shape, and surface-to-volume ratio. In order to improve the stability of Au catalysts, coating them with a compact shell to form core–shell,4 or yolk–shell5 structures has been identified as effective. The active sites of the core would be kept well under the protection of the shell. Early methods are mainly focused on a “seeding growth” or a bottom-up self-assembly process. However, these processes are strongly limited by their complex steps, the use of expensive ligands, and the poor water-solubility of products. Therefore, it seems more meaningful to use the facile aqueous synthesis strategy to obtain hydrophilic products, though there are few works that have successfully prepared metal–CeO$_2$ nanohybrids in a one-pot process.

Self-assembled hybrids of zero-dimensional NPs into one-, two-, and even three-dimensional networks have shown novel collective performance on optical, electrical and catalytic properties as compared with their nanoparticle building blocks.11–17 However, for either Au or CeO$_2$, it becomes difficult to form multidimensional ordered nanostructures due to the lack of an intrinsic driving force, so a long-time aging and strictly kinetics-controlled process is quite necessary for overcoming the disadvantages in crystal structures to achieve a secondary configuration. The most representative work has been recently reported on the Ag–CeO$_2$ nanohybrids with super core–shell structures,18 and their greatly improved capability on catalysis of carbonaceous soot oxidation. Interestingly, the final spherical rice-balls are composed by the secondary structured aggregates of Ag–CeO$_2$ core-shell NPs, in which the core and the shell are also aggregates self-assembled by several Ag and CeO$_2$ NPs, respectively. Not only the stability, but also the chemoselective catalytic capability of the as-prepared Ag–CeO$_2$ catalysts is highly improved. This greatly inspired us to develop novel CeO$_2$ supported noble metal catalysts with more stable super-structures as well as a better catalytic performance.

Herein, we describe a facile one-pot aqueous method for the synthesis of Au–CeO$_2$ nanohybrids that are completely composed by Au and CeO$_2$ NPs. All the Au NPs are firmly embedded in the close arranged CeO$_2$ NPs that have spontaneously self-assembled into sheet-like networks. Experimentally, cerium(III) nitrate and l-lysine were mixed together in water to form a transparent solution, followed by adding dropwise the aqueous solution containing HAgCl$_4$ and PVP. Here, PVP served as the structure-directing agent. Then, butylamine was introduced into the system slowly to speed up the nucleation and growth of CeO$_2$ NPs. Afterwards, the solution was quickly heated to 80 °C and kept at this temperature for one hour. At last, acetone was used as an anti-solvent to deposit the products that could be purified by centrifugation (details see ESI†).

Fig. 1 shows the transmission electron microscopy (TEM) images of the samples prepared while using 0.1 mmol HAgCl$_4$. It can be seen that the as-prepared products are graphene-like nanosheets with a lateral dimension up to 20 μm. Some drapes seen in Fig. 1A might be caused by self-folding of the nanosheets. The high-resolution TEM image (HRTEM, Fig. 1D) shows that every nanosheet is not a single crystal, and is composed of numerous ultra-small closely arranged NPs with a size less than 4 nm. The clear lattice fringes of these ultrasmall NPs correspond well with the crystal facets (111) and (200) of a cubic fluorite CeO$_2$. In addition, lots of black monodisperse Au NPs with an average diameter of about 20 nm have been also clearly observed to be uniformly embedded in the CeO$_2$ nanosheets, and no isolated or surface scattered Au NPs can be found. In good consistence with the HRTEM analysis the powder XRD diffraction pattern (Fig. S1†) identifies the Au and CeO$_2$ NPs are both in a cubic phase. ADF analysis shown in Fig. S2† indicates that the thickness of the hybrid nanosheets is about 170 nm in average, however the thinnest area is less than 30 nm. In good agreement with the observation from Fig. 1A and 2D, this result confirms the largely existent self-folding phenomenon of the...
The molar ratio of [Au] : [Ce] in the nanosheets is about 1 : 3.1 determined by ICP analysis, which is much smaller than the adding ratio. This means not all the CeO$_2$ NPs self-assembled into the final nanosheets. In addition, if further increasing the amount of HAuCl$_4$, for example, if 0.15 mmol or more HAuCl$_4$ were used, it results in the disappearance of Au wrapped structures, and more aggregated Au NPs seem to be scattered on the CeO$_2$ nanosheets (Fig. S3†). However, no size change of either Au or CeO$_2$ NPs has been observed by varying the amount of HAuCl$_4$.

The color changes of the reaction system intuitively reveal the whole reaction progress. Our previous work has illustrated the key role of l-lysine as a linker for the formation of Pt–CeO$_2$ nano-hybrids. The bio-molecule l-lysine has strong coordination capability with both noble metals and CeO$_2$. Therefore, it can be seen after the addition of HAuCl$_4$ the colorless solution immediately turned to be light yellow, caused by the formation of Au$^{3+}$–l-lysine complex. Then it became salmon pink while adding butylamine. However, TEM analysis (Fig. 2A) showed that there were only 4 nm CeO$_2$ NPs but no Au produced at this time. When the temperature reached to 57 °C, the solution suddenly appeared as dark green and, meanwhile, 20 nm Au NPs closely wrapped by the pre-produced CeO$_2$ NPs could be clearly observed in the TEM images (Fig. 2B). Afterwards, the solution became purple at the final temperature of 80 °C, and the CeO$_2$ NPs gradually self-assembled into the nanosheets seen in Fig. 2C and 2D. This indicates l-lysine molecules increased the reduction potential of Au$^{3+}$, and after the formation of the Au$^{3+}$–l-lysine complex, Au$^{3+}$ could be only reduced at a temperature higher than 57 °C. In the absence of l-lysine the solution would suddenly turn from yellow to wine red after the addition of butylamine, even without heating, and, meanwhile, the nucleation and growth of Au NPs quickly happened. In those circumstances we cannot get the ideal products because of the break of growth balance between Au and CeO$_2$ counterparts, because as the temperature increased to 80 °C only scattered Au and CeO$_2$ NPs could be observed rather than the ordered hybrid structures.

After the above analysis, it is concluded that the formation of Au–CeO$_2$ nanosheets experienced the following process: the low-temperature nucleation and growth of CeO$_2$ NPs, the high-temperature nucleation and growth of Au NPs, and finally the spontaneous self-assembly of CeO$_2$ and Au NPs to form Au–CeO$_2$ nanosheets. That means CeO$_2$ undergoes a rapid nucleation and growth process, and afterwards the CeO$_2$ NPs began to continuously coat Au NPs on their surfaces until a stable dimension. As the temperature increased, more and more scattered CeO$_2$ NPs were observed and finally self-assembled together into the sheet-like hybrid structures under the guidance of PVP molecules as templates. Without the PVP only irregular Au–CeO$_2$ core–shell structures could be obtained as seen in Fig. S4.† The UV-vis absorption spectra of the products at different stages correspond well with this process, which are related to the typical Au NPs plasma response. They have shown an obvious blueshift during the reaction evolution (Fig. 3). It can be seen that at the very beginning at 80 °C there were only a few scattered CeO$_2$ NPs, and others are completely coated on the Au NPs (Fig. 2C), and finally after being at 80 °C for one hour they formed nanosheets (Fig. 2D). However, the corresponding TEM analysis (Fig. 2) identifies that the particle size of Au does not change any more, just the numbers of its surface assembled CeO$_2$ NPs. Since the Au plasma responses strongly depend on its environment around the Au surface, thus the continuously increased numbers of self-assembled CeO$_2$ NPs should be responsible for the blueshift phenomenon of the Au NPs. The similar phenomenon has been discussed in the case of Au@TiO$_2$ nanostructures in detail.⁹

Stability and activity are the most important two factors for evaluating catalysts. In this work, the typical reduction of p-nitrophenol (4-NP) into p-aminophenol (4-AP) by NaBH$_4$ as the
A model reaction has been chosen to evaluate the catalytic performance of our products. Four Au–CeO₂ catalysts are taken as samples: the Au–CeO₂ catalysts obtained using 0.1 mmol HAuCl₄ (Sample-1), after treating Sample-1 with HCl (pH = 3, aq.) for 24 h (Sample-2), after treating Sample-1 with NaOH (pH = 12, aq.) for 24 h (Sample-3), and obtained using 0.15 mmol HAuCl₄ (Sample-4). In this reaction, NaBH₄ was used in large excess to make sure the kinetic process followed the first order reaction equation, just a function between C (concentration) and t (reaction time). The kinetic constant was tested by UV-vis absorbance associated with 4-NP as a function of time. The concentration of 4-NP was kept as 0.1 mmol mL⁻¹. If 10 μL (2 mg mL⁻¹) of Sample-1 were added, the bright yellow solution faded very fast. The characteristic absorption of 4-NP at 400 nm continuously weakened until it disappeared (Fig. 4, inset). We also calculated the turnover frequency (TOF), which is defined as the number of moles of reduced 4-NP per mole of Au atoms per hour when the conversion has reached 90%. Fig. 4 shows the catalytic performance of the four catalysts in ten successive cycles of catalytic reactions. All the samples were thoroughly washed and purified by centrifugation before a next catalytic cycle. In the first cycle, the four samples (Sample-1 to -4) exhibited close catalytic activities. However, the TOF value of Sample-4 drops rapidly in the following cycles. This is probably caused by serious damage of the surface of the Au NPs that are aggregated, and ineffective CeO₂ protection. In obvious contrast, Sample-1 exhibits better activity and stability for ten cycles even after being treated by the acid or the alkali for 24 hours.

In conclusion, we have successfully prepared highly active and stable Au–CeO₂ hybrid nanosheets via a facile, rapid, one-pot aqueous method. L-Lysine plays a key role in our synthesis to modify Au and CeO₂ NPs, and further to connect the two counterparts. As used for the catalytic reduction of p-nitrophenol into p-aminophenol by NaBH₄, the obtained Au–CeO₂ hybrids exhibited high activity and stability even after the strong acid and alkali treatment for 24 hours. Additionally, our approach is expected to be a viable and low-cost strategy to fabricate noble metal–metal oxide catalysts in one-pot. It is believed that such stable hybrid nanocatalysts and the facile synthesis strategy have great potential for applications in the future.

Acknowledgements

The work is supported by the National Natural Science Foundation of China (Grant no. 20901075 and 21001101).

References