Colloidal deposition synthesis of supported gold nanocatalysts based on Au–Fe_3O_4 dumbbell nanoparticles†

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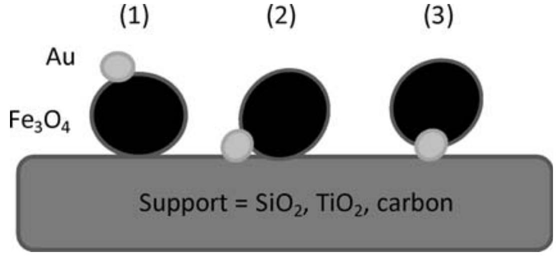
Highly active Au catalysts with a dumbbell-like heterostructure for CO oxidation were prepared through colloidal deposition method; both activities and stabilities were investigated under different experimental conditions.

Since Haruta's pioneering work in 1987 on the extraordinary catalytic activity of nanoscale gold particles for CO oxidation at low temperature,[1–5] synthetic methodologies for the preparation of gold nanoparticle catalysts have been extensively investigated.[2] These include precipitation deposition,[1,4,6–9] co-precipitation, ligand-assisted deposition,[10,11] ion exchange,[12,13] and colloidal deposition.[14,15] Among these synthetic methods, colloidal deposition (CD) is relatively new and has recently gained an increased popularity due to the advancement in solution-phase syntheses of monodisperse Au nanoparticles and deposition of these nanoparticles on various supports without the constraint of support surface properties (*e.g.*, isoelectric point). In this CD methodology, gold nanoparticles are pre-synthesized and subsequently deposited on supports *via* wet impregnation or incipient wetness.[15] The key drawback associated with the CD technique is that the pre-synthesized gold nanoparticles are only physically dispersed on oxide supports and the resultant gold catalysts lack direct metal–support interactions.[16] Furthermore, these catalytic systems have limited thermal stabilities and often sinter under high-temperature catalytic reaction conditions.[14,17] To overcome this intrinsic deficiency in the current supported Au catalysts, we herein report a new CD methodology for the synthesis of sintering-resistant nanocomposite Au catalysts. Highly active gold catalysts for CO oxidation were prepared on carbon, silica and titania. The silica-supported catalysts showed a dramatic enhancement in stability under acidic conditions.

The essence of our new CD methodology is based on the solution/suspension deposition of dumbbell-like Au–Fe_3O_4 nanoparticles on various supports (Scheme 1).[18] The key structural feature of these nanoparticles is that each dumbbell consists of a strongly interacting heterostructure with a gold nanoparticle at one end and an iron-oxide nanoparticle at another end. Due to the epitaxial growth of Fe_3O_4 on Au, a strong metal–oxide interaction exists at the interface of the dumbbell heterostructure. The dumbbell nanoparticles intrinsically entail a highly stable metal–oxide interface and therefore there is no need for these heterostructured nanoparticles to develop metal–support interactions with high surface area supports.[16,19]



Scheme 1 Three possible interactions between Au–Fe_3O_4 dumbbell nanoparticles and supports.

Au–Fe_3O_4 dumbbell nanoparticles were prepared according to a literature method *via in situ* decomposition of $HAuCl_4$ and $Fe(CO)_5$.[18] By adjusting the Au/Fe molar ratio to 1 : 10, we have obtained the nanoparticles with Au particle size of 2.5–3.5 nm and Fe_3O_4 particle size of 15–16 nm (both in diameter), as analyzed by transmission electron microscopy (TEM) (see Fig. S1, ESI†) and X-ray diffraction (XRD) (see Fig. S2, ESI†) techniques. The dumbbell nanoparticles were then washed with hexane–ethyl alcohol to remove extra surfactants (the catalysts made from unwashed Au–Fe_3O_4 nanoparticles had limited catalytic activities in CO oxidation until the reaction temperature reached 200 °C) and their hexane dispersion was deposited on amorphous silica, carbon or titania supports. Solvent evaporation gave powders that

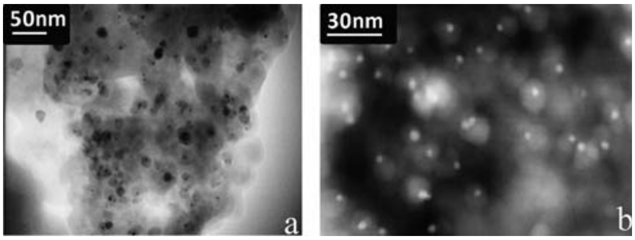


Fig. 1 TEM images of Au–Fe_3O_4 supported on SiO_2: (a) bright field, (b) dark field. The dumbbell-like nanoparticles were highly dispersed on the support.

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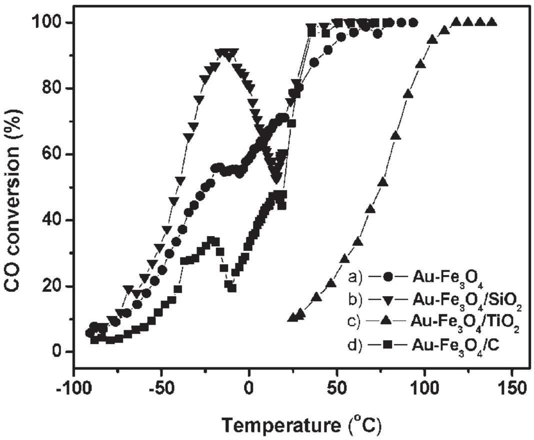

Fig. 2 CO oxidation conversion light-off curves of Au–Fe_3O_4 deposited on SiO_2, TiO_2 and carbon: (a) Au–Fe_3O_4: Au–Fe_3O_4 nanoparticles calcined at 300 °C for 1 h; (b) Au–Fe_3O_4/SiO_2: Au–Fe_3O_4 deposited on SiO_2 was calcined at 500 °C for 1 h; (c) Au–Fe_3O_4/TiO_2: Au–Fe_3O_4 deposited on TiO_2 was calcined at 300 °C for 1 h; (d) Au–Fe_3O_4/C: Au–Fe_3O_4 deposited on carbon was calcined at 300 °C for 1 h.

appeared black for Au–Fe_3O_4/SiO_2 and Au–Fe_3O_4/C and purple for Au–Fe_3O_4/TiO_2. As seen from TEM images (Fig. 1 and Fig. S1 in ESI†), Au–Fe_3O_4 dumbbell nanoparticles are highly dispersed on the surface of these supports.

Energy-dispersive absorption X-ray (EDAX) spectroscopy analysis revealed that Au loadings on the above three supports were all close to 1.6%. The catalysts were further calcined at 500 °C for Au–Fe_3O_4/SiO_2 and 300 °C for Au–Fe_3O_4/C and Au–Fe_3O_4/TiO_2 in 8% O_2/He for 1 h to remove the residue of any organic surfactant on the particle surface. The treated nanoparticles showed significant activities for CO oxidation at room temperature. Fig. 2 summarizes the light-off curves for CO oxidation measured for the supported dumbbell nanoparticles. It can be seen that different supports give different light-off curves. If supports play a negligible role in determination of catalytic activities for these heterostructured active centers, the pure dumbbell Au–Fe_3O_4 nanoparticles should have a similar light-off curve as those of the supported catalysts. However, even though the gold loadings of the supported catalysts are only 1/4 of that for the pure dumbbell particles (Table S1, ESI†), the catalytic activities for the dumbbell catalysts supported on SiO_2 and carbon are equal to or even higher than that of the pure dumbbell nanoparticles. This indicates that the supports are involved in the formation of active sites by support–Au–Fe_3O_4 interfaces *via* surface reactions [Scheme 1 (2) and (3)]. However, no new XRD peaks, which correspond to the formation of Fe_3O_4–support compounds, were observed in the XRD patterns of our catalysts treated under high-temperature conditions. This observation suggests that no surface-induced bulk reaction between the Fe_3O_4 and support oxide phases happens during the various catalyst treatments.

The light-off curve for Au–Fe_3O_4/SiO_2 calcined at 500 °C exhibits a hump at −25 °C, which is reminiscent of silica-supported Au catalysts[20] rather than iron-oxide-supported Au catalysts. This observation further indicates the effect of supports on the catalytic activities of these supported dumbbell catalysts. The observed deviation of our light-off curves from sigmoidal shapes can be attributed to the different catalytic mechanisms at low and high reaction temperatures as recently studied by Qian *et al.*[21] It is well known that Au nanoparticles directly loaded on carbon supports are inactive for CO oxidation because of the lack of metal-oxide interfaces.[3,22] In contrast, the dumbbell nanoparticles supported on carbon are highly active for CO oxidation, showing 100% CO conversion at 50 °C (Fig. 2). This successful preparation of the carbon-supported Au catalyst again demonstrates the advantage of the application of dumbbell-like nanoparticles in the CD methodology.

The dumbbell-like Au–Fe_3O_4 catalysts supported on SiO_2 and TiO_2 are stable against deactivation by acid vapors, which is ubiquitous to the common supported Au catalysts.[20] The vapors of acids, such as HNO_3, were proved to effectively deactivate the commercial Au/Fe_2O_3 catalyst of World Gold Council (Fig. S9, ESI†). When treated with HNO_3 vapor for 12 h, its T_{50} value was increased from 10 °C to 129 °C. In sharp contrast, under the same exposure condition, our Au–Fe_3O_4/SiO_2 or Au–Fe_3O_4/TiO_2 catalysts did not change their light-off curves for CO oxidation. No change of Au particles sizes was observed during this acid treatment, reflecting remarkable tolerance of the SiO_2- or TiO_2-supported dumbbell-like catalysts against corrosive acid vapors. However, the carbon-supported dumbbell catalyst showed no such stability against HNO_3 vapor as its T_{50} value was increased to 138 °C upon the treatment with concomitant growth of Au particle size from 3.0 ± 0.1 nm to 4.2 nm. This indicates that the acid tolerance of the Au–Fe_3O_4/SiO_2 and Au–Fe_3O_4/TiO_2 catalysts result from the unique interfacial structures and synergistic interplay of the silica/titania supports and the dumbbell nanoparticles. The instability associated with carbon-supported dumbbell catalysts can be attributed to the weak interface of the Au–Fe_3O_4 heterostructure with the carbon surface.

The supported dumbbell nanocatalysts are also quite stable against thermal deactivation. The light-off curves of the Au–Fe_3O_4/SiO_2 catalyst did not change after each of three sequential calcinations to 500 °C for 1 h. This high stability is consistent with the recent computational study by Liu *et al.*, which indicated the unique role of nanostructured dual-oxide supports in the enhancement of catalyst stabilities against sintering.[23,24] Liu *et al.* computationally demonstrated that the extra activation energy against the sintering of metal nanoparticles on dual-oxide supports was induced by the difference in the metal–support interactions of gold with Fe_3O_4 and SiO_2.[23]

In conclusion, we developed a new CD methodology to introduce Au catalysts on supports *via* dumbbell-structured nanoparticles. This strategy is a bottom-up approach to the recent discovery that the active sites for a highly stable Au catalyst supported on dual-oxide supports consist of a dumbbell-like heterostructure derived from surface restructuring.[23,24] Highly active Au catalysts for CO oxidation were prepared using TiO_2, SiO_2, or even C as supports through our new CD methodology. The observed catalytic activity differences among these three supported catalysts indicate a support effect induced by the development of different secondary interfaces between supports and heterostructured nanoparticles (Scheme 1). The catalysts also showed enhanced stabilities against acid vapor treatment and high temperature annealing conditions. This enhanced stability is consistent with the prediction of the theoretical modeling by Liu *et al.*[23] Further study on interfacial structures of these supported dumbbell nanocatalysts is underway.

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