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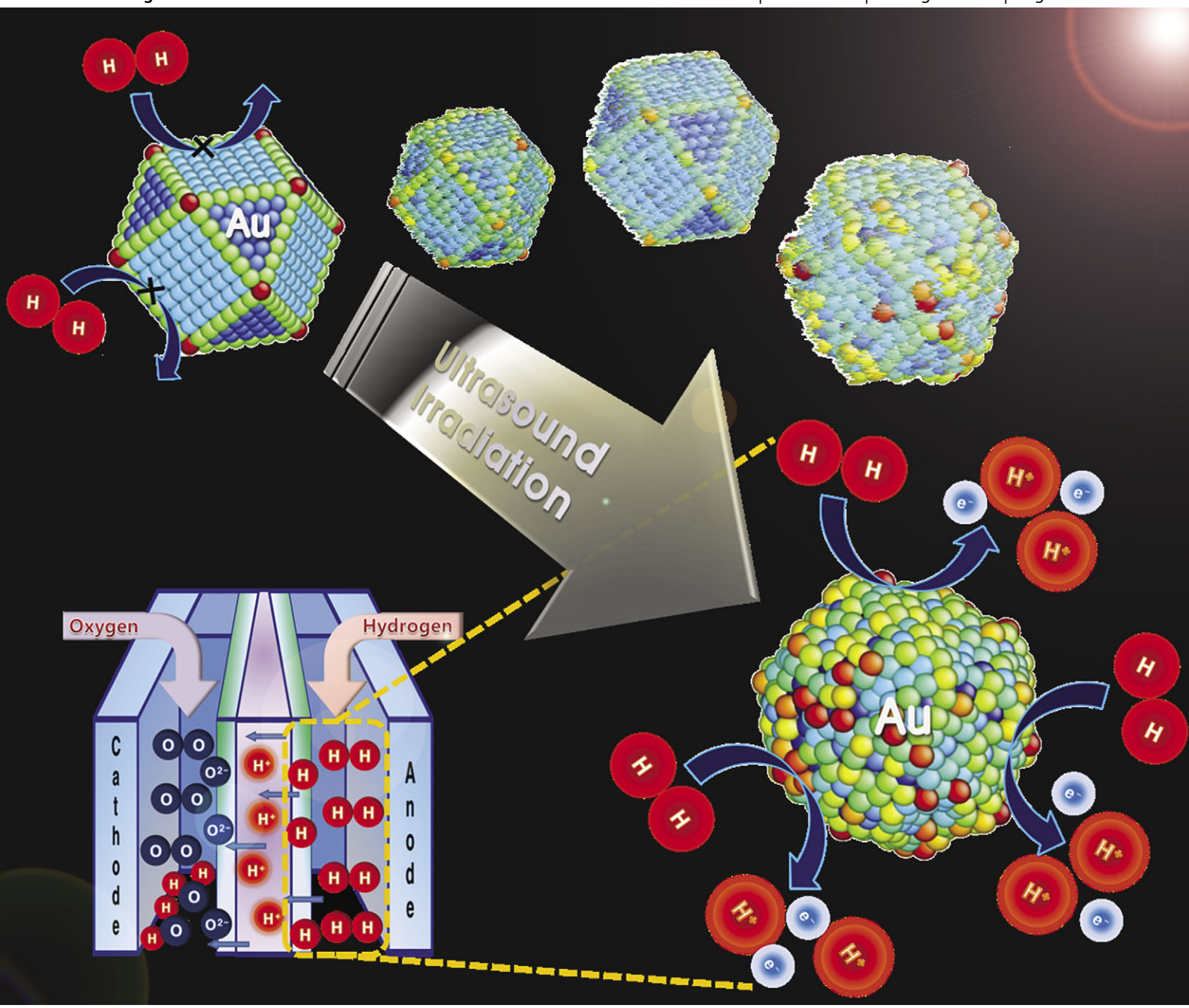

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Enhancement of electrocatalytic activity of gold nanoparticles by sonochemical treatment†

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We demonstrate that gold nanoparticles can become catalytically active for the electrochemical hydrogen oxidation reaction by a sonication treatment. Experimental data and theoretical calculations indicate that the activity arises from the supercooled molten state of gold nanoparticles which are enriched with coordinatively unsaturated gold atoms.

The emergence of catalytic activity of gold upon downsizing to nanoparticles (NPs) has been of great scientific and technological interest.[1–5] Gold NPs have been reported to catalyze hydrogenation and dehydrogenation reactions often with superior selectivity.[6] Most of the studies indicate that the activity is associated with the coordinatively unsaturated atoms at the edges and corners of gold NPs. This means that only a small fraction of the surface atoms of gold NPs are utilized for catalysis and the majority at the faces are inactive. Reducing the particle size may be a way to increase the proportion of active sites. However, this approach is bound to face problems such as synthetic difficulties and instability of small NPs. The smallest gold NPs so far synthesized by solution-based methods are 1.7 nm in diameter,[7] for which size only 49% of the surface atoms are on potentially catalytically active sites and the fraction decreases precipitously on increasing the size.[8] Certainly, there are limitations in enhancing the catalytic activity of gold NPs by reducing the size alone. Methods to activate the atoms at the faces will be able to help this situation.

There have been a few reports on catalytic activity of bulk gold by high temperature treatments. Catalytic decomposition of H_2 by a gold filament at 1200 K was reported in 1960.[9] More recently, it has been shown that treatment of a gold electrode with flame followed by quenching enhances the electrocatalytic activity for the hydrogen oxidation reaction.[10] Apparently, the high temperature conditions produce a large number of coordinatively unsaturated gold atoms on the surfaces. These results on bulk gold suggest that the activity of gold NPs can also be enhanced when treated at high temperatures. However, this would be a challenge because the conventional methods of high temperature treatments cannot avoid the growth of gold NPs into larger particles.

In this work, we sought the solution to this problem from sonochemical principles. The acoustic cavitation process of sonication produces extreme conditions of up to 5000 K of heat. The energy pulse is extremely short-lived with a decay rate of 10^{10} K s^{-1}.[11–14] These characteristics of sonication make it possible to produce gold NPs in a supercooled molten state. Such gold NPs are enriched with active sites and show strong activity for the hydrogen oxidation reaction (HOR).

In order to see whether the molten surface of gold can be indeed catalytically active, we performed theoretical calculations on the interaction between H_2 and gold NPs with faceted and molten surfaces in two steps. First, the structure of a gold NP with a molten surface was generated by classical molecular dynamics simulations. Starting from a model structure of a $\sim$3 nm-sized gold NP with cuboctahedral (Ch) symmetry, we increased the temperature in steps from 300 K to 1100 K with an increment of 200 K for each step. At each temperature step, the equilibrated structure was obtained by running 10^4 iterations with each iteration run for 1 fs. The details of the calculations are in the Supplementary Information (Fig. S1–S4†). The NP starts to show disordered atoms at 700 K and becomes completely molten at 1100 K (Fig. 1). This result is consistent with the report by Barnard *et al*. in which 3 nm-sized gold NPs are quasi-molten at $\sim$1100 K.[15] The fraction of coordinatively unsaturated gold atoms has increased considerably by this process. In the 1100 K structure, for example, about 10% of the total gold atoms both on the surface and inside have coordination numbers smaller than 7, while the 300 K structure has less than 1% of such atoms. Next, the interaction of so-generated gold NPs with H_2 molecules was investigated by first-principles total energy calculations based on the density functional theory. The 300 K structure with the Ch symmetry does not show any significant interaction with H_2. The H–H bond distance (d_{H-H}) was 0.75 Å, the same as that of free H_2. The gold atoms at an edge induced a slightly lengthened d_{H-H} of 0.77 Å, but there was no electron transfer between the gold NP and H_2. On the contrary, the 1100 K structure resulted in a d_{H-H} of 0.83 Å, and the distance between the gold NP and H_2 became 1.85 Å. According to our Löwdin population analysis, each hydrogen atom donated 0.2 e^- to the gold NP. These theoretical results strongly suggest that molten gold surfaces can be catalytically active.

We prepared samples of gold NPs on porous carbon supports without and with a following sonochemical treatment, which are denoted as Au/C and Au/C(s), respectively. The gold NPs

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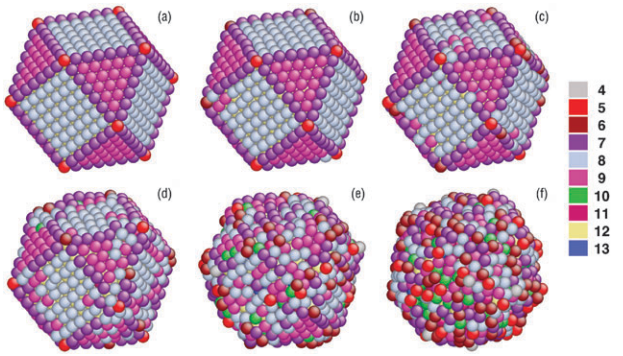

Fig. 1 Coordination numbers of gold atoms of calculated structures of gold NPs equilibrated at 0 K (a), 300 K (b), 500 K (c), 700 K (d), 900 K (e), and 1100 K (f).

were synthesized by reacting $AuCl_4^-$ with $NaBH_4$ as a reducing agent in water according to the literature method.[16] Au/C was prepared by stirring the solution with a carbon support added for 48 h, followed by filtration and vacuum-drying. For the preparation of Au/C(s), Au/C was dispersed in distilled water and irradiated with ultrasound for 30 min, and treated in the same way as for Au/C.

The powder X-ray diffraction patterns of Au/C and Au/C(s) (Fig. S5†) show broad peaks due to the carbon support and the gold NPs. Using the Scherrer equation, the particle sizes are calculated to be 3.8 nm for both samples. The transmission electron microscopy (TEM) data produced the same results for the particle size (Fig. S6†). The energy dispersive X-ray spectroscopy data (Fig. S7†) show that the compositions of the two samples are close to each other with 1 at% of Au. Therefore, in terms of the particle size and composition, Au/C and Au/C(s) do not show any difference. On the contrary, the TEM images taken at 100 K show differences between the two samples. While the gold NPs in Au/C (Fig. 2a) show facets and lattice fringes (mostly of the (111) planes), the gold NPs in Au/C(s) (Fig. 2b) are round shaped and show no lattice fringe, suggestive of poor crystallinity. This transformation of gold NPs can be understood as the result of the melting induced by the sonication treatment.[17] Based on these observations, one can conclude the following: (1) Gold NPs in Au/C are formed in ordered structures with facets and lattice fringes. (2) They can be melted by the sonication treatment. (3) The heating by sonication does not have undesirable side effects such as the growth of gold NPs or their loss. These prove that sonication treatment is an efficient method to induce the molten state of gold NPs without inducing the growth or aggregation of the gold NPs to reduce the surface area. The supercooled molten state of gold NPs is expected to have much better catalytic effects.

We studied the electrochemical properties of Au/C and Au/C(s) with cyclic voltammetry (CV) and HOR measurements (Fig. 3) under various conditions. The electrodes were prepared by placing Au/C or Au/C(s) on a rotating disk electrode (RDE) with a Nafion solution. The measurements were done in a 0.5 M $HClO_4$ aqueous solution as the electrolyte. The potential values are with reference to that of Ag/AgCl standard electrode (+0.254 V).

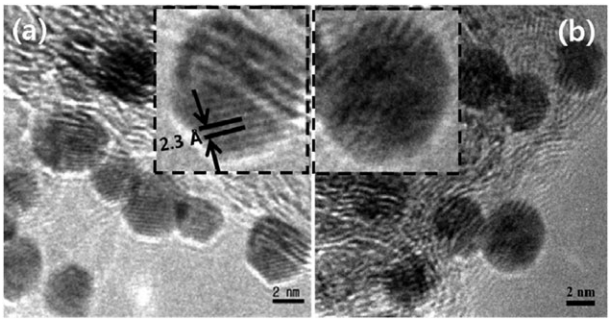

Fig. 2 TEM data on Au/C and Au/C(s). Low temperature (100 K) TEM images of (a) Au/C and (b) Au/C(s). The insets are enlarged views of single NPs.

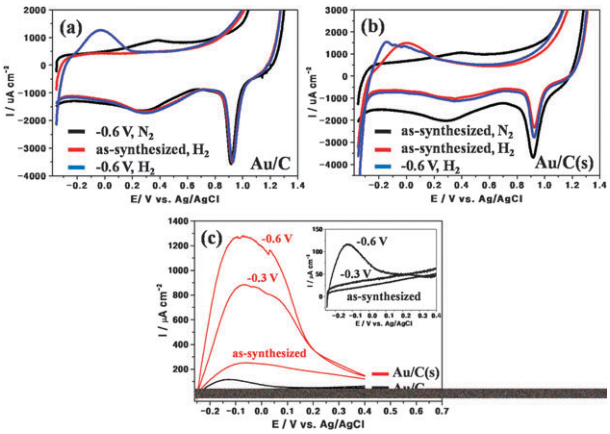

Fig. 3 Cyclic voltammograms of (a) Au/C and (b) Au/C(s) under various conditions and (c) HOR plots of Au/C and Au/C(s) with cathodic treatments at various potentials. Inset in (c) is an enlarged view to show the HOR plots of Au/C.

Au/C does not show any signal in the range between −0.2 and 0.1 V (Fig. 3a), consistent with the well-known inactivity of gold NPs for hydrogen species. It has been reported that the electrocatalytic activity of gold NPs (for oxidation of H_2O_2) can be induced by either reaction with $NaBH_4$ or treatment with a strongly cathodic potential (< −0.6 V).[10,18,19] In our case, cathodic treatment of Au/C at −0.6 V for 600 s induced a cathodic peak in the range between −0.2 and 0.1 V when the electrolyte was saturated with H_2. The cathodic current disappears when the electrolyte is saturated with N_2. These data indicate that as-synthesized gold NPs are catalytically inactive, but can be activated for the oxidation of H_2 by the cathodic treatment. Das *et al.* explained the effect of the cathodic treatment as the roughening of the surface of gold NPs.[18] The HOR data on Au/C in Fig. 3c agree with the CV data. This figure shows that Au/C is HOR inactive in the as-synthesized state and after the cathodic treatment at −0.3 V, but becomes active after the cathodic treatment at −0.6 V (inset of Fig. 3c).

Quite contrarily, Au/C(s) shows an activity for hydrogen even without cathodic treatment as can be seen in the cathodic peak in the −0.2–0.1 V range under the H_2 saturated condition (Fig. 3b). This peak disappears when H_2 is replaced by N_2. The cathodic treatment of Au/C(s) at −0.6 V broadens the potential range of this peak (Fig. 3b).

All of the CV curves in Fig. 3 show an anodic peak at 0.9 V arising from the reduction of oxygenated Au species. The area of this peak has been used to obtain the electrochemically active surface areas (ESAs) of a gold electrode.[20] Since we kept the amount of gold NPs loaded on the RDE constant (at 10 μg) in all of the electrochemical measurements, the more or less constant peak areas regardless of the measurement conditions indicate that neither the cathodic nor sonochemical treatment influences the ESA of Au NPs. Therefore, we can conclude that the appearance of the activity for hydrogen is not related to the change of the ESA, but to the change of the surface state.

The HOR plots in Fig. 3c give a clear comparison between Au/C and Au/C(s). The current densities in these plots are normalized values based on the areas of the anodic peak at 0.9 V (420 C cm^{-2}). All of the Au/C(s) samples with different cathodic treatments show higher HOR currents than Au/C. The highest HOR current density of Au/C, after the cathodic treatment at −0.6 V, is 117 A cm^{-2}. In contrast, the as-synthesized Au/C(s) without any cathodic treatment shows a more than twice higher peak current density of 256 A cm^{-2}. Upon the cathodic treatments at −0.3 and −0.6 V, the HOR current density is further increased to 886 and 1280 A cm^{-2}, respectively. When the data of Au/C and Au/C(s) cathodically treated at −0.6 V are compared, the peak current density of Au/C(s) is more than 10 times larger than that of Au/C. Combined with the low temperature TEM data, the electrochemical data indicate that the sonochemical treatment produced supercooled molten gold NPs with greatly enhanced catalytic activity for HOR. Since the activity of the as-synthesized Au/C(s) is more than two times higher than that of Au/C after the treatment at −0.6 V, we can conclude that sonication is effective in activating the gold NPs.

It is noteworthy that the HOR peaks of Au/C(s) are broader than that of Au/C. The potential range of the peaks of Au/C(s) is extended to a more positive potential region in addition to the region covered by Au/C. This indicates that Au/C(s) has a different type(s) of active gold atoms in addition to the type present in Au/C. Although more elaborate studies are required, we believe that the activation of Au/C by the cathodic treatment is restricted to the atoms at the edges and corners of the regularly shaped gold NPs while the activity of the Au/C(s) arises from all over the surface because the molten structure does not have such distinction among the surface atoms. This is probably the reason why the activity of the as-synthesized Au/C(s) is more than two times higher than that of Au/C after the treatment at −0.6 V.

We found that the HOR current density of Au/C(s) increased with the increase of the time period used for the sonochemical treatment up to 2 h (Fig. S8†). We also tried the same method with Pt by treating a similarly prepared Pt/C sample with ultrasound, but failed to see any noticeable change in the activity of Pt (Fig. S9†). Probably, Pt NPs are already active all over the available surface so that further roughening by sonochemistry does not make much difference. In addition, because Pt melts at a higher temperature than Au, the effect of ultrasound on Pt may be weaker than that in the case of Au.

In conclusion, we demonstrate that gold NPs can become an active electrocatalyst by sonication treatment. Our data show that sonochemistry is a very efficient method to heat-treat nanoparticles without affecting the particle size. This is the first time use has been made of the heating effect of sonication. Because the supercooled molten gold NPs have a large fraction of coordinatively unsaturated atoms all over the surface, they show high HOR activity. We believe that the sonochemical heating of the present study can find applications in altering the properties of various nanomaterials, opening up a new horizon for the studies on nanomaterials.

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