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J. Am. Chem. Soc., **Just Accepted Manuscript** • DOI: 10.1021/jacs.7b05476 • Publication Date (Web): 08 Sep 2017

Downloaded from <http://pubs.acs.org> on September 12, 2017

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Catalytic Activity Control via Crossover between Two Different Microstructures

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ABSTRACT: Metal nanocatalysts hold great promise for a wide range of heterogeneous catalytic reactions, while the optimization strategy of catalytic activity is largely restricted by particle size or shape control. Here, we demonstrate that a reversible microstructural control through the crossover between multiply-twinned nanoparticle (MTP) and single crystal (SC) can be readily achieved by solvent post-treatment on gold nanoparticles (AuNPs). Polar solvents (e.g. water, methanol) direct the transformation from MTP to SC accompanied by the disappearance of twinning and stacking faults. A reverse transformation from SC to MTP is achieved in non-polar solvent (e.g. toluene) mixed with thiol ligands. The transformation between two different microstructures is directly observed by in-situ TEM and leads to a drastic modulation of catalytic activity towards the gas-phase selective oxidation of alcohols. Based on the combined experimental and theoretical investigations of alcohol chemisorption on these nanocatalysts, we propose that the exposure of {211}-like microfacets associated with twin boundaries and stack faults accounts for the strong chemisorption of alcohol molecules on MTP AuNPs and thus the exceptionally high catalytic activity.

1. INTRODUCTION

Nanometer-sized gold particles have attracted great fundamental research interests due to their diverse structures and fascinating catalytic properties¹⁻³. Despite their identical face-centered cubic (f.c.c.) atomic packing pattern, the catalytic activities are highly sensitive to the non-periodic structural features, such as crystal facets, grain/domain boundaries and defects⁴. Actually, most studies indicate that only a small fraction of the total metallic sites on a gold nanoparticle frequently contributes to its catalytic activity⁵. For example, the low coordinated perimeter⁶ and corner sites of gold nanoparticles⁷ have been reported to exhibit extremely high catalytic activity. On the other side, gold nanostructures in the form of MTP consist of f.c.c. structured tetrahedra joined by twin boundaries with elastic strain to give decahedra or icosahedra⁸⁻¹⁰. Such MTPs are rich in twin boundaries exposed with high-index {211}-like facets¹¹, along with a high probability of stacking faults (SFs) in the vicinity of the {111} coherent twin boundaries (TBs) due to the low SF energy¹², and thus exhibit very different properties with respect to their single-crystals counterparts¹³. It is interesting to note that in some cases, the presence of twin defects (i.e. TBs and SFs) imposes a stronger impact on the catalytic activity than the type of facet¹⁴. For instant, Choi *et al.* investigated the catalytic formic acid oxidation activities of Pd nanocrystals with different shapes and twin structures and revealed that both decahedra and

icosahedra exhibited higher specific activities than cubes even though the {111} facets were less active than the {100} facets¹⁵. Wang *et al.* compared the catalytic activities of Au₇₅Pd₂₅ icosahedrons and octahedrons for the aerobic oxidation of cyclohexane and demonstrated that twins in icosahedrons predominately generated tensile surface structure and highly negatively charged surface, which could enhance the catalytic activity¹⁴. However, in both cases, the structure-activity correlation is mainly supported by theoretical calculations while clear experimental evidence is rarely reported. A comprehensive understanding of the twin effect on catalysis is yet implemented due to the plagued composition and facet effect as well as the poorly controlled twin structures.

Different from their single-crystalline counterparts, the growth of nanoparticles that contain twin defects can be quite difficult to control because multiple competitive growth pathways can evolve such structures¹⁵. In traditional bottom-up approaches, the twin defects of nanoparticles are tuned by various experimental parameters including type of seeds, stabilizers, additives, solvent, and temperatures, following a "nucleation and growth" or "seeded growth" mechanism^{16,17}. The complex mechanism makes it difficult to rationally and reproducibly manipulate the process and thus the populations of MTP and SC. Besides, uncertainty in the loading process could also affect the catalytic performance and thus hinders the investigation of twin effects.

Here we report a simple post-synthesis method to manipulate the populations of MTP versus SC of AuNPs. We find that the water treatment leads to a drastic structural change from MTP to SC, which significantly reduces the proportion of MTP (from 86% to 26%). Meanwhile, the binding with thiols in non-polar solvent results in a reverse SC-to-MTP conversion of AuNPs. The crossover of these two microstructures allows a facile control over the defects associated with the twin boundaries of AuNPs, and helps us to reveal the importance of twin boundary effects on gas-phase catalytic oxidation of alcohols. Kinetic studies indicate that the chemisorption of alcohols on MTP is significantly stronger than that on SC, which is further confirmed by temperature-programmed desorption (TPD) and solid state nuclear magnetic resonance (NMR) measurements. This simple solvent post-treatment method has also been validated to improve the catalytic performance of other supported gold catalysts for the oxidation of alcohols by tuning their microstructures.

2. EXPERIMENTAL SECTION

2.1 Materials synthesis

Synthesis of AuNPs. The synthesis of AuNPs is similar to the method reported by Zheng et al.¹⁸. In a typical synthesis, 100 mg of AuPPh₃Cl was mixed with 400 μ L of dodecanethiol in 20 mL of benzene to form a clear solution. Then, 84 mg of NaBH₄ was added into the solution in one portion. The mixture was heated at 55 °C for 7 h before it was cooled down to the room temperature. AuNPs were precipitated out from the reaction mixture as black solid powder by addition of 20 mL of ethanol. The products were separated by centrifugation and washed several times with ethanol. The size of AuNPs is 3.3 ± 0.5 nm as determined by TEM.

Synthesis of silica microspheres. Silica microspheres were synthesized by a classic Stöber method¹⁹. Typically, 3.14 mL of ammonia water (25%) was mixed with 80 mL of ethanol (containing 5 mL of water), followed by vigorously stirring for 30 min at 25 °C. Subsequently, 6 mL of tetraethyl orthosilicate was added to this solution. The mixture was stirred vigorously for 1 h and was then filtered and dried at room temperature. The particle size is ~ 100 nm as determined by TEM.

Synthesis of 0.5 wt% Au/SiO₂. AuNPs were loaded on the silica microspheres by a colloid deposition method as previously reported²⁰. Typically, 5.0 mg of AuNPs were dissolved in 25 mL of chloroform or toluene at 25 °C, followed by the addition of 1.0 g of silica microspheres. After 30 min stirring, the solid product was collected by centrifugation and dried in air. The loading efficiency is more than 99% as determined by inductively coupled plasma-mass spectroscopy (ICP-MS). The as-synthesized Au/SiO₂ was calcined at 350 °C for 5 h to remove surface capping agents before using in post-treatment processes and catalytic reactions.

Post-treatment process for Au/SiO₂. Generally, 50 mg of Au/SiO₂ samples were washed 3 times with 2 mL of the desired solvent (e.g. water, methanol, ethanol,

chloroform and toluene) and centrifuged at 10000 rpm for 5 min, followed by drying and annealing at 350 °C for 5 h.

Process of thiol/toluene treatment. In a typical treatment process, Au/SiO₂ catalysts (200 mg) were soaked in 5 mL of toluene containing 50 μ L of dodecanethiol for 3 h at 60 °C and centrifuged at 10000 rpm for 5 min, followed by drying and annealing at 350 °C for 5 h. For treatment of toluene, no thiol was added.

2.2 Characterization

Wide-angle X-ray diffraction (XRD) patterns were recorded on a Rigaku Ultimate IV diffractometer using CuK α radiation (40 kV, 40 mA, 5° min⁻¹ from 30 to 50°). Transmission electron microscopy (TEM) images were recorded on the Tecnai G2 F20 S-TWIN transmission electron microscope, operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed in a VG Scientific ESCALAB Mark II spectrometer. All binding energies were referenced to the C1s peak at 284.8 eV of the surface adventitious carbon to correct the shift caused by charge effect. ICP-MS was performed on a PerkinElmer NexION 300XX spectrometer. In-situ heating experiment was carried out on a FEI Titan S-Twin transmission electron microscope working at 300 kV using a Gatan 628 single tilt heating holder. Solid-state NMR spectroscopy was carried out on a Bruker Avance HD III 9.4 T spectrometer with a 3.2 mm triple-channel probe. The ¹H and ¹³C signal resonances are at 400.13 MHz and 100.62 MHz, respectively. The chemical shifts of ¹³C were referenced to adamantane at 38.5 ppm.

2.3 Catalytic Reaction

The gas-phase oxidation of benzyl alcohol (n-hexanol, n-heptanol, n-octanol) was carried out in a fixed bed vertical glass reactor (h = 250 mm, d = 12 mm), fitted with a glass frit carrying the catalyst (20 mg for 0.5 wt% Au/SiO₂) and provided with an electronically controlled furnace. The oxygen stream (30 mL min⁻¹) was controlled by a mass flow instrument and the liquid reagent (1.8 mL h⁻¹) was supplied through a syringe pump. Liquid vaporization occurred on the reactor wall prior to the catalytic bed. The tests were performed at 220 °C. The products were accumulated for every hour and analyzed by gas chromatography (GC). The selectivity was calculated as mol of produced benzaldehyde per mol of reacted benzyl alcohol. The carbon balance was > 99% in the case of selectivity near 99%. The similar activities for catalysts with different masses under the same contact time suggest that the diffusion effect has been eliminated in these catalytic tests.

2.4 Partial pressure experiments

The partial pressure experiment was carried out at 240 °C. The charging rate of gas streams and benzyl alcohol (BA) were controlled by a mass flow instrument and syringe pump, respectively. For the control of O₂ partial pressure, N₂ was used as balance gas and total flow rate was kept at 30 mL min⁻¹, of which the O₂ flow rate (0 to 30 mL min⁻¹) was adjusted to certain ratios with benzyl alcohol (1.8 mL min⁻¹). In contrast, to determine the reaction rate of benzyl alcohol, oxygen flow rate was fixed at 30 mL min⁻¹ while the charging rate of benzyl alcohol was

adjusted (0 to 1.8 mL min⁻¹). Liquid vaporization occurred on the reactor wall prior to the catalytic bed. The liquid products and unreacted benzyl alcohol were periodically (every hour) collected during the reaction and analyzed quantitatively by gas chromatography. The selectivity was calculated as mole of produced benzaldehyde per mole of reacted benzyl alcohol and the carbon balance was > 99% in the case of selectivity near 99%.

2.5 TPD measurement

The adsorption and desorption of benzyl alcohol was performed in a fixed bed vertical glass reactor fitted with a glass frit carrying the catalyst (1 g for 0.5 wt% Au/SiO₂). Nitrogen was used as carrier gas and was controlled by a mass flow instrument. To remove the surface hydroxyl groups and the adsorbed oxygen, the catalyst was swept by nitrogen at 250 °C at a speed of 40 mL min⁻¹ for 1 h. After pretreatment, the samples were cooled in the carrier gas to 210 °C. Subsequently, benzyl alcohol was supplied through a syringe pump at a speed of 0.6 mL h⁻¹. The adsorption of benzyl alcohol was performed for 1 h at different speeds (40 mL h⁻¹, 80 mL h⁻¹ and 120 mL h⁻¹). Then, the nitrogen continued to purge for 1 h without the flowing of benzyl alcohol to remove the weakly adsorbed species. After this step, the temperature program desorption was carried out from 210 °C to 420 °C with a heating rate of 5 °C min⁻¹. The outlet of the reactor was sealed by cold trap filled with ethanol solution to collect the desorbed molecules. The collected solution was accumulated and detected by GC-FID every five minutes. Toluene was used as the internal standard for quantitative analysis of the desorbed molecules.

2.6 DFT calculations

Density functional theory (DFT) calculations were carried out using the Vienna Ab-initio Simulation Package (VASP)²¹. The spin-polarized projector augmented wave (PAW) method²² and the Perdew-Burke-Ernzerhof (PBE)²³ electron exchange-correlation functional of the generalized gradient approximation (GGA)²⁴ were applied in our calculations. The kinetic energy cut-off for the wave function expanded in the plane-wave basis was set as 400 eV. To optimize the structures, the calculation was performed until the maximum force upon each relaxed atom was less than 0.05 eV Å⁻¹. The vacuum height was set as 15 Å to eliminate the interaction between neighboring slabs. The spin-polarized calculations were carried out with the DFT (PBE) - D3 (BJ) scheme^{25,26} as implemented in VASP. Default values of the dispersion coefficient (C₆) and the vdW radii (R_o) parameters given by Grimme^{25,26} were employed. The optimized bulk lattice constant for Au was determined to be 4.116 Å, in good agreement with the experimental value of 4.078 Å²⁷.

The adsorption energy (E_{ads}) was calculated as follows:

$$E_{\text{ads}} = -(E_{\text{total}} - E_{\text{substrate}} - E_{\text{gas-phase adsorbate}})$$

where E_{total} is the calculated total energy of the adsorption system, E_{substrate} is the energy of the clean substrate and E_{gas-phase adsorbate} is the energy of the gas-phase molecule.

In order to study the adsorption of different alcohols on gold surfaces, we used the following models: a 3×3 surface cell was used to construct a three-layer Au(100) slab, a 5×4 surface cell was used to construct a six-layer Au(111) slab and a 2×4 surface cell was used to construct a ten-layer Au(211) slab. The top two layers of the Au(100) slab, the top three layers of the Au(111) slab, and the top five layers of the Au(211) slab were allowed to relax. The Brillouin-zone integration was performed along with a 2×2×1 Monkhorst-Pack grid for the different surface slabs.

3. RESULTS AND DISCUSSION

3.1 Solvent-driven MTP to SC reversible transformation. AuNPs synthesized by a NaBH₄ reduction method¹⁸ in the presence of dodecanethiol show uniform size distribution (3.3 ± 0.5 nm). The high-resolution transmission electron microscopy (HRTEM) image of a representative particle shows five-fold symmetry (Figure 1a), along with apparent stacking faults, indicating that the particles are MTPs. Besides, the spots (Figure 1b) in the Fast Fourier Transform (FFT) pattern also follow an arrangement similar to the reported fivefold symmetry for MTPs²⁸. Based on TEM images obtained at three different tilting angles (Figure S1), an icosahedra structure is proposed for AuNPs as demonstrated by the atomic structure model in Figure 1c. We further measured 100 particles in this sample with HRTEM and carefully counted the frequency of MTP. The concentration of MTP is as high as 94% (Figure S2), suggesting that MTP is the dominant product synthesized by this method.

The as-synthesized AuNPs were loaded onto silica support (denoted as Au/SiO₂) by a colloid deposition method²⁰, followed by a calcination at 350 °C to remove surface capping agents. After calcination, the particle size increases from 3.3 ± 0.5 nm to 5.2 ± 0.8 nm due to the sintering problem. Interestingly, the supported AuNPs are still MTP dominant (86%, Figure S3), implying that the loading process has limited influence on the MTP concentration.

It is important to note that post-synthesis modifications of Au/SiO₂ with solvents could dramatically alter the microstructures of AuNPs. The solvent treatment was carried out by washing Au/SiO₂ in different solvents for 3 times, followed by a 5 h calcination at 350 °C. XPS data (Figure S4) show the absence of sulfur on the surface of AuNPs after the thermal treatment at 350 °C, indicating the complete removal of thiols after calcination. This result is well consistent with Khlobystov's report²⁹, which shows that thiols capping on the gold begin to vaporize below 300 °C and can be completely removed at nearly 400 °C.

TEM

Figure 1. Characterization of solvent-driven MTP-to-SC reversible transformation. (a) HRTEM image, (b) FFT pattern and (c) schematic model of a representative particle in Au/SiO₂-86%; (d) HRTEM image, (e) FFT pattern and (f) schematic model of a representative particle in Au/SiO₂-26%; (g) The MTP concentration (%) as a function of polarity of solvents using for post-synthesis modifications; (h) The MTP concentration (%) of Au/SiO₂-26% after post-synthesis modifications by different nonpolar solvents. (i-p) HRTEM images of gold NPs grown in situ at 350 °C after water treatment. All scale bars in Figures ii-p are 2 nm. (i, A) Fresh gold NP and its FFT pattern; (j~m) water-adsorbed AuNPs heated at 350 °C for first few minutes; (n~o) water-adsorbed AuNPs with prolonged time of heating at 350 °C, and (p) single crystal domain in region B.

and XRD analysis suggested that no visible particle aggregation occurred during the post-synthesis processes (Figures S5 and S6). Figure 1d shows the HRTEM image of a representative particle of Au/SiO₂ after water treatment. Unlike the spherical morphology of untreated AuNPs, the water-treated AuNPs become faceted as labeled in Figure 1d. Meanwhile, the exposed {111} and {100} facets labeled in the HRTEM image as well as the FFT pattern unambiguously confirm that the particle has become single-crystal with a truncated octahedral morphology (Figures 1e and 1f). Importantly, statistical data revealed that only 26% of AuNPs in water-treated Au/SiO₂ were MTP (Figure S7), suggesting that the water treatment caused an obvious MTP-to-SC transformation. The sharply decreased MTP concentration (from 86% to 26%), which also means less TBs and SFs, were found to cause different catalytic performance as will be discussed later. For the convenience of writing, all the silica supported AuNPs were denoted as Au/SiO₂-X, where X is the concentration of MTP.

To further understand the water-driven structural evolution of gold icosahedra, in situ HRTEM was employed to monitor the heating process of water-adsorbed AuNPs at 350 °C. Control experiments on untreated AuNPs show no noticeable structural change, which confirm the good thermal stability of small sized MTP^{30,31} and excludes the electron irradiation effect (Figures S8 and S9). AuNPs treated by polar solvents without thermal annealing have similar structures with those of untreated samples, indicating that the structural evolution occurs during the thermal annealing process. The interaction between solvent molecules and the surface of Au NPs, together with the desorption of solvents during thermal annealing might greatly facilitate the MTP-to-SC transformation.

Figures ii-p show a time series of the restructuring process of as-synthesized gold NPs with a size of ~ 10 nm after adsorbing water molecules. The fresh gold NP was multiply twinned along with a high probability of SFs as indicated by the FFT from region A. The contrasts for TBs were marked by red arrows (Figure ii). When heated at 350 °C, only a slight morphology change was observed in the first few minutes, which included the appearance of concave and convex surface features (Figures ij~m). After prolonged heating, the NP was elongated, accompanied by the movement of TBs (Figure in). Further heating led to the gradual disappearance of TBs and SFs (Figures io and ip), which was evidenced by the FFT of region B. At the same time, the NP crystallized from one single-crystal segment of the MTP and continued to grow to a larger crystal with faceted edges protruding from the NP surface (Figure ip). The gold NPs finally experienced a complete MTP-to-SC restructuring similarly as observed in Figure 1d. We note that the mechanism of MTP-to-SC transformation merit detailed study and will be presented elsewhere.

Interestingly, Au/SiO₂ treated by different solvents (e.g. toluene, chloroform, ethanol, methanol and water) show different MTP concentrations (Figures S7 and S10). Figure 1g plots the concentration of MTPs as the function of the polarity of the treatment solvents³². The quasi-linear plot suggests that the MTP-to-SC transformation is correlated to the polarity of the solvent molecules. The higher of the polarity, the lower of the MTP concentration. It is likely that polar solvents have stronger interaction with AuNPs which drive more significant restructuring as compared to nonpolar solvents³³. Similar structural evolution has been reported in other systems. Banfield and her

coworkers described that water can drive ZnS nanoparticle undergo structural change with significantly reduced surface and interior distortion owing to its strong interaction with the ZnS surface³⁴. Li *et al.* demonstrated that solvent exchange of ethanol by hexane leads to quick selective desorption of the thiolate layers from Au nanocluster surface which subsequently results in an icosahedral to cuboctahedral structure transformation³⁵.

From the viewpoint of surface science, it is also of great interest to know the reversibility of this transformation. To this end, we employed SC dominant gold sample (Au/SiO₂-26%) as a source material and treated it with nonpolar solvents. It turns out that toluene treatment could increase the MTP concentration from 26% to 44% (Figure 1h). Moreover, the MTP concentration could be doubled to 58% with a treatment with thiol/toluene solution (Figure S11). It is likely that the treatment of thiol/toluene and prolonged annealing at 350 °C will facilitate the SC-to-MTP transformation. According to a previous study carried out by Zhu *et al.*, the thiol ligands tend to bond strongly with the densest Au {111} facets to minimize the surface energy³⁶, which acts as a thermodynamic driving force here for the SC-to-MTP transformation due to the maximization of {111} facets in the Au MTPs. These results not only confirm the good reversibility of the MTP-to-SC transformation, but also demonstrate a practical approach to enrich the MTP concentration and thus the TBs and SFs of AuNPs. MTPs are rich in twin boundaries exposed with high-index {211}-like facets, along with a internal lattice strain^{11,37}. Such structures will directly influence the bonding strength for adsorbates, and may result in a major modification of their catalytic properties.

3.2 Gas-phase selective oxidation of alcohols with molecular oxygen. Gas-phase selective alcohol oxidation is widely recognized as one of the most fundamental transformations in both laboratory and industrial synthetic chemistry since the partial oxidation products (aldehyde/ketone) serve as most important molecules in cosmetics, perfumery, food and pharmaceutical industries³⁸. During recent years, an increasing effort has been made to apply “green” methods and to replace traditional stoichiometric oxidants by molecular oxygen.³⁹ The most challenging part of the gas-phase oxidation with molecular oxygen remains in its limited activity and selectivity as compared to the liquid-phase processes^{40–42}. Supported AuNPs catalysts have been explored as promising candidates for this reaction²⁰, but the origin of their excellent activity is still unclear. There is limited information about active sites for BA and O₂ chemisorption, let alone the rate-determining step of the reaction. In addition, a comprehensive understanding on the structure-activity relationship is still unavailable.

Previous studies revealed that the activity and selectivity of gold NPs not only depend on the particle size and the exposed crystallographic facets, but also correlate to additional structural features, such as the degree of particle rounding or the multiple twinning properties^{13,14,43,44}. Luckily, the post-synthesis method has negligible influ-

ence on the particle size and valence state of the supported AuNPs as confirmed by TEM, XRD and XPS analysis (Figures S5, S6 and S12). Besides, control experiments also confirmed the complete removal of surface ligand (Figure S4 and Table S1). Therefore, these AuNPs with variable MTP concentrations could serve as an excellent model to investigate the twin effect on their catalytic properties.

Figure 2. Catalytic tests and kinetic studies of AuNPs/SiO₂ with different MTP concentrations. (a) TOF (220 °C) value as a function of the MTP concentration for catalytic selective oxidation of BA. Catalytic results of toluene and thiol/toluene treated Au/SiO₂-26% are indicated by red stars. Reaction conditions: catalyst = 20 mg, benzyl alcohol = 1.8 mL min⁻¹, O₂ = 30 mL min⁻¹, T = 220 °C. (b) The Arrhenius plots of Au/SiO₂-86%, Au/SiO₂-60% and Au/SiO₂-26%; (c) The influence of oxygen and (d) BA partial pressure on catalytic selective oxidation of BA over the 0.5 wt% Au/SiO₂-86%, Au/SiO₂-60% and Au/SiO₂-26%. In all cases, the selectivity is > 98%.

Figure 2a plots the turnover frequency (TOF) values as the function of the MTP concentrations. Here, TOF values are defined as benzyl alcohol reacted per hour per surface Au atom. By taking the gold particle as a sphere, the ratio between the surface gold atoms and the total gold atoms (i.e. dispersion, D) was roughly calculated by $D = 1.3/d_{Au}$ (nm), where d_{Au} is the average particle size determined from XRD patterns by Scherrer equation.⁴⁵ Generally, the TOF values decrease with the decline of the MTP concentrations. The supported AuNPs with high MTP concentration show excellent catalytic activity towards gas-phase benzyl alcohol oxidation even at relatively low temperature (220 °C). The highest turnover frequency (Au/SiO₂-84%) is up to ca. 6500 h⁻¹ (220 °C). Though this value cannot compare to the state-of-art one^{41,42} in liquid-phase oxidation of benzyl alcohol, it actually surpasses the TOF for most of supported gold catalysts in gas-phase oxidation of benzyl alcohol⁴⁶. AuNPs with the lowest MTP concentration (Au/SiO₂-26%) give the lowest TOF value (2030 h⁻¹), which is only one third of that of Au/SiO₂-86%. Nevertheless, the TOF is still higher than that reported by Rossi *et al.*³⁸. Notably, there is a quasi-linear relationship between TOFs and MTP concentrations, demonstrating that MTPs play a

Figure 3. Quantitative analysis of BA adsorption on Au/SiO₂-86% and Au/SiO₂-26%. (a) TPD of BA at a N₂ flowing speed of 40, 80 and 120 mL min⁻¹ in the temperature range of 240 - 400 °C; (b) The total amount of desorbed BA and BAD at a speed of 120 mL min⁻¹ from 240 to 400 °C in the atmosphere of N₂ and O₂; (c) ¹³C solid-state NMR spectra of adsorbed BA molecules on different catalysts acquired under quantitative direct polarization.

significant role in selective oxidation of benzyl alcohol. As has been extensively discussed above, MTPs are rich in SFs and TBs which are accompanied by high-index {211} facets. Such sites usually exhibit lower coordination number and thus high activities. It is reasonable to hypothesize that the presence of TBs and SFs as defects in nanosized gold icosahedra mainly accounts for their low temperature activity towards the gas phase alcohol selective oxidation. Passivating these sites by solvent-induced restructuring could dramatically deactivate the gold catalyst.

Besides, we also tested the catalytic performances of toluene and thiol/toluene treated Au/SiO₂-26%. In line with the SC-to-MTP transformation, those samples exhibit superior catalytic performance than Au/SiO₂-26%. More interestingly, they also fall into the quasi-linear plot of TOFs and MTP concentrations as indicated by red stars in Figure 2a. The TOF values for pure MTP and SC AuNPs can be calculated according to the linear correlation. As can be seen from Figure 2a, the pure MTP is highly active (TOF > 7000 h⁻¹) while pure SC is almost inert. These results then further emphasize the importance of TBs and SFs. It also implies that only MTP AuNPs are responsible to the high activity for low-temperature gas-phase BA oxidation.

3.3 Comparison studies of the reaction kinetic on Au/SiO₂-86%, Au/SiO₂-60% and Au/SiO₂-26%. To monitor reaction profiles and analyze reaction kinetics is very useful for illuminating mechanistic details. Figure 2b shows the Arrhenius plots of Au/SiO₂-86%, Au/SiO₂-60% and Au/SiO₂-26%. The apparent activation energies of BA oxidation over Au/SiO₂-86% (82.2 kJ mol⁻¹), Au/SiO₂-60%(72.4 kJ mol⁻¹) and Au/SiO₂-26% (75.0 kJ mol⁻¹) are almost the same, indicating identical active sites for BA oxidation in these cases. This result leads us to the conclusion that the difference in TOFs among Au/SiO₂-86%, Au/SiO₂-60% and Au/SiO₂-26% is mainly determined by the number of active sites. Interestingly, if TBs and SFs (defect) sites are the active sites as one may expect, the phenomenon can be well understood since the number of defect sites decreases proportionally to the MTP concentrations.

Additionally, we carried out partial pressure experiments to determine the apparent reaction order of each reactant. As shown in Figure 2c, there is a small

change of the reaction order of O₂ molecules on Au/SiO₂-86%, Au/SiO₂-60% and Au/SiO₂-26% (0.57, 0.61 and 0.62), suggesting that O₂ activation is not significantly influenced by the MTP concentration. In contrast, the reaction order of BA molecules closely depends on the MTP concentration (Figure 2d). The reaction order of BA on Au/SiO₂-86% is as low as 0.13, which is only one third of Au/SiO₂-26% (0.45). According to the classic theory, lower reaction order indicates stronger adsorption on the surface of the catalyst³⁵. Therefore, the MTP-to-SC transformation eventually decreases the BA adsorption strength. In other words, Au/SiO₂-86% could adsorb more BA molecules than Au/SiO₂-26% due to its more abundant defect sites.

The BA chemisorption was then determined by TPD measurement and solid-state NMR spectrum analysis. The convenience in controlling the flowing speed and atmosphere facilitates the separation of physical adsorption from chemisorption and thus can help determine the reaction mechanism. As shown in Figure 3a, at lower space velocity (40 mL min⁻¹) in the N₂ atmosphere, there was a large amount of desorbed BA molecules on both Au/SiO₂-86% and Au/SiO₂-26% over the full temperature range, which mainly comprised of the physical adsorption. In contrast, at higher flowing speeds (80 and 120 mL min⁻¹), considerable desorption took place only at temperatures higher than 325 °C, likely due to the strong interaction between chemisorbed BA and AuNPs. Notably, at both flowing speeds, the amount of desorbed BA molecules on Au/SiO₂-86% is larger than that on Au/SiO₂-26%. Specifically, the concentration of chemisorbed BA on Au/SiO₂-86% is 24.2 mg g_{Au}⁻¹, which is about 4-5 times as much as that on Au/SiO₂-26% (3.2 mg g_{Au}⁻¹), coinciding with the MTP concentrations. Based on the amount of chemisorbed BA molecules and the loading of AuNPs, the ratio of BA molecules to surface gold atoms (BA/Au_{surf}) on Au/SiO₂-86% and Au/SiO₂-26% is identified to be ca. 0.16 and ca. 0.04, respectively. This result, in line with the kinetic study, reveals different BA-chemisorption capacities of MTP and SC. More interestingly, after we switched the carrying gas from N₂ to O₂, most of the adsorbed BA molecules (78%) converted into benzaldehyde (Figure 3b). It unambiguously confirms their chemisorption nature and that these chemisorption sites also act as active sites for

Table 1. Aerobic oxidation of various alcohols.

Reactants	$H_{\text{chemisorption}}$ (eV) ^a			TOF (h ⁻¹) at 220 °C		
	Au(100)	Au(111)	Au(211)	Au/SiO ₂ -26%	Au/SiO ₂ -58%	Enhancement
BA	1.33	1.23	1.52	1925	4841	2.51
n-hexanol	1.15	1.03	1.14	1132	3700	3.26
n-heptanol	1.27	1.32	1.34	1156	1504	1.30
n-octanol	1.44	1.48	1.55	488	1184	2.64

Reaction conditions: O₂ flowed at a rate of 30 mL min⁻¹, liquid alcohols were supplied by a syringe pump at a rate of 1.8 mL h⁻¹ and catalysts masses were 20 mg. In all cases, selectivities are > 99%. ^aThe chemisorption energies of alcohols on Au(100), Au(111) and Au(211) were predicted by DFT calculations.

BA selective oxidatn. We can thus correlate the catalytic performance to the ability of chemisorption which is determined by the structure (e.g. MTP, SC) of the catalyst. In specific, MTP has a strong chemisorption capability for benzyl alcohol and then acts as the active phase. SC cannot chemisorb benzyl alcohol and is thus inactive for this reaction, consistent with the extrapolation shown in Figure 2a. Fundamentally, the post-treatment approach adjusts the activity of Au/SiO₂ by tuning the number of active sites (i.e. MTP concentration).

More accurate quantitative characterization of the chemisorbed BA molecules on catalysts was conducted by solid-state NMR. BA-adsorbed catalysts were pretreated by a high flowing speed of N₂ for 1 h to remove most physical adsorbed BA molecules. The methyl carbon in BA molecule was 50% enriched by ¹³C isotope for clear signal. Adamantane was used as an internal calibration material and pure SiO₂ was employed as the control. Solid-state NMR spectra of BA-adsorbed Au/SiO₂ show three distinct signals (Figure 3c). The one appearing at ~ 64.5 ppm belongs to the physical adsorbed BA molecule, and it was further confirmed by the control experiment on pure SiO₂. Two lower peaks (65.5 ppm, 67.3 ppm) are assigned to the chemisorbed BA molecules that have stronger interaction with Au/SiO₂. Notably, the ratio of chemisorbed molecules to surface gold atoms on Au/SiO₂-86% and Au/SiO₂-26% is ca. 0.15 and ca. 0.04, respectively, in good agreement with the results obtained by TPD measurement (0.16 and 0.04).

In gas-phase catalytic reaction, BA molecules have firstly to be brought to the surface active sites of AuNPs, where they can be chemisorbed in the right form and with minimum energy, to ensure that their adsorbed states are sufficiently reactive. To rationalize the experimental observations, we further performed density functional theory (DFT) calculations to determine the adsorption properties of model gold surfaces. As suggested by Choi and his coworkers, the icosahedron with a gap of 1.54 steradians will cause large elastic lattice strain and result in the appearance of multiple twin boundaries that are frequently accompanied with adjacent stacking faults and nanotwinning domains. Such twin domains could expose {211} facets while other active sites might expose {111} and {100} facets¹¹. The optimized configurations and adsorption energies are summarized in Figure 4. The adsorption energy of benzyl alcohol on Au(211) is higher than those on Au(100) and Au(111) by 0.19 and 0.29 eV, respectively. Consequently, the MTP-rich catalyst (more Au(211) sites) could adsorb more benzyl alcohol molecules than the SC-rich catalyst. Besides, as the number of adsorbed BA molecules increases, the calculated adsorption energies have almost no change (Figure S13), showing no obvious coverage effect of benzyl alcohol on such surface. In addition, when two molecules of benzyl alcohol were adsorbed on Au(211), each molecule takes 9~10 Au atoms. The ratio of chemisorbed molecules to surface gold atoms is ca. 0.10, close to the value determined by NMR and TPD measurements.

3.4 Optimize gold catalysts for alcohol oxidation by tuning their microstructures. Understanding the factors that influence the growth and final shape of noble metal nanostructures is important for tuning their properties. As has been extensively discussed above, the unique interaction between thiol/toluene and AuNPs could drive the restructuring of SC-to-MTP to increase the twin defects and subsequently enhance their catalytic performance for selective oxidation of BA. On the other hand, we also evaluated the adsorption properties of 1-hexanol, 1-heptanol and 1-octanol on the Au surfaces by DFT calculations. As shown in Figure 4, the adsorption energies on Au(211) are always higher than those on Au(111) and Au(100) regardless of the type of alcohols. It then can be expected that MTP-dominant Au catalysts might also exhibit better catalytic performance for the oxidation of other alcohols. In this work, we also conducted the catalytic oxidation of 1-hexanol, 1-heptanol and 1-octanol

Figure 4. Different binding configurations and corresponding adsorption energies of alcohols on Au(100), Au(111) and Au(211). Au (golden), C (grey), O (red), H (white).

Table 2. TOF values of different gold catalysts before and after thiol/toluene treatment.

Catalysts	MTP concentration		TOF (h ⁻¹) at 220 °C		
	before	after	before	after	enhancement
Au/SiO ₂ -26%	26%	58%	1925	4841	2.51
Au/SiO ₂ -DP ⁴⁸	18%	52%	2189	4146	1.89
Au/SiO ₂ -Im ⁴⁷	-	-	850	1933	2.27
Au/SiO ₂ -CP ⁴⁹	-	-	1044	1956	1.87

Reaction conditions: O₂ flowed at a rate of 30 mL min⁻¹, benzyl alcohol was supplied by a syringe pump at a rate of 1.8 mL h⁻¹ and catalysts masses were 20 mg. In all cases, selectivities to benzaldehyde are > 99%.

on both Au/SiO₂-26% and Au/SiO₂-58% catalysts. The Au/SiO₂-58% is obtained by post-treating Au/SiO₂-26% with thiol/toluene. The MTP concentration is determined by HRTEM. Table 1 lists the TOF values of Au/SiO₂-26% and Au/SiO₂-58%. An enhancement over 1.3 (typically, >2.5) in TOFs were obtained for all these alcohols (1-hexanol, 1-heptanol and 1-octanol), confirming the potential application of this post-synthesis method to optimize their interaction with reactants and corresponding activity.

More importantly, the solvent-driven SC-to-MTP transformation is also valid for supported AuNPs prepared by other methods including impregnation (Au/SiO₂-Im)⁴⁷, deposition precipitation (Au/SiO₂-DP)⁴⁸ and coprecipitation (Au/SiO₂-CP)^{49,50}. As indicated in Table 2, the catalytic activities are roughly enhanced by a factor of 1.87 - 2.51 after thiol/toluene treatment, consistent with the typical increased MTP concentration (2.2 times). This result then serves as a proof for the structure-activity correlation, and it also greatly expands the applications of the post-synthesis approach in practical cases.

4. CONCLUSIONS

Here we describe a simple post-synthesis approach to reshape the AuNPs with two different microstructures. The binding of polar solvents, especially water, to the MTP-dominant Au catalysts leads to a transformation of MTP to SC, while the binding of thiol/toluene results in a reversible SC-to-MTP transformation. The crossover of the two microstructures allows a facile tuning of their population and reveals the twin effect in catalytic alcohol selective oxidation. A quasi-linear relationship between MTP concentration and catalytic activity implies that twin boundaries exposed with {211}-like facets are essential for the selective oxidation of alcohols. Experimental evidences as well as DFT calculations confirm that such sites can significantly enhance the chemisorption of alcohol molecules and therefore greatly improve the selective chemical conversion.

ASSOCIATED CONTENT

Supporting Information. Materials, synthetic details for Au/SiO₂-Im, Au/SiO₂-DP and Au/SiO₂-CP, experimental details for solid-state NMR, XRD patterns, XPS data, additional TEM images and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

This work was supported by National Natural Science Foundation of China (21271153, 21421004, 21373181, 21222307, U1402233), Major Research Plan Of National Natural Science Foundation of China (91545113, 91545103), Fok Ying Tung Education Foundation (131015) and the Fundamental Research Funds for the Central Universities (2014XZZX003-02). The authors are grateful to the King Abdullah University of Science and Technology (KAUST) in Saudi Arabia for providing the characterization of the in situ HRTEM.

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