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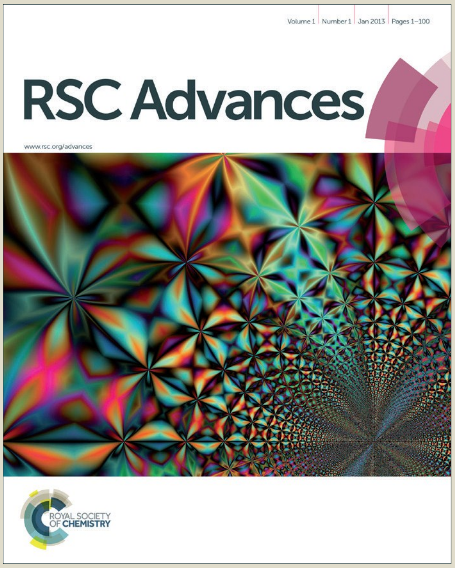

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Surface clean gold nanoflower obtained by complete removal of capping agent: active catalyst for alcohol oxidation

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Yoshiro Imura*[a,b], Shinya Furukawa[c], Kenichi Ozawa[a], Clara Morita-Imura[b], Takeshi Kawai[b] and Takayuki Komatsu*[a]

Shape-controlled metal nanocrystals, such as nanowires and nanoflowers (NFs), are attractive due to their potential novel catalytic properties. However, catalytic activity is limited due to capping agents adsorbed on the metal surface, which are necessary for the preparation and dispersion of shape-controlled nanocrystals in solution. Recently, *surface clean* shape-controlled nanocrystals, which is obtained by removal of almost all of the capping agent, is very interested to bring out the intrinsically novel catalytic property. In this study, to prepare *surface clean* shape-controlled nanocrystals, firstly, Au NFs obtained by surfactant-free synthesis were supported on γ-Al_2O_3 to increase dispersibility and morphological stability, because unsupported Au NFs formed aggregates by removal of capping agent. Then, we removed the capping agent from the surface of Au NFs by a calcination procedure and a water extraction procedure, in order to improve their catalytic activity. The water extraction procedure succeeded in removing the capping agent from Au NFs/γ-Al_2O_3 without morphological change and in providing *surface clean* Au NFs/γ-Al_2O_3, while the calcination procedure changed the morphology from NFs to spherical Au nanoparticles (Au NPs). *Surface clean* Au NFs/γ-Al_2O_3 was used for the aerobic oxidation of 1-phenylethyl alcohol, and the extraction procedure resulted in an eleven-fold increase in catalytic activity. Furthermore, formation rate of acetophenone on *surface clean* Au NFs/γ-Al_2O_3 was ten-fold higher than that on *surface clean* Au NPs/γ-Al_2O_3 having almost the same diameter, indicating the catalytic superiority of *surface clean* Au NFs.

Introduction

Morphological control of noble metal nanocrystals (NCs) is important in the development of modern materials chemistry, because their physical and chemical properties can be easily and widely tuned by tailoring their particle size and shape.[1,2] There have been many reports of fabrication of shape-controlled NCs, such as rods,[3,4] wires,[5-9] plates,[10,11] and cubes.[12-14] Recently, anisotropically structured NCs have been applied as catalysts in expectation of novel catalytic properties.[15-24] In general, these shape-controlled NCs are prepared by a colloidal synthesis method in solution using a capping agent that has selective adsorption properties on metal surface, such as cetyltrimethylammonium bromide (CTAB),[3,4] poly(vinylpyrrolidone) (PVP),[25,26] or melamine.[20] The capping agent is essential for morphological control and inhibition of aggregates in the preparation of metal NCs.[21,27,28] However, catalytic activity is depressed due to adsorption of the capping agent on the metal surface, because the capping agent acts as a physical barrier, restricting free access by the reactants.[21,27] Therefore, in order to use NCs prepared by colloidal synthesis as catalysts, their preparation has to be carried out using a capping agent which is adsorbed weakly on a metal surface and/or removing the capping agent from the surface after preparation.[15,20,27-30] The former preparation is called as surfactant-free method.

Recently, there have been some reports on the preparation of shape-controlled NCs, such as nanoflowers (NFs) and dendritic nanowires, under surfactant-free conditions using melamine and ascorbic acid.[15,20,23] Generally, the removal of capping agents from NCs for catalysis has been done by calcination and extraction procedures, with the result that the catalytic activity of the NCs improves upon removal of the capping agent.[30-32] However, morphological stability and dispersibility of metal NCs are easily affected not only by organic/inorganic additives and temperature changes but also by the removal of capping agent.[28,33-37] Therefore, in order to know intrinsically novel catalytic properties of shape-controlled NCs, it is necessary to remove the capping agents without change in their morphology and dispersion. The NCs, which is removing almost the entire capping agent after preparation by surfactant-free synthesis, are called as *surface clean* NCs, and expected as novel nanocatalysts with high catalytic activity.

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[a] Department of Chemistry and Material Science, Tokyo Institute of Technology, 2-12-1-E1-10 Ookayama, Meguro-ku, Tokyo 152-8551, Japan. E-mail: komatsu.t.ad@m.titech.ac.jp.
[b] Department of Industrial Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan. E-mail: imura@ci.kagu.tus.ac.jp.
[c] Department of Chemistry, Tokyo Institute of Technology, 2-12-1-E1-10 Ookayama, Meguro-ku, Tokyo 152-8551, Japan.

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The dispersibility and morphological stability of metal NCs is improved by the use of a support, such as carbon nanotubes, SiO_2, or Al_2O_3.[31,38] Hutchings *et al.* showed that a capping agent, polyvinyl alcohol, was removed from gold spherical nanoparticles (Au NPs) supported on TiO_2 by calcination and water extraction procedures.[30] The water extraction procedure was capable of removing the capping agent without changing the morphology of the Au NPs, while the calcination procedure did change the morphology.[30] In general, morphology of shape-controlled Au NCs was easily changed compared with Au NPs. For catalytic application, it is a worthy challenge to keep the morphology during the removal of capping agent through the effective approach such as extraction procedure, which could supply the shape-controlled *surface clean* Au NCs with high catalytic activity.

The purpose of this study is to clarify the effect of NF shape on the catalytic properties of Au particles. For achieving this purpose, it is necessary to remove capping agents from the surface of Au NFs, namely, to prepare *surface clean* NFs. We attached NFs on the surface of γ-Al_2O_3 support to improve the stability against the removal of the capping agent. Furthermore, we applied the mild treatment, water extraction, to remove the capping agent at room temperature. Through these considerations, we finally revealed the higher catalytic activity of *surface clean* Au NFs than that of *surface clean* spherical Au NPs in the oxidation of 1-phenylethyl alcohol.

Experimental

Materials

Hydrogen tetrachloroaurate tetrahydrate ($HAuCl_4$•$4H_2O$) was obtained from Wako Pure Chemical Industries. Melamine (Kanto Chemicals), γ-Al_2O_3 (JRC-ALO-8, Sumitomo Chemical, BET surface area of 148 $m^2\ g^{-1}$), SiO_2 (Cariact G-6, Fuji Silysia Co., BET surface area of 640 $m^2\ g^{-1}$), ascorbic acid (Tokyo Chemical Co.), and 1-phenylethyl alcohol (Tokyo Chemical Co.) were used without further purification.

Preparation of Au NFs/γ-Al_2O_3

Au NFs were prepared by a previously reported surfactant-free method[20] using melamine as a capping agent which has a weak adsorption power on Au surface. 10 mM aqueous solution of $HAuCl_4$•$4H_2O$ (5.0 mL) was added to a 10 mM aqueous solution of melamine (175 mL). Then, 10 mM ascorbic acid aqueous solution (20 mL) was slowly injected into the above solution. The colour of the solution quickly turned to blue. γ-Al_2O_3 (1.0 g) was added to the Au NF dispersion (200 g) and stirred for 24 h. When the dispersion was heated to 80°C, Au NFs/γ-Al_2O_3 powder was obtained.

Removal procedure for capping agent

We carried out removal of the capping agent by two methods, a calcination procedure and a water extraction procedure. The calcination procedure was conducted by heating the as-prepared Au NFs/γ-Al_2O_3 at 100, 200, 300, 400, or 500°C for 1 h in air. The water extraction procedure was carried out using the following method. The as-prepared Au NFs/γ-Al_2O_3 (0.4 g) was added to water (40 g) and stirred for 10 min at room temperature. Au NFs/γ-Al_2O_3 was recovered from the solution by centrifugation at 4000 rpm for 10 min. After several repetitions of these treatments, Au NFs/γ-Al_2O_3 powder was obtained by heating at 80°C for 5 min to remove water.

Catalytic activity before and after extraction procedure

Aerobic oxidation of 1-phenylethyl alcohol (1-PA) was carried out at 60°C in a batch reactor under an air atmosphere. After addition of K_2CO_3 (0.1 g, 0.72 mmol) to 10 mL of 1.5 mM 1-PA aqueous solution (15 μmol), the mixture was stirred at 60°C. Au NFs/γ-Al_2O_3 (50 mg) before or after the water extraction procedure were added, and the mixture was stirred at 60°C under air. After quenching the reaction with 1 M HCl, the products were extracted five times with toluene. The yield of the products was determined by gas chromatography using the internal standard method.

Characterization

Transmission electron microscopy (TEM) observation was carried out using a JEOL JEM-1011 instrument operating at 100 kV. High-resolution TEM (HR-TEM) was performed using a JEOL 2100 instrument equipped with an energy-dispersive X-ray spectrometer (EDX) operated at 200 kV. UV-vis absorption and reflectance spectrum measurements were carried out using a JASCO V-570. γ-Al_2O_3 was used as base sample for UV-vis reflectance spectroscopy (incident and reflectance angle: 30°). FT-IR measurement was carried out using a JASCO FT/IR4200 instrument. The sample (a 20 mm disk) was prepared by pressing Au NCs/γ-Al_2O_3 (3 mg) with KBr (300 mg). TG-DTA measurements were conducted using a SII TG/DTA 7200 instrument. The sample was heated from room temperature to 800°C at a rate of 10°C/min under a flow of air.

Results and Discussion

Au NFs with an average size of 75 nm were synthesized by reducing $HAuCl_4$ in a solution of melamine as capping agent (Figure 1a and b). UV-vis spectroscopy is very useful for examining the shape of Au NCs, because the surface plasmon (SP) band of Au NCs is strongly dependent on their shape.[2,39-41] For example, the SP band of spherical Au NPs appears at ~530 nm, while that of Au NFs appears at ~600 nm.[20,41-45] Therefore, we examined the SP band of the Au NF dispersion by UV-vis spectroscopy. UV-vis measurements showed that peak position of the SP band was at ~630 nm, indicating the formation of Au NFs (Figure 2).[20,42] This is in good agreement with the blue colour of the as-prepared solution (Figure 1a).[20,42] TEM-EDX spectra showed that the Au NFs were composed of pure gold (Figure S1). HR-TEM image of Au NFs showed fringes with a periodicity of 0.235 nm, which corresponds to (111) lattice spacing in Au (Figure S2).[7,8,36,46] Predominant growth along the [111] direction was due to weak adsorption of melamine on the Au (111) crystal facet compared with (100) and (110) crystals facets.[20]

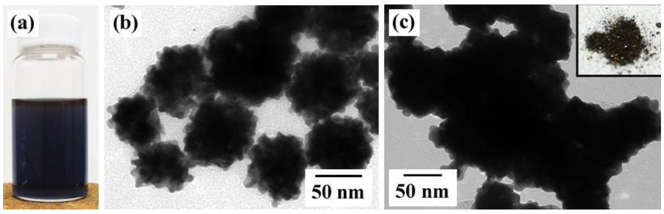

Figure 1. (a) Photographic and (b) TEM images of as-prepared Au NFs before the water extraction. (c) TEM and inserted photographic images of unsupported Au NFs after third extraction.

When we carried out removal of the capping agent from the Au NF dispersion by the water extraction three times, the Au NFs formed aggregates because Au surface were exposed due to desorb capping agent (Figures 1c). The black precipitate did not re-disperse into the solution upon shaking and stirring (Figures 2b). These results indicate that it is very difficult to remove melamine from an unsupported Au NF dispersion without change in morphology and dispersion ability.

Dispersion of NCs can be improved by ligand exchange, coating with silica, or attaching to a support such as silica or γ-Al_2O_3.[31,37,38,47] Au NFs were not supported on silica. Therefore, we supported Au NFs on γ-Al_2O_3, which shows relatively strong interactions with metal particles.[48,49] The Au NFs/γ-Al_2O_3 dispersion was obtained by adding γ-Al_2O_3 to the Au NF dispersion and stirring for 20 h (Figure 3a and b). After leaving it for 8 h, the colours of the solution and the precipitate were colourless and blue, respectively, indicating that almost all of the Au NFs had been adsorbed onto γ-Al_2O_3 (Figure 3c). The blue precipitate (Au NFs/γ-Al_2O_3) was easily redispersed by stirring (Figure 3e). When the Au NFs/γ-Al_2O_3 dispersion was heated to 80°C to evaporate the solvent, Au NFs/γ-Al_2O_3 was obtained in the form of a purple powder, as shown in Figure 3d. TEM observation showed that the morphology of Au NFs did not change after the evaporation of water at 80°C (Figure 3d). The Au NFs/γ-Al_2O_3 powder was easily redispersed by adding water, and the colour changed back to blue after redispersion (Figure 3f). Generally, the SP band of Au NCs is affected by the environment, such as the solvent used.[50-54] Therefore, we examined the SP band of Au NFs/γ-Al_2O_3 using UV-vis reflectance spectra before and after the addition of water. The SP band of Au NFs/γ-Al_2O_3 was shifted from 575 nm to 640 nm upon addition of water, and was in good agreement with that of as-prepared Au NFs. (Figures 3, S3, and S4).

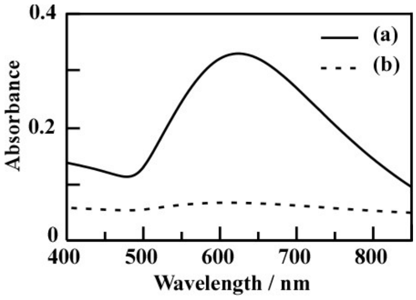

Figure 2. UV-vis absorption spectra of unsupported Au NFs (a) before the water extraction (solid line) and (b) after third extraction (dashed line).

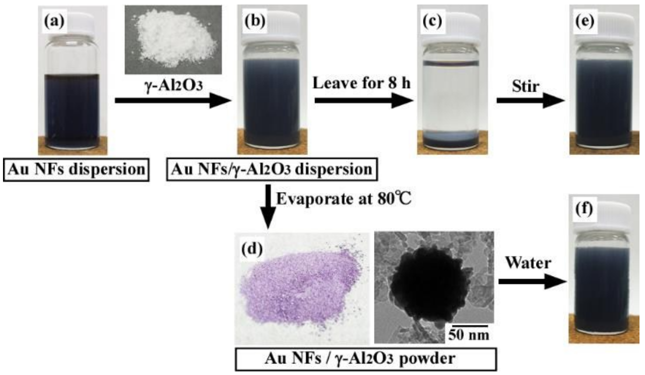

Figure 3. Photographic and TEM images of (a) Au NFs dispersion, (b) Au NFs/γ-Al_2O_3 dispersion, (c) Au NFs/γ-Al_2O_3 precipitate, (d) Au NFs/γ-Al_2O_3 powder, and (e, f) Au NFs/γ-Al_2O_3 redispersion.

Au NFs/γ-Al_2O_3 contains large amounts of melamine as capping agent. We tried to remove the melamine without significant morphological change by two procedures such as calcination and water extraction.

TG-DTA measurement showed that decomposition of melamine occurred at ~300°C (Figure S5). Thus, to remove the capping agent by the calcination procedure, it is required that NF morphology remains stable even above 300°C. We examined the morphological stability of Au NFs by calcining Au NFs/γ-Al_2O_3 in air for 1 hour at 100–500°C. At 100°C, the Au NFs/γ-Al_2O_3 powder retained its purple colour, but at 200°C it changed to purple-red (Figure 4a and b), and above 300°C it changed to red (Figure 4c–e). In addition, UV-vis spectra showed that the peak position (~575 nm) after calcination at 100°C was almost the same as that obtained for as-prepared Au NFs/γ-Al_2O_3, while the peak positions at 200, 300, 400, and 500°C were ~548, 532, 520, and 520 nm, respectively (Figures 5 and S6). TEM observation showed that the morphology of Au NFs was retained at 100°C, while it gradually changed to spherical NPs as the temperature increased from 200 to 400°C (Figure 4). Above 400°C, the morphology was almost spherical (Figure 4). These results indicate that the morphology of Au NFs is retained after calcination at 100°C but that deformation takes place above 200°C. In addition, FT-IR measurement showed that melamine was not removed from Au NCs/γ-Al_2O_3 upon calcination at 100 and 200°C but was removed after 500°C (Figure S7).

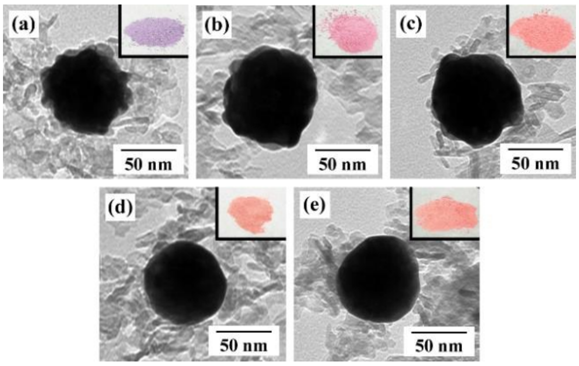

Figure 4. TEM and photographic images of Au NCs/γ-Al_2O_3 after calcination at (a) 100, (b) 200, (c) 300, (d) 400, and (e) 500°C.

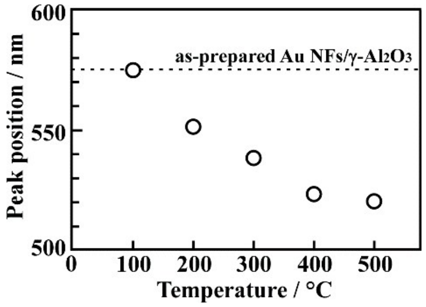

Figure 5. Peak position of SP band before and after calcination. Black dotted line is peak position of as-prepared Au NFs/γ-Al_2O_3.

Because the morphology of Au NFs changed upon calcination at 200°C, as mentioned above, the calcination procedure is not suitable for the removal of capping agents without morphological change. Then, we attempted the removal of the capping agent using the water extraction procedure. In the first extraction, Au NFs/γ-Al_2O_3 was immersed into water and centrifuged. TEM images showed that the morphology, including the shape and diameter, of NFs did not change after the first extraction (Figures 6a and 7). Upon repeated extraction procedures, the morphology of Au NFs/γ-Al_2O_3 was still retained (Figure 6). In addition, the UV-vis spectra of them showed that the peak position of the SP band (575 nm) did not change after repeated extraction, indicating a good agreement with the observed colour of purple (Figures 6, 7, and S8). This corresponds to the unchanged colour upon the repeated extraction. Thus, the water extraction procedure by using Al_2O_3 support was revealed to retain the morphology of Au NFs.

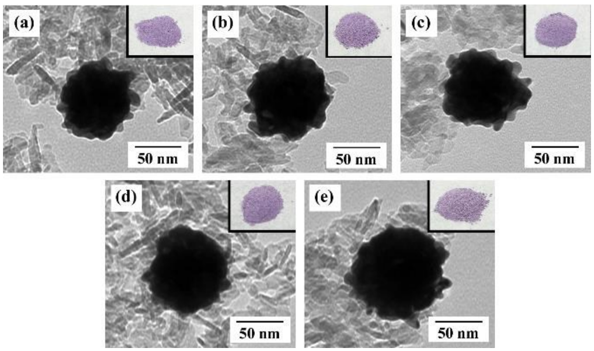

Figure 6. TEM and photographic images of Au NFs/γ-Al_2O_3 after water extraction procedure carried out (a) one, (b) two, (c) three, (d) four, and (e) five times.

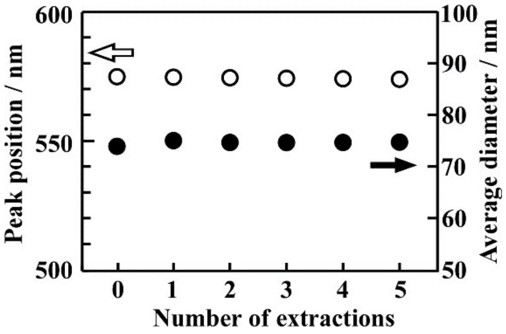

Figure 7. Peak positions of surface plasmon band (open circles) and average diameter (filled circles) of Au NFs on Al_2O_3 before and after water extraction procedure.

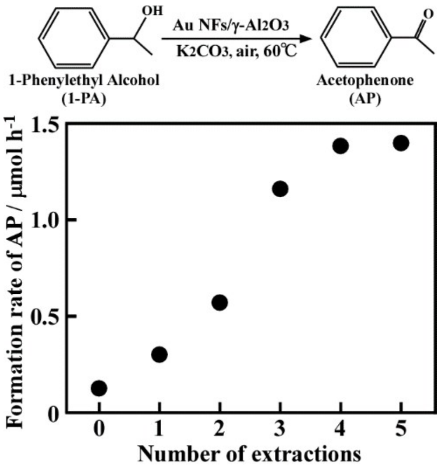

Figure 8. Change in formation rate of acetophenone at 6 h in 1-phenylethyl alcohol oxidation with number of repeated extractions.

We subsequently examined the catalytic activity of Au NFs/γ-Al_2O_3 for aerobic oxidation of 1-phenylethyl alcohol before and after the water extraction procedure (Figure 8). The yield of acetophenone increased with the number of extractions up to four times (Figure S9 and Table S1). Similarly, the formation rate of acetophenone was also improved by washing (Figure 8 and Table 1). As a result, the formation rate after fifth extraction showed an eleven-fold increase over that before the extraction. Because the water extraction procedure did not change the morphology of the Au NFs, the improvement in catalytic activity would be due to remove the melamine, which capping agent decreased catalytic activity, in every extraction. We also carried out elemental analyses (Table 1) and FT-IR measurements (Figure S10) to confirm the amount of melamine in Au NFs/γ-Al_2O_3. Elemental analyses showed that almost all of melamine (> 98%) was removed after fourth extraction (Table 1). This result was well agreed with the disappearance of the peaks assigned with melamine in FT-IR spectra after extraction procedure (Figure S10). Namely, *surface clean* Au NFs were obtained by this washing method.

Table 1. Amount of melamine in 0.05 g of Au NFs/γ-Al_2O_3, and formation rate of acetophenone at 6 h in 1-phenylethyl alcohol oxidation.

Number of extraction	Melamine / μmol	Formation rate / μmol h^{-1}
0	57.38	0.12
1	14.40	0.30
2	1.90	0.57
3	0.18	1.16
4	0.12	1.38
5	0.12	1.40

The effect of melamine on the catalytic activity was further investigated by titration of melamine to the washed catalyst; aerobic oxidation of 1-phenylethyl alcohol was carried out after the addition of melamine to Au NFs/γ-Al_2O_3 that had undergone the extraction procedure five times. The formation rate of acetophenone decreased as the amount of melamine increased (Figure 9). Interestingly, the dependence of the formation rate of acetophenone on the amount of melamine well agreed with that for the extraction procedure. These results strongly indicate that (1) the removal and addition procedures are reversible; (2) the change in catalytic activity depends exclusively on the amount of melamine. Therefore, we conclude that the extraction procedure using γ-Al_2O_3 as support can remove the capping agent and improve catalytic activity, without changing the morphology of Au NFs.

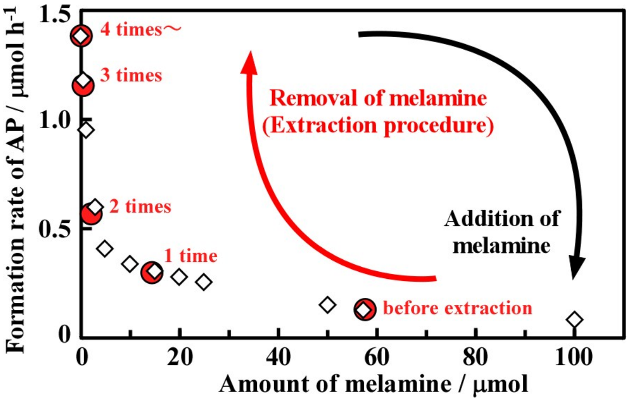

Figure 9. Change in the formation rate of acetophenone in 1-phenylethyl alcohol oxidation over Au NFs/γ-Al_2O_3 with amount of added (open squares) or residual (filled circles) melamine. Reaction conditions: 1-phenylethyl alcohol (15 µmol), catalyst (50 mg), K_2CO_3 (0.1 g), water (10 g), air (1 atm), 60°C, 6 h.

Finally, we compared the catalytic activity of *surface clean* non-spherical Au NFs/γ-Al_2O_3 with that of *surface clean* spherical NPs (Au NPs/γ-Al_2O_3) for 1-phenylethyl alcohol oxidation. The former catalyst was prepared by repeating the extraction procedure for five times, and the latter one was obtained by heating the former catalyst at 200°C in air for 1 h. FT-IR showed no peak from melamine (Figure S11). Figure 10 shows the TEM images of typical NF and NP. The average diameter of spherical NPs was about 70 nm, which was close to that of NFs, indicating that no aggregation of Au particles occurred during the deformation of NFs into NPs at 200°C. Figure 10 also shows the change in acetophenone yield with reaction time on *surface clean* Au NFs/γ-Al_2O_3 and *surface clean* Au NPs/γ-Al_2O_3. The former exhibited much higher acetophenone yield. The formation rates of acetophenone were 1.40 (NFs) and 0.135 µmol/h (NPs), respectively. The shape of Au particles indicates a significant decrease in Au surface area during the thermal treatment. However, the difference between the Au surface areas would be much smaller than that between formation rates. The Au atoms on NFs must have higher intrinsic activity than those on NPs. Au atoms at corner and/or edge sites may be such highly active sites, because the NF particle looks like an aggregate of smaller crystallites having higher proportion of these sites. These results clarify the advantage of NF structure as the catalyst for aerobic oxidation. In addition, after washing the recovered Au NFs catalyst by water extraction, the catalyst was reused under same catalytic reaction condition. The formation rate of acetophenone was 1.33 µmol/h without significant loss of activity.

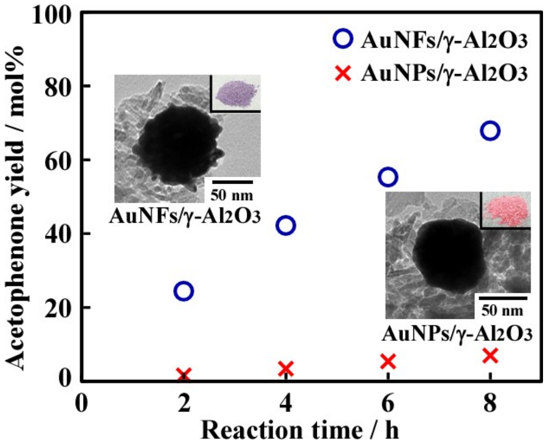

Figure 10. Acetophenone yield of *surface clean* Au NFs/γ-Al_2O_3 and Au NPs/γ-Al_2O_3. Reaction conditions: 1-phenylethyl alcohol (15 µmol), catalyst (50 mg), K_2CO_3 (0.1 g), water (10 g), air (1 atm), 60°C.

Conclusions

This article reveals the advantage of *surface clean* Au nanoflowers over *surface clean* spherical particles as metal catalysts. Au NFs supported on the surface of γ-alumina have higher morphological stability than unsupported ones. With the help of γ-alumina support and by using capping agent weakly bound to NFs, the capping agent is removed completely by moderate water extraction treatments keeping the morphology of NFs intact. A bare nanoflower particle thus obtained consists of small crystallites, which have higher proportion of edge and corner sites as well as higher surface area than a spherical nanoparticle with the same particle size. This must be the reason for the much higher catalytic activity of Au NFs for the alcohol oxidation. The findings in this article will open new possibilities of shape-controlled nanocrystals as novel metal catalysts.

Acknowledgements

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Table of contents

Morphological stability and catalytic activity of gold nanoflowers (Au NFs) were improved by using γ-Al_2O_3 support and water extraction procedure. Furthermore, formation rate of acetophenone on Au NFs/γ-Al_2O_3 was ten-fold higher than that on spherical Au NPs/γ-Al_2O_3 having almost the same diameter, indicating the catalytic superiority of Au NFs.