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Continuous Fabrication of Novel Polyimide Nanoparticles Confining Highly Dispersed Gold Nanoparticles by a Multistep Microfluidic Reaction System and Their Catalytic Application

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Novel polyimide nanoparticles confining maximum 12.5 wt % of highly dispersed Au nanoparticles (size: 5.6 nm) were continuously fabricated by using a multistep microfluidic reaction system; the particles show good activity for the hydrogenation in $scCO_2$ with excellent yields and selectivity without leaching and agglomeration of Au nanoparticles.

Gold nanoparticles (Au NPs) have been shown to be highly active catalysts for many important industrial reactions such as low-temperature oxidation of CO, hydrogenation, epoxidation of alkenes, oxidation with molecular oxygen, and synthesis of H_2O_2 using hydrogen and oxygen.[1] In general, metal NPs, including Au NPs, are supported on the surface of different metal oxide supports such as TiO_2, SiO_2, Al_2O_3, ZrO_2 or carbon (charcoal). Although supported metal NPs are thought to be active, these solid-supported catalysts still have some drawbacks such as desorption of metal NPs from supports, coalescence with neighboring metal NPs during repeated use in reactions and inaccessibility of the organic substrate to the catalysts.[2] To overcome the drawbacks, surface coverage of metal NPs with shell materials, which allow permeation of substrates, has received significant attention as an alternative. For example, β-D-glucose-stabilized Au NPs dispersed in water were used for the reduction of 4-nitrophenol in the presence of $NaBH_4$.[3] Recently, we also developed Au NPs in water, stabilized with block copolymer (P123: $EO_{20}PO_{20}EO_{20}$) for the effective oxidation of benzyl alcohol using molecular oxygen.[4] Furthermore, fabrication of other metal NPs, such as Pd and Pt NPs, encapsulated by dendrimer and polystyrene, and their stability against catalytic reactions have been reported.[5]

In recent years, fabrication of polyimide (PI) particles has been attracting much attention because of their wide range of applications.[6] These PI particles are a promising material for the next generation and might have potential to act as a support of heterogeneous catalyst due to their excellent physical properties like high thermal stability, high mechanical durability, exceptional chemical resistance, and high elasticity, which could be employed extensively as a representative high-performance polymer in microelectronics, photonics, optics, and aerospace industries.[7] Previously, we have successfully developed not only a method of preparation of Au NPs[8] but also the PI NPs[9] using a continuous microfluidic system,[10] and large-scale (ca. 1 kg/day) synthesis was also possible even in laboratory. In this communication, we thus applied the microfluidic preparation technique to the formation of highly dispersed Au NPs in PI NPs (Au NPs/PI NPs). This method is facile and obtained NPs demonstrated a good catalytic performance for the hydrogenation of nitrobenzene in supercritical CO_2 ($scCO_2$).

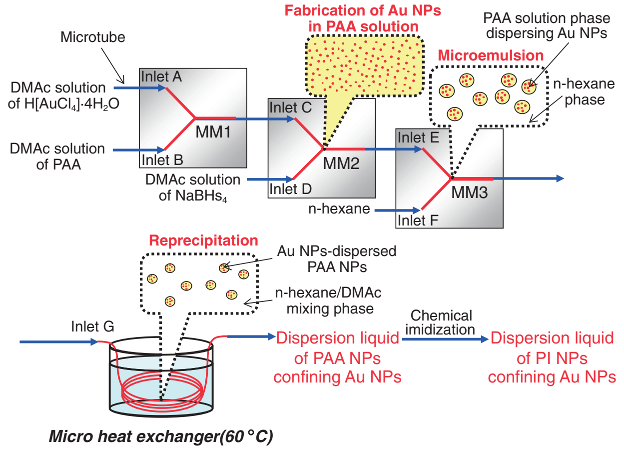
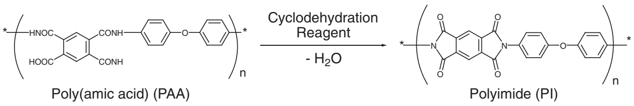


Figure 1. Schematic diagram of PI nanoparticles confining Au nanoparticles via emulsion reprecipitation using a microfluidic system.



Scheme 1. Reaction scheme of synthesize polyimide from poly(amic acid) by dehydration.

Figure 1 illustrates the fabrication process of Au NPs/PI NPs under rapid mixing, streaming and heating conditions by micromixers, microtubes and a micro heat exchanger. First, Au NPs were formed in *N*,*N*-dimethylacetamide (DMAc) solution of the polymer precursor, poly(amic acid) (PAA, Scheme 1), by $NaBH_4$ reduction. Subsequently, PAA NPs confining Au NPs were synthesized by the emulsion reprecipitation method as reported earlier.[9] PAA NPs were converted to PI NPs by cyclodehydration reaction, i.e., chemical imidization (Scheme 1). In a typical experiment, Y-type micromixers (Teflon; YMC Co., Ltd., Japan, channel width: 500 µm) and a micro heat exchanger (Teflon tube; i.d. = 1000 µm, length: 3 m) connected serially by Teflon tubes (i.d. = 1000 µm, length: 0.15 m). $H[AuCl_4]\cdot 4H_2O$ (1.24×10^{-2} mol L^{-1}, 0.3 mL min^{-1}) and DMAc solution of PAA (2 wt %, 1.0 mL min^{-1}) were introduced into inlets A and B (Figure 1) at the first micromixer (MM1) by pumps, and homogeneously mixed solution was prepared. The resultant solution was continuously introduced

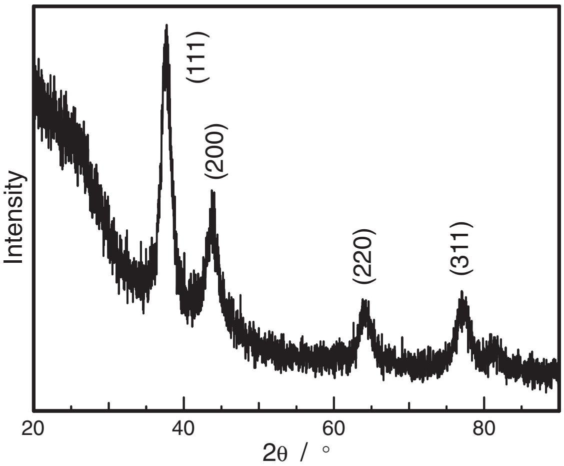


Figure 2. XRD pattern of powder of PI nanoparticles confining Au nanoparticles.

into the second micromixer (MM2) through the inlet C and mixed with DMAc solution of $NaBH_4$ ($2.48 \times 10^{-2}\,mol\,L^{-1}$, $0.3\,mL\,min^{-1}$) from inlet D. At this stage, homogeneously dispersed Au NPs were formed in PAA solution. Subsequently, the stream of PAA solution dispersing Au NPs was introduced into the third micromixer (MM3) and was struck against *n*-hexane ($20\,mL\,min^{-1}$) at room temperature to form microemulsion. After that the emulsion was heated at 60 °C in the micro heat exchanger through a water bath. During passing through the heat exchanger, DMAc was miscible in *n*-hexane, followed by the reprecipitation of PAA molecules in DMAc droplets due to dissolution of DMAc into *n*-hexane. As a result, nanoparticles of PAA along with confined Au NPs are formed and dispersed in *n*-hexane/DMAc. This dispersion liquid was then collected into a glass vessel heated at 60 °C, followed by the addition of pyridine and acetic anhydride into the vessel. After stirring for 1 h, PAA was converted into PI (Scheme 1). A reddish brown dispersion liquid of PI NPs was obtained and then cooled to room temperature without stirring. The complete phase separation of *n*-hexane and DMAc including suspension of PI NPs confining Au NPs occurred. Finally, *n*-hexane phase was removed, and Au NPs/PI NPs were separated simply by filtration of DMAc phase with a membrane filter.

We investigated the morphology of the Au NPs/PI NPs by X-ray diffraction (XRD), dynamic light scattering (DLS), UV–vis reflection spectrum and transmission electron microscopy (TEM) images. Figure 2 shows a powdered XRD pattern of Au NPs/PI NPs. Typical peaks of Au were observed at $2\theta = 37.7$, 43.7, 64.6 and 77.6°, attributed to (111), (200), (220) and (311) face, respectively. Average size of Au NPs was 6.4 nm estimated from full width at half-maximum of (111) peak using Scherer's equation.

The PI NPs average size of 449.3 nm, and the variation coefficient of 0.21 were estimated by DLS measurement (Figure S1).[11] Figures 3a and 3b show TEM images of Au NPs/PI NPs at different magnifications. Each image shows low-density large particles (ca. 200 nm to 1 μm, average 486 nm) and high-density small particles (3 to 10 nm, average 5.6 nm) representing the PI NPs and Au NPs, respectively. Both particle sizes were in good agreement with the DLS and XRD measurements. In Figure 3b, very few Au NPs can be seen on the surface of PI NPs, which implies that most of the Au NPs exist in PI NPs and are stabilized by PI structure. According to the UV–vis reflection spectrum (Figure S2[11]), a peak appeared around 540 nm. It is well known that a state of Au NPs is reflected by the position of a surface plasmon resonance peak from the UV–vis spectrum. Individual Au NPs give a peak around 530 nm, and a peak of agglomerated particles red-shifted.[8,12] Therefore, the result of the reflection spectrum implies that the Au NPs are almost isolated and highly dispersed in PI NPs, and it is in good agreement with the TEM observation. The homogeneous dispersion state of Au NPs in PI NPs was attributed to the weak ability of the carboxy group in PAA molecules as a dispersion stabilizer. It has been reported that carboxy groups in polymer can stabilize metal NPs.[13] Thus, when Au NPs were formed without PAA, Au NPs have very poor stability in DMAc. Therefore, when the mixing order of precursor solutions was changed from Au salt → PAA → $NaBH_4$ to Au salt → $NaBH_4$ → PAA, Au NPs agglomerated rapidly between the point of Au NPs formation and mixing point with PAA (i.e., mixing points of MM1 and MM2 in Figure 1, and see Figure S3).[11] Furthermore, it is difficult to fabricate PI NPs with well-dispersing Au NPs using a batch process,[14] because in the batch process longer time (10 s) is necessary to prepare, and the stabilization effect of PAA is insufficient for restricting agglomeration of Au NPs for several minutes (Figure S4).[11] Thus, rapid and sequential control of state in stream with a microfluidic system plays an important role in the synthesis of Au NPs/PI NPs.

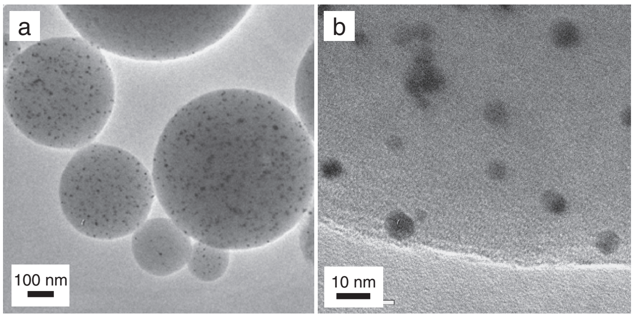
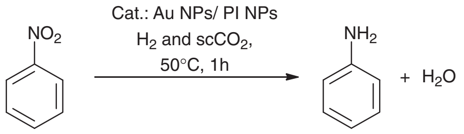


Figure 3. TEM images PI nanoparticles confining Au nanoparticles.

On the other hand, all the PI NPs were spherical with the average particle size of 449.3 nm. In the present study, average particle size was larger than that of NPs consisting of only PI as described earlier (100–180 nm).[9] Final particle size is decided by emulsion droplet size just before fabrication of PAA NPs. Since the emulsion is prepared by collision of PAA solution with *n*-hexane, the droplet size is influenced by viscosity of PAA solution. Namely, solution of higher viscosity gives larger droplets. In the present study, viscosity of PAA solution changed because Au NPs were contained in the solution. As mentioned above, carboxy groups act as a weak stabilizer of Au NPs. This stabilizing effect is induced by the weak interaction between PAA molecules and Au NPs in DMAc, resulting in a higher viscosity solution. Therefore, final particle size became larger.

To check the catalytic activity of Au NPs/PI NPs, we have primarily investigated the hydrogenation of nitrobenzene to



Scheme 2. Reaction path of hydrogenation of nitrobenzene to aniline in the presence of PI nanoparticles confining Au nanoparticles catalyst.

Table 1. Hydrogenation of nitrobenzene to aniline in the presence of PI nanoparticles confining Au nanoparticles in supercritical CO_2[a]

Run	Catalyst[a]	P_{CO_2} /MPa	P_{H_2} /MPa	Reaction time/h	Reaction temp/°C	Conv. /%	Selectivity /%
1	Au NPs/PI particles	12	4	1	50	89.8	100[c]
2	Au NPs/PI particles[b]	12	4	1	50	87.6	100[c]
3	PI particles	12	4	1	50	0.8	100[c]

[a] Catalyst:substrate (nitrobenzene) 100 mg:500 mg. Loading amount of Au is 2.5 wt %. [b] Au NPs/PI particle catalyst is reused after the reaction in Run 1. [c] No other product was detected by GC analysis.

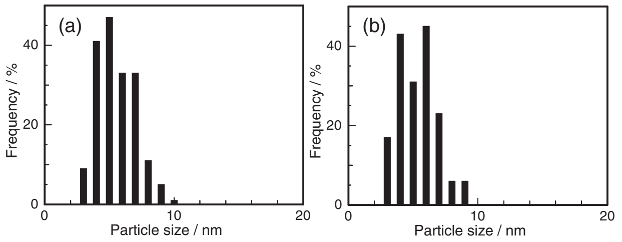


Figure 4. Size distributions of Au nanoparticles confined in PI nanoparticles before (a) and after (b) use in catalytic reaction.

aniline in $scCO_2$ in the presence of the Au NPs/PI NPs as a model reaction (Scheme 2),[15] and the results are shown in Table 1. Nitrobenzene could be successfully hydrogenated into aniline with 89.8% conversion and excellent selectivity of 100% to aniline within 1 h at 50 °C in the presence of Au NPs/PI NPs (Run 1). Figure 4 shows size distributions of Au NPs confined in PI NPs before and after the hydrogenation, which suggested that no agglomeration of Au NPs occurred. When the PI NPs without Au NPs were used, hydrogenation hardly preceded (Run 3). Therefore, Au NPs are necessary to achieve catalytic activity stabilized in PI NPs. The studied catalyst could be recycled without any loss of activity (Run 2) and attributed to the stability of the catalyst.

In conclusion, we developed a continuous microfluidic fabrication system for the highly dispersed Au NPs confined with PI NPs. In the described system, loading amount of Au NPs could be easily tuned up to 12.5 wt % by changing the flow rates and concentrations of starting materials. The Au NPs/PI NPs showed high catalytic activity in the hydrogenation of nitrobenzene in $scCO_2$ and were devoid of leaching and agglomeration of Au NPs after reaction. This method might be useful for large-scale production of Au NPs in PI NPs, and it is also possible to apply for other series of metal NPs.

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