

Self-organization of Organic-inorganic Hybrid Nanomushroom by Simple Synthetic Route at Organic/water Interface

Hiroshi Shiigi,^{*,a} Ryosuke Morita,^a Yojiro Yamamoto,^a Shiho Tokonami,^a
Hidenobu Nakao,^b and Tsutomu Nagaoka^a

^aFrontier Science Innovation Center, Osaka Prefecture University, 1-2 Gakuen-cho, Sakai,
Osaka 599-8570, Japan.

^bNational Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

*Fax: 81 72 254 9875; E-mail: shii@riast.osakafu-u.ac.jp

AuNP was prepared by using a reducer such as aniline at an interface of aqueous and respective organic medium. An aniline/organic solution such as benzene, hexane, benzyl alcohol, and nitrobenzene was added to an aqueous 0.1 mM chloroauric acid solution (10 mL) with a 1:30 molar ratio of the reactants and stirred at 353 K for 30 min, as shown in Fig. S1.

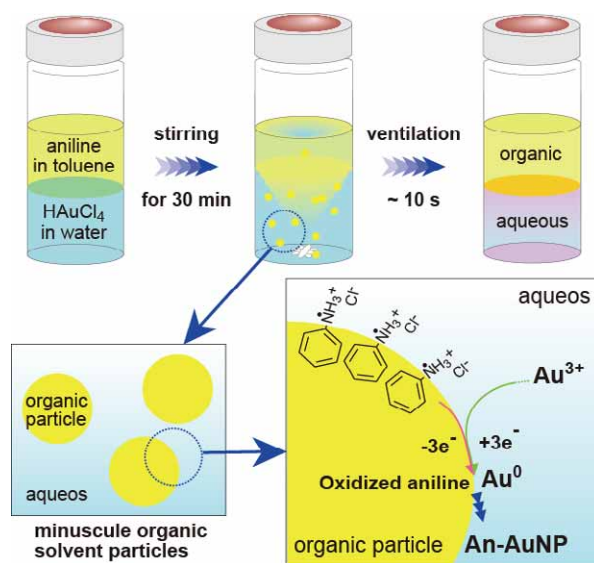


Fig. S1 Schematic representations of the procedure for preparation and the minute reaction fields at the surface of the organic droplets in the aqueous medium.

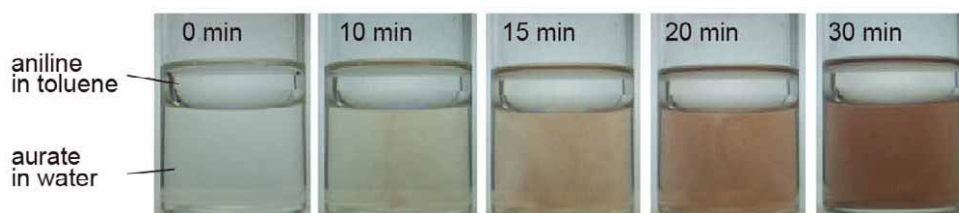


Fig. S2 Change in the color of the reaction solution without stirring at 353 K.

Aurate was reduced to gold particles by aniline, and the aniline monomer was oxidized with self-stabilized dispersion polymerization in a heterogeneous biphasic mixture containing organic and aqueous phases.¹ Organic solvents used are listed in Table S1. The constant stirring at 350 rpm yielded minuscule organic solvent particles in an aqueous medium and many reaction-active interfaces.

The resultant mixture was left at rest in order to separate the phases completely, and then the aqueous phase was pipetted for removing the organic phase. The AuNPs were characterized by using a transmission electron microscope (TEM) at an accelerating voltage of 200 kV. To reveal the composition and structure of the nanoparticles, powder X-ray diffraction (XRD) experiments were carried out using a Rigaku RINT2400 X-ray diffractometer incorporating CuK α radiation with an applied voltage and current of 40 kV and 40 mA, respectively. Thermogravimetric/mass (TG/MS) analysis was performed on a Bruker AXS TG-DTA/MS 9600 system under an ultra-pure helium atmosphere. Temperature was changed from 20–800 °C at the programmed heating rate of 10 °C min⁻¹. 2 mg of the vacuum-dried mushroom powder was placed on a Pt sample holder.

Table S1 Relative permittivity (ϵ_r) of organic solvents

Solvent	Relative permittivity (ϵ_r) / F m ⁻¹	Density / g mL ⁻¹	Color of aqueous solution
Hexane	1.88	0.77	Purplish red
Toluene	2.38	0.87	Purplish red
Benzene	2.38	0.86	Purplish red
Benzylalcohol	11.9	1.04	None
Nitrobenzene	35.6	1.20	Purplish red
Water	78.4	1.00	—

These values were reported in ref. [2].

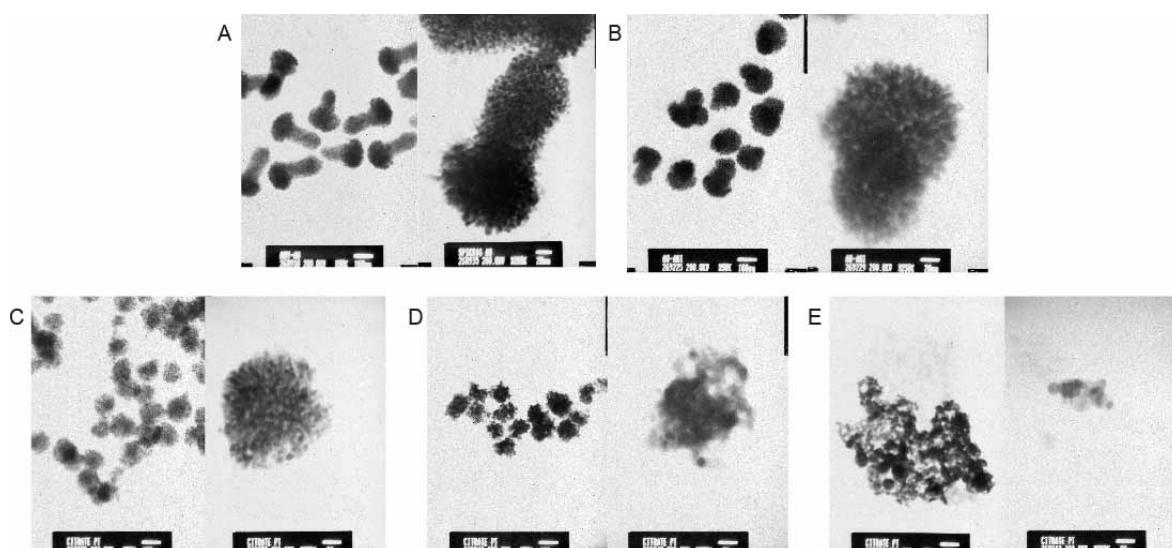


Fig. S3 TEM images of the aggregate prepared at the water/organic solvent interface. (A) Toluene, (B) benzene, (C) hexane, (D) nitrobenzene, and (E) benzyl alcohol were used as the organic solvent. The magnifications of the left-hand-side and right-hand-side images were 50 k and 200–250 k, respectively.

The aqueous and organic phases were studied by using a TEM, and the existence of the assembled AuNPs was observed in the aqueous phase. The resultant aggregates have different shapes, as shown in Fig. S3; however, no other metal product was obtained in the organic phase. Although various shapes of the structure were observed with different solution systems, the resulted aggregates were formed of nanoparticles. In the cases of toluene and benzene, which were used as organic solvents, uniform mushroom- and acorn-like aggregates were observed; a raspberry-like aggregate was observed when hexane was used. In the other cases, when nitrobenzene and benzylalcohol were used, irregularly shaped aggregates were observed. It was found that the shape of the aggregates depended on the solution property of the organic solvent. The difference in the relative permittivity between organic solvents and water controlled the size or shape of minuscule organic solvent particles yielded in an aqueous medium, which had an intimate involvement in the formation of the AuNPs aggregate. However, the question that needs to be answered is “Why was the aggregate mushroom shaped”? Further examination under various conditions will help us to understand this phenomenon and provide more details, and this is our priority for study in the near future. It is highly necessary to report the formation of strange-shaped aggregates in this study.

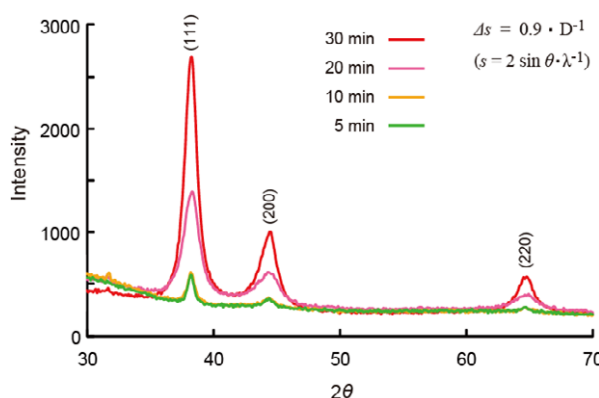


Fig. S4 XRD spectra of nanomushroom prepared in a toluene/water system.

In process of the growth of AuNP in a PANI matrix, the XRD measurements were carried out, as shown in Fig. S4. The peak intensity increased dramatically with an increase in the reaction time of more than 10 min, and a typical XRD pattern of the AuNP was observed after 30 min. This implies that the reduction of Au^{3+} occurred here and there in the solution at the early reaction stage and that the crystal grew considerably with the reaction time of more than 10 min. According to the TEM measurement, the aggregates of AuNP formed after 30 min had a mean particle diameter of 3.42 and standard deviation of 0.56 nm. This mean particle diameter value corresponded approximately to the diameter calculated by the *Scherrer correlation* (3.88 nm).³

The FTIR spectrum of PANI in KBr is shown in Fig. S5 in which the sample was prepared in a toluene/water system. The PANI shows a quinoid ring (**Q**) stretching at 1592 cm^{-1} and a benzenoid ring (**B**) stretching at 1500 cm^{-1} , typical features of a semiquinoid structure of emeraldine type.⁴⁻⁷ The peaks at 1311 and 1241 cm^{-1} were attributed to the C–N stretching and deformation modes of the aromatic amine.⁷ The peak at 1157 cm^{-1} , was

attributed to the $\text{B-NH}^+=\text{Q}$ vibration, which is smaller than that of the high doping level of emeraldine salt, since the PANI has been synthesized at the interface between a mild acidic aqueous phase (pH 3.6) and toluene.⁵

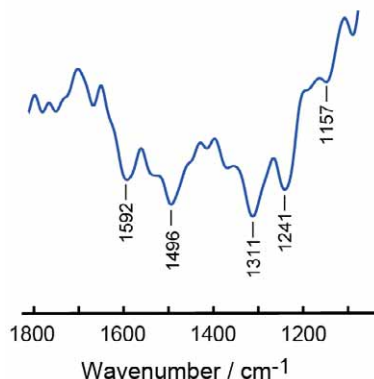


Fig. S5 FTIR spectrum of nanomushroom prepared in a toluene/water system.

While there are no fragments of low-molecular-weight structures, which are attributable to the aniline oligomer in the lower-temperature region ($< 250\text{ }^{\circ}\text{C}$), the large weight loss attributed to the degradation of the PANI backbone over $300\text{ }^{\circ}\text{C}$ was observed on the basis of the TG/MS analysis. This implies that the PANI in the mushroom had a relatively large polymerization degree, as compared to the oligomer.⁶⁻⁸

References

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