Ionic Liquid-in-Water Emulsion-Templated Synthesis of Gold Nanoshells
at the Liquid-Liquid Interface between Water and Primary Ammonium-based Ionic Liquids

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Au nanoshells have been synthesized at the liquid-liquid interface between primary ammonium-based ionic liquids and water. Ionic liquid-in-water emulsions, which are spontaneously formed on the water side of the interface, function as a template for the synthesis of Au nanoshells. Selective adsorption of the primary amine group on the Au surface plays an important role in the formation of Au nanoshells.

Ionic liquids (ILs) are salts in the liquid state and have been investigated as promising materials owing to their exceptional properties such as low volatility, high ionic conductivity, and designability.[1] When IL ions are designed to be highly hydrophobic, the ILs are immiscible with water (W) and the IL|W interface is formed. By employing the IL|W interface as redox reaction field, various kinds of metal nanostructures have been synthesized.[2-7] During the synthesis, IL ions act as capping agents, which lead to stabilization of nanostructures[8] and tunable morphology ascribed to designability of ILs.[9]

Gold nanostructures have unique optical and catalytic properties which are not found in the bulk form. It is important to establish a method to control the morphology of gold nanostructures because their unique properties depend on their size and shape.[10] To utilize the features of gold, such as biocompatibility and easy surface modification, for the applications such as biomedical areas, gold nanostructures with well-defined morphology are desirable. Especially, gold nanoshells have been studied for their applications in cancer treatment[11] and drug delivery systems[12] because they show localized surface plasmon resonances in the near-infrared region and high photothermal efficiency.[13]

Gold nanoshells have been synthesized with a wide range of templates. When nanoparticles (NPs) of less-noble metals such as Ag[14] and Co[15] are selected as the template, gold is reductively precipitated onto the NPs via galvanic replacement reaction. Gold nanoshells have been synthesized by taking advantages of surfactant aggregates.[16] For other NPs such as silica NPs[17] and polystyrene NPs[18], the growth of gold proceeds on the surface of the template via the selective adsorption of primary amine group (-NH$_2$ group) or thiol group (-SH group) on the Au surface. Oil-in-water (O/W) emulsions have also been employed as the template for the synthesis of Au nanoshells via the selective adsorption of -NH$_2$ group[19] or -SH group[20] on the Au surface.

In the present study, in order to control the morphology of gold nanostructures by utilizing the selective adsorption of -NH$_2$ group on the Au surface, primary ammonium (-NH$_3^+$) based hydrophobic ILs were designed and synthesized. Gold was reductively precipitated at the IL|W interface where the -NH$_3^+$ group of the IL cation is deprotonated to be -NH$_2$ group in neutral aqueous condition. Spontaneous emulsification driven by mass transfer across the liquid-liquid interface[21] was observed in the present study as IL-in-W (IL/W) emulsions on the W side of the IL|W interface. Although in a previous study the IL/W emulsions have been utilized as the template of nanostructures of inorganic salts,[22] in the present study, the IL/W emulsions functioned as the template for the synthesis of Au nanoshells. The formation mechanism of Au nanoshells has been discussed.

An IL with -NH$_3^+$ group, protonated L-phenylalanine methyl ester bis(nonafluorobutanesulfonyl)amide ([N$_{000\text{-L-Phe-OMe}}^+$][C$_4C_4N^-$]) was prepared[23] and purified[24] by the similar procedures described previously (the structures of ions are shown in Fig. S1). Tris(4-methylphenyl)amine (CH$_3$-TPA, 10 mmol kg^{-1}) was dissolved in IL as a reducing agent (Fig. S1). AuCl$_3$ (2.5 mM) and LiCl (100 mM) were dissolved in W as a gold precursor and stabilizer for AuCl$_3$ to form AuCl$_4^-$, respectively. 0.20 g of IL and 0.50 mL of W were made contact in a sample bottle to form the IL-W two-phase system and kept for 7 days (labeled as Neutral sample). Another sample using HCl (100 mM) instead of LiCl as the stabilizer was also prepared (labeled as Acidic sample), where the deprotonation of -NH$_3^+$ group into -NH$_2$ group is prevented. Au nanostructures formed at the IL|W interface was washed repeatedly with methanol and acetonitrile, and then observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

SEM images of Au nanostructures are shown in Fig. 1. The deposits for Neutral sample were spherical with an average diameter of 300 nm (Fig. 1a). A fraction of the spheres were broken (circled in Fig. 1a and Fig. S5c) or with a hole on their surface (Fig. 1b), which illustrates that the spheres are hollow Au nanoshells. The wall thickness of the nanoshells was several tens of nm (Fig. 1 and Fig. S5c). In contrast, the deposits for Acidic sample were Au nanofibers (Fig. S4), whose morphology resembles that of metal nanofibers formed at the IL|W interface in our previous studies.[5-7] Accordingly, the morphology of the synthesized Au nanostructures has significant pH dependence, implying that the IL cation having weakly acidic -NH$_3^+$ group plays an important role during the nanostructure formation.
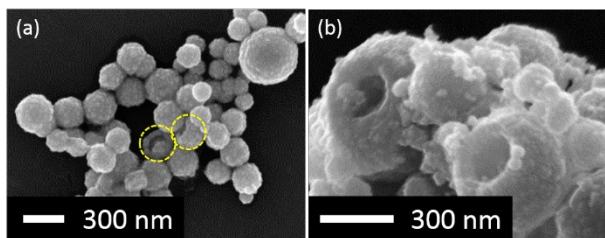
Figure 1. (a, b) SEM images of Au nanoshells obtained from Neutral sample. The yellow dashed circles in (a) illustrate the structure of the Au nanoshells.

TEM images of Au nanoshells obtained from Neutral sample are shown in Fig. 2. Their surface was found to be uneven with a roughness of 10 nm scale (Fig. 2a). Since Au NPs with a diameter of 10 nm were also observed (Fig. 2b), the uneven surface of the Au nanoshells seems to be ascribed to aggregation of the Au NPs.
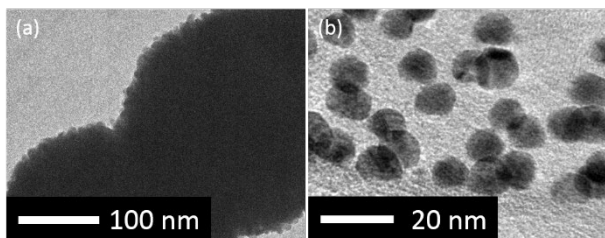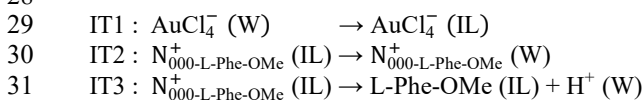

Figure 2. TEM images of (a) Au nanoshells with an uneven surface and (b) Au nanoparticles with a diameter of 10 nm obtained from Neutral sample.

The reductive deposition of $AuCl_4^-$ at the liquid-liquid interface is explained as simultaneous ion transfer (IT) and electron transfer (ET) processes occurring across the interface.[5-7] The ET across the interface between the metal precursor ($AuCl_4^-$) in W and the reducing agent (CH_3-TPA) in IL is expressed as follows:

ET : $AuCl_4^-$ (W) + 3Red (IL) → Au + 4Cl$^-$(W) + 3Ox$^+$(IL)
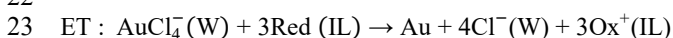
Judging from the hydrophobicity of ions used in the present study, possible ITs across the IL|W interface are the following three:

IT1 : $AuCl_4^-$ (W) → $AuCl_4^-$ (IL)
IT2 : $N_{000\text{-}L\text{-}Phe\text{-}OMe}^+$ (IL) → $N_{000\text{-}L\text{-}Phe\text{-}OMe}^+$ (W)
IT3 : $N_{000\text{-}L\text{-}Phe\text{-}OMe}^+$ (IL) → L-Phe-OMe (IL) + H$^+$ (W)

where the deprotonated form of $N_{000\text{-}L\text{-}Phe\text{-}OMe}^+$ is abbreviated as L-Phe-OMe. The positive charge flow from W to IL phase is defined as positive current as in the convention of electrochemistry at the liquid-liquid interface, and therefore the ET is treated as positive current and the IT1, IT2, and IT3 as negative current. To maintain electroneutrality, the ET has to be coupled with either of the ITs.

Which IT entirely occurs can be judged from the formal ion transfer potential, which is the measure of the hydrophobicity of ions. When the potential, $\Delta_O^W \varphi$, is defined as the Galvani potential in W with respect to that in IL, the IT with the most positive formal potential among the three is likely to occur and coupled with the ET. The formal potentials of ITs are estimated from reported[29,30] and predicted[31] data for related ions and molecules (the estimation details are discussed in SI) and the results are shown in Fig. 3. IT3 is thermodynamically advantageous in neutral aqueous condition (pH = 7), while IT2 is dominant in acidic aqueous condition (pH = 1). Therefore, -NH$_3^+$ groups are expected to be deprotonated to be -NH$_2$ groups via IT3 in Neutral sample while not in Acidic sample.
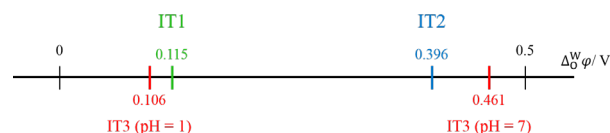
Figure 3. Estimated formal ion transfer potentials of IT1, IT2, and IT3.

Spontaneous formation of IL/W emulsions was confirmed during the synthesis (Fig. 4). The IL/W emulsions were clearly visible at 12 h after the contact of the two phases while decreased in the number at 24 h and totally disappeared at 7 days. A control experiment in the absence of CH_3-TPA did not show the IL/W emulsions, indicating that gradients in chemical potentials,[21] IT and ET across the interface in the present study, are indispensable for the spontaneous formation of the IL/W emulsions. It has been reported that IT of surface-active ions gives rise to the in-plane nonuniformity of the interfacial tension and causes Marangoni convection.[25,26] The Marangoni convection induced by ITs is likely to be responsible for the spontaneous formation of the IL/W emulsions.
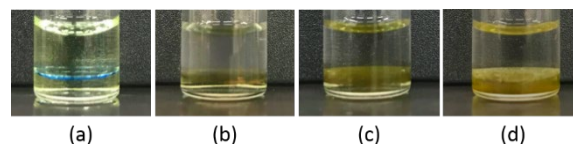

Figure 4. The two-phase system composed of the W (upper) and IL (lower) phases for Neutral sample at t = (a) 0, (b) 12 h, (c) 24 h, and (d) 7 days after the contact of the two phases. The blue color at the IL|W interface in (a) is due to oxidized CH_3-TPA.

The -NH$_3^+$ group of IL cation, $N_{000\text{L-Phe-OMe}}^+$, is the polar and charged part of the ion and therefore likely to be protruded toward the outside (W phase) at the surface of the IL/W emulsion. In neutral aqueous condition, the -NH$_3^+$ groups at the IL/W emulsion surface are deprotonated to become -NH$_2$ groups via IT3. In a previous study, O/W emulsions whose surfaces were functionalized with -NH$_2$ group has been utilized as the template for the synthesis of Au nanoshells via the selective adsorption of -NH$_2$ group on the Au surface.[19] In the present study, the IL/W emulsions function as the template for the synthesis of the Au nanoshells. To compare the size of Au nanoshells and IL/W emulsions, the average diameter of the IL/W emulsions was measured by dynamic light scattering and turned out to be 296 ± 14 nm.

1 The IL/W emulsions and Au nanoshells (Fig. 1a and 2a) are
2 almost the same in size, indicating that Au nanoshells were
3 formed on the surface of the IL/W emulsions.
4 　　We propose a formation mechanism of Au nanoshells
5 consisting of the following three steps. First, IL/W emulsions
6 were formed spontaneously on the W side of the IL|W
7 interface via IT3 (Fig. 5a). To maintain electroneutrality, the
8 ET also proceeded with IT3 and led to the generation of the
9 Au nanoparticles (Fig. 2b) at the IL|W interface. Second, the
10 surface of the IL/W emulsions were functionalized with $-NH_2$
11 group. Since $-NH_2$ group is known to be specifically adsorbed
12 on the Au surface, the Au NPs formed in step 1 are adsorbed
13 and grown further via ET on the surface of the IL/W
14 emulsions, resulting in the Au nanoshells with an uneven
15 surface (Fig. 5b). Third, some Au nanoshells stop their
16 growth in the form of a snowman because adjacent IL/W
17 emulsions mutually interfere with the growth of the metallic
18 Au. The snowman-like Au nanoshells are split into two
19 during the washing process, resulting in the hollow Au
20 nanoshells (Fig. 5c).
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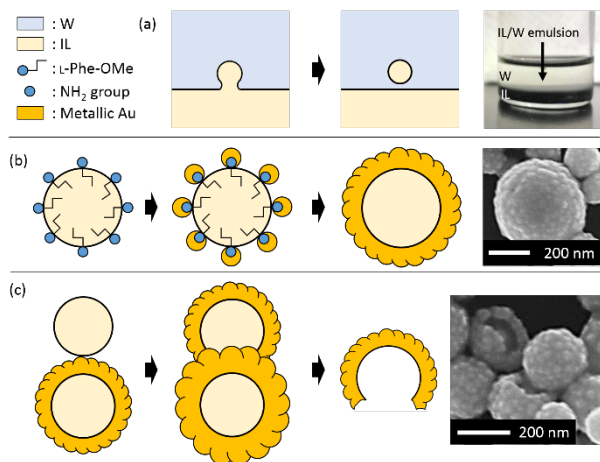
22 **Figure 5.** A possible formation mechanism of Au nanoshells.
23

24 　　Au nanoshells were not obtained in the case of Acidic
25 sample (Fig. S4). The $-NH_3^+$ groups at the surface of the IL|W
26 emulsions cannot be deprotonated to be $-NH_2$ groups in acidic
27 aqueous condition because IT3 is thermodynamically
28 disadvantageous (Fig. 3), indicating that the selective
29 adsorption of $-NH_2$ group on the Au surface is crucial to the
30 formation of Au nanoshells. Our previous studies revealed
31 that IT of metal precursor ions (IT1 in the present case) leads
32 to the formation of metal nanofibers at the IL|W interface.[5-7]
33 Although IT1 is disadvantageous even in acidic aqueous
34 condition based on the formal potential estimation (Fig. 3),
35 the formation of the Au nanofibers (Fig. S4) demonstrates the
36 progress of IT1.
37 　　Some control experiments have been conducted to
38 validate the formation mechanism of Au nanoshells. The
39 proposed mechanism predicts that Au nanoshells are not
40 obtained without the specific adsorption of the amine group
41 on the Au surface. We synthesized a quaternary ammonium-
42 based IL, $[N_{111\text{-L-Phe-OMe}}^+][C_4C_4N^-]$, in which the $-NH_3^+$ group
43 of $N_{000\text{-L-Phe-OMe}}^+$ was quaternized to $-NMe_3^+$ group (Fig. S1)

44 by a previously reported procedure.[27] Gold was reductively
45 precipitated at the $[N_{111\text{-L-Phe-OMe}}^+][C_4C_4N^-]$|W interface in a
46 similar manner. The nanostructures formed are shown in Fig.
47 S5. No Au nanoshells were observed as predicted. Moreover,
48 the proposed mechanism expects that ILs with $-NH_3^+$ group
49 other than $[N_{000\text{-L-Phe-OMe}}^+][C_4C_4N^-]$ also produce Au nano-
50 shells. We synthesized three primary ammonium-based ILs,
51 $[N_{000\text{-L-Met-OMe}}^+][C_4C_4N^-]$, $[N_{000\text{-L-Leu-OMe}}^+][C_4C_4N^-]$ and
52 $[2EHA^+][C_4C_4N^-]$ which incorporate $-NH_3^+$ group (Fig. S1).
53 The Au nanostructures formed at the IL|W interface are
54 shown in Fig. S6. Au nanoshells were not obtained in acidic
55 aqueous condition but obtained in neutral aqueous condition.
56 These control experimental results support the formation
57 mechanism of Au nanoshells.
58 　　In conclusion, $[N_{000\text{-L-Phe-OMe}}^+][C_4C_4N^-]$ was designed
59 and synthesized to take advantage of the specific adsorption
60 of the amine group on the Au surface for the control of the
61 morphology of Au nanostructures. Au nanoshells have been
62 successfully synthesized at the $[N_{000\text{-L-Phe-OMe}}^+][C_4C_4N^-]$|W
63 interface. The formation mechanism of Au nanoshells was
64 explained by IL/W emulsions as the template and the specific
65 adsorption of the amine group on the Au surface. Further
66 study is being conducted to control the diameter of Au
67 nanoshells by changing the size of IL/W emulsions which is
68 expected to be tuned with the design of the hydrophobicity of
69 IL ions.[16] It has been reported that Pt porous film with
70 nanocavities made by chiral molecules shows
71 electrochemical recognition toward chirality.[28] Au nanoshells
72 in the present study formed by the specific adsorption of the
73 chiral molecule, L-Phe-OMe, may possess such chiral
74 nanocavities of L-Phe-OMe and show chiral recognition.
75 Further study is being conducted in our laboratory.
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80 Supporting Information is available on
81 http://dx.doi.org/10.1246/cl.******.

82 **References and Notes**
83 1　R. D. Rogers and K. R. Seddon (eds) : "Ionic Liquids Industrial
84 　　Applications to Green Chemistry"; ACS Symposium Series 818;
85 　　American Chemical Society, **2002**.
86 2　T. Soejima and N. Kimizuka, *Chem. Lett.*, **2005**, 34, 1234.
87 3　I. Kaminska, J. Niedziolka-Jonsson, A. Roguska, M. Opallo,
88 　　*Electrochem. Commun.*, **2010**, 12, 1742.
89 4　Y. Chen, M. Chen, J. Shi, J. Yang, D. Zhang, *Mater. Lett.*, **2014**,
90 　　132, 153.
91 5　N. Nishi, T. Kakinami, T. Sakka, *Chem. Commun.*, **2015**, 51,
92 　　13638.
93 6　Y. Zhang, N. Nishi, K. Amano, T. Sakka, *Electrochim. Acta*, **2018**,
94 　　282, 886.
95 7　N. Nishi, I. Yajima, K. Amano, T. Sakka, *Langmuir*, **2018**, 34,
96 　　2441.
97 8　T. Torimoto, K. Okazaki, T. Kiyama, K. Hirahara, S. Kuwabata,
98 　　*Appl. Phys. Lett.*, **2006**, 89, 243117.
99 9　K. Yao, Z. Li, X. Li, W. Lu, A. Xu, H. Zhang, J. Wang, *Cryst.*
100 　　*Growth Des.*, **2017**, 17, 990.
101 10　Y. Tang and W. Cheng, *Langmuir*, **2013**, 29, 3125.
102 11　S. Lal, S. E. Clare, N. J. Halas, *Acc. Chem. Res.*, **2008**, 41, 1842.
103 12　B. Singhana, P. Slattery, A. Chen, M. Wallance, M. P. Melancon,
104 　　*AAPS PharmSciTech*, **2014**, 15, 741.

13   V. P. Pattani and J. W. Tunnell, *Lasers Surg. Med.*, **2012**, 44, 675.

14   A. L. Durán-Meza, D. S. Moreno-Gutiérrez, J. F. Ruiz-Robles, A. Bañuelos-Frías, X. F. Segovia-González, A. M. Longoria-Hernández, E. Gomez, J. Ruiz-García, *Nanoscale*, **2016**, 8, 11091.

15   H. P. Liang, L. J. Wan, C. L. Bai, L. Jiang, *J. Phys. Chem. B,* **2005**, 109, 7795.

16   W. Wang, Y. Hun, M. Tian, Y. Fan, Y. Tang, M. Gao, Y. Wang, *Appl. Mater. Interfaces*, **2013**, 5, 5709.

17   Q. Chen, Y. Rao, X. Ma, J. Dong, W. Qian, *Anal. Methods*, **2011**, 3, 274.

18   W. Shi, Y. Sahoo, M. T. Swihart, P. N. Prasad, *Langmuir*, **2005**, 21, 1610.

19   Y. Guan, Z. Xue, J. Liang, Z. Huang, W. Yang, *Colloids Surf. A*, **2016**, 502, 6.

20   C. Zimmermann, C. Feldmann, M. Wanner, D. Gerthsen, *Small*, **2017**, 3, 1347.

21   C. Solans, D. Morales, M. Homs, *Curr. Opin. Colloid Interface Sci.*, **2016**, 22, 88.

22   M. Kowacz, J. M. S. S. Esperança, L. P. N. Rebelo, *Soft Matter*, **2014**, 10, 3798.

23   E. Elfassy, Y. Basel, Y. Mastai, *CrystEngComm*, **2016**, 18, 8769.

24   M. J. Earle, C. M. Gordon, N. V. Plechkova, K. R. Seddon, T. Welton, *Anal. Chem.*, **2007**, 79, 758.

25   T. Kakiuchi, N. Nishi, T. Kasahara, M. Chiba, *ChemPhysChem*, **2003**, 4, 173.

26   T. Kasahara, N. Nishi, M. Yamamoto, T. Kakiuchi, *Langmuir*, **2004**, 20, 875.

27   I. Fuchs, N. Fechler, M. Antonietti, Y, Mastai, *Angew. Chem. Int. Ed*., **2016**, 55, 408.

28   C. Wattanakit, Y. B. S. Côme, V. Lapeyre, P. A. Bopp, M. Heim, S. Yadnum, S. Nokbin, C. Warakulwit, J. Limtrakul, A. Kuhn, *Nat. Commun.*, **2014**, 5, 3325.

29   A. Uehara, S. G. Booth, S.Y. Chang, S. L. M. Schroeder, T. Imai, T. Hashimoto, J. F. W. Mosselmans, R. A. W. Dryfe, *J. Am. Chem. Soc*., **2015**, 137, 15135.

30   F. Reymond, V. Chopineaux-Courtois, G. Steyaert, G. Bouchard, P. Carrupt, B. Testa, H. H. Girault, *J. Electroanal. Chem.*, **1999**, 462, 235.

31   Advanced Chemistry Development (ACD/Labs) Software V11.02.

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Title(required)	**Ionic Liquid-in-Water Emulsion-Templated Synthesis of Gold Nanoshells** **at the Liquid-Liquid Interface between Water and Primary Ammonium-based Ionic Liquids**
Authors' Names(required)	Seiji Takagi, Naoya Nishi,[*] and Tetsuo Sakka

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