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Dendritic nanofibers of gold formed by the electron transfer at the interface between water and highly hydrophobic ionic liquid

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Gold nanofibers have been found to be formed from heterogeneous electron-transfer reaction at ionic liquid|water interface. The tips of the nanofibers show dendritic structure and the dendrites are bundled to nanofibers except around the tips. The roles of the ionic liquid for the dendritic nanofiber formation have been discussed.

Gold nanostructures have specific optical, electrical, and catalytic properties different from those in bulk and have been extensively studied for the application to catalyst, sensors, and bioimaging.^{1,2} The formation of gold nanostructures has been effectively performed by the reduction of Au ions such as AuCl₄⁻ by a reducing agent. For the reaction media of the reduction, oil(O)-water(W) two-phase systems have been utilized since more than a century ago³ and such studies have boomed after the development of the “Brust-Schiffrin” method for the formation of Au nanoparticles.⁴ Among such two-phase systems for the Au nanostructure formation, the reaction is able to be spatially restricted at the O|W interface, e.g., by using metal ion only soluble in one phase and reducing agent only soluble in the other phase.⁵ For the Au deposition at the O|W interface, we may choose a combination of metal ion and reducing agent that lead to either of spontaneous reaction or the reaction driven by the externally-controlled phase-boundary potential across the interface. The latter has been adopted to control and analyze the kinetics of the reduction at the O|W interface.⁶⁻⁹ Most often studied Au nanostructures formed at the O|W interface are nanoparticles, but more complicated Au nanostructures have also been found to be formed at the O|W interface. Rao et al. prepared 2-D fractal and dendritic nanostructures formed by Au “nanocauliflowers” at toluene|W interface in the presence of tetraoctylammonium bromide (TOAB) or cetyltrimethylammonium bromide (CTAB),¹⁰ which is one of the results of their extensive studies for the preparation of metal nanostructures using oil-water two-phase system.¹¹ Soejima et al. utilized linear aggregates of tetrabutylammonium Au(OH)₄⁻ ion pairs formed at chloroform|W interface for the photoreductive formation of holey Au nanowires.¹² In the

present study, we will introduce another nanostructure, dendritic nanofibers of gold, that are formed by the electron transfer at another kind of liquid-liquid interface where we used a highly hydrophobic ionic liquid (IL) instead of molecular organic solvents (oil).

ILs are liquid salts that are entirely composed of ions and are promising materials replacing conventional organic solvents in many scientific fields.¹³⁻¹⁵ When ILs are composed of highly hydrophobic cations and anions the ILs are immiscible with W¹⁶ and furthermore when the IL-ions are highly hydrophobic the IL|W interface is able to be electrochemically polarizable.^{17,18} The development of highly hydrophobic ILs has enabled to perform electrochemical measurements at the IL|W interface,^{19,20} using the same methodology as that at the O|W interface.²¹⁻²³ For example, the transfer of ions^{17,18,24-30} and the facilitated transfer of metal ions in W by ligand in IL³¹⁻³⁴ across the IL|W interface has been studied. The electron transfer across the IL|W interface has also been studied between redox species in IL and those in W,³⁵⁻³⁹ which prompted us to measure electron-transfer current due to electrodeposition of metal ion at the IL|W interface in the present study.

Aside from the viewpoint of electrochemistry at liquid-liquid interface, ILs have some characteristics that provide benefits to the formation of unique metal nanostructures. First, ILs have high viscosity, typically hundreds times higher than W, which leads to slow mass transfer of the reactants in ILs for the metal deposition. This will induce significant imbalance of the mass transfer rates from W side and IL side of the IL|W interface where metal ion and reducing agent reacts and such mass transfer imbalance has been discussed as a key factor to prepare 1-D nanostructure of metal at the O|W interface.⁴⁰⁻⁴² Second, ILs form a specific structure, ionic multilayers at interfaces.^{43,44} By virtue of this property researchers have successfully prepared well-dispersed metal nanoparticles in ILs without any additives to prevent aggregation.⁴⁵ This remarkable stabilization of metal nanoparticles in ILs has been discussed in the viewpoint of the ability of IL-ions acting as “capping reagents”.⁴⁵ Regarding the role of IL-ions as the capping reagent, we may also anticipate the influence of IL ions on the final metal nanostructures because some IL-ions are surface-active but others are not. In fact, Yao et al. recently prepared Ag films, by reducing Ag⁺ in W with a reducing agent in IL at the IL|W interface, whose morphology depends on the used IL-ions.⁴⁶ Finally, ILs are regarded as dense electrolyte solutions with an ionic strength of several mol dm⁻³ and thus possess the ability to screen electric field (i.e. ...)

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electrical double layer). This screening ability is expected to make metal nanostructures in ILs easily assembled, without aggregation because of capping ability described above. In the present study, we will show that the formation of Au nanofibers becomes possible because of the above-mentioned characteristics of ILs.

The highly hydrophobic IL used in the present study, trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide ([TOMA⁺][C₄C₄N⁻]), was prepared⁴⁷ and purified^{48,49} in the same way as literature method. In [TOMA⁺][C₄C₄N⁻] tri-*p*-tolylamine (TPTA, TCI) was dissolved as a reducing agent. AuCl₃ (Shimadzu) was dissolved in aqueous solution of HCl to form AuCl₄⁻ in W as a source of metal (metal precursor). The details of the electrochemical measurements for the ion and electron transfer at the IL|W interface and scanning electron microscope (SEM) analysis of the Au deposits are written in ESI.

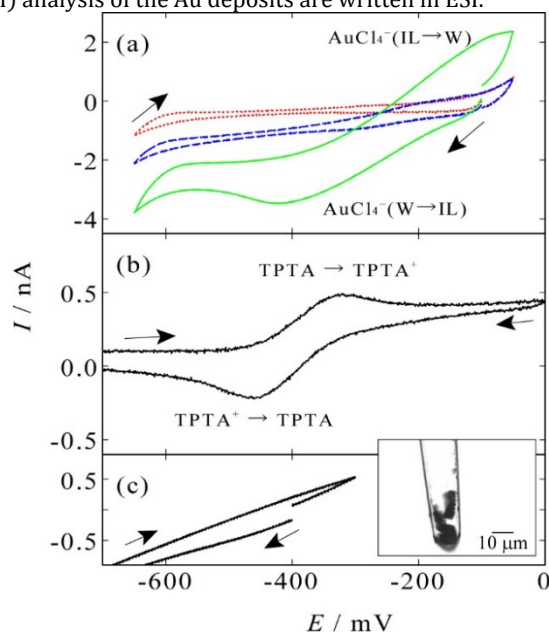


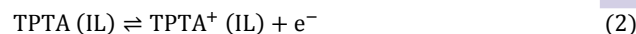
Fig. 1 Cyclic voltammograms at the IL|W interface (a) for the ion transfer recorded using Cell I with $(x,y)=(0,0)$ (red dotted), $(0,1)$ (blue dashed), and $(0,10)$ (green solid), (b) for the electron transfer recorded using Cell II with $(x,y)=(40,10)$, and (c) for both of them recorded using Cell I with $(x,y)=(40,10)$. Inset in (c) is an optical microscope image of the micropipette tip after the voltammetric measurement shown in (c). Scan rate: 100 mV s⁻¹.

Fig.1a shows cyclic voltammograms at the IL|W interface using Cell I (see ESI) in the absence of TPTA in IL ($x=0$, where x denotes the molality of TPTA in the IL in the unit of mmol kg⁻¹). Without TPTA, the reducing agent in the present study, no electron transfer occurs at the IL|W interface and ion transfer across the IL|W interface is detected as current. For the case with $(x,y) = (0,0)$ (red curve in Fig.1a), also in the absence of AuCl₄⁻, one can see potential windows with a width of 500 mV⁴⁷ (where y denotes the molarity of AuCl₄⁻ in W in the unit of mmol dm⁻³). In the presence of AuCl₄⁻ in W, cyclic voltammograms with $(x,y) = (0,1)$ (blue) and $(0,10)$ (green) show negative current at forward scan and positive current at backward scan. The negative and positive current reflects the transfer of AuCl₄⁻ from W to IL and from IL to W, respectively, as was previously observed at the O|W interface.^{5,50–53}



The shape of voltammograms is not as simple as those limited by linear or radial mass transfer, because of truncated conical geometry of the micropipette tip and also small diffusion coefficient of the ion outside the micropipette caused by high viscosity of the IL (2000 mPa s at 25.0 °C).^{47,54} With a slower scan (e.g. 0.1 mV s⁻¹) and a smaller micropipette tip (2 μm) we would record sigmoidal voltammograms, judging from previous experimental²⁴ and simulation⁵⁴ results. In such a complicated case we cannot precisely determine the mid-point potential (or half-wave potential) for the transfer of AuCl₄⁻, however, we roughly estimate it to be -250 mV.

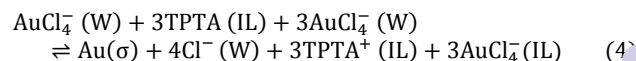
In order to focus on the electron transfer at the IL|W interface, we used the ECSOW system where liquid-liquid interface is separated by electron conductor to prevent the ion transfer.^{53,55} In our case, Au wire and Pt microelectrode, which are electrically connected, were immersed into W and IL, respectively (see ESI for details). Fig.1b shows electron-transfer cyclic voltammogram, where the current is limited by mass transfer and redox of TPTA⁺/TPTA. One can see semi-infinite linear diffusion limited voltammogram having a positive and negative current peaks, indicating simple redox of TPTA.^{52,56}



The peak separation was 130 mV, greater than ideal 59.2 mV for reversible one-electron transfer, reflecting the residual IR drop in the IL even with microelectrode setup due to its low conductivity. That is also why the shape of the cyclic voltammogram is not sigmoid that is usually recorded for microelectrode; high viscosity of the IL limits the diffusion zone close to the surface of microelectrode, leading to more linear diffusion condition rather than radial-diffusion one.^{24,54} The net electron transfer reaction between IL and W is⁵²



where σ denotes the IL|W interface. The mid-point potential for the electron transfer process is -390 mV. Since this mid-point potential is more negative than that for the ion transfer (-250 mV, Fig.1a), one can expect that the ion transfer (1) and the electron transfer (3) couples and that the following net reaction spontaneously proceeds.



It should be noted here that AuCl₄⁻ transferred from W to IL cannot undergo homogenous electron transfer reaction with TPTA in IL because the net reaction (4) is partly driven by release of hydrophilic Cl⁻ ions to W,⁹ which is impossible in IL. The occurrence of this spontaneous reaction was checked by cyclic voltammogram using Cell I in the presence of both AuCl₄⁻ and TPTA shown in Fig.1c. The cyclic voltammogram shows non-polarized behavior, indicating that even in the zero net current condition around at -400 mV the electrochemical reactions (1) and (3) occurs simultaneously at the interface with maintaining the electroneutrality of both of IL and W phases. In order to check the Au deposition at the interface, after the measurement shown in Fig.1c we observed the tip of the micropipette using an optical microscope. The inset in Fig.1c is the image, clearly showing deposit at the tip of the micropipette, as were the cases with Ag deposition observed in the electron transfer and ion transfer coupled at the O|W interface formed at the tip of micro-⁵⁷ and nano-pipette.^{57,58}

To obtain an analyzable amount of the deposit for the morphology analysis, the deposit was prepared at macro IL|W

interface with an area of 1.1 cm². After the contact of the W phase with the IL phase, the formation of gold-coloured deposits at the IL|W interface was observed by the naked eye. SEM images for the deposit are shown in Fig.2a and 2b. The deposits are highly anisotropic 1-D nanostructures whose diameter is 600 nm on average and whose length is from 10 to 30 μm (Fig.2a). The tips of the nanostructures have feather-like dendritic structure whose trunks and branches are 50-100 nm in size (Fig.2b). The dendritic structures is bundled to nanofibers except around the tips (Fig.2ab), keeping small gaps between trunks and branches in the bundles. It should be noted here that these structures are observed by ex-situ SEM and may be somewhat different from those present at the IL|W interface. EDX analysis performed simultaneously with SEM measurements only detected x-ray fluorescence of Au without signal from other elements, illustrating that the nanofibers are made of Au metal (see ESI for the EDX images). To check the existence of any peculiar roles of the IL for the Au nanofiber formation, we performed similar experiments using dichloromethane (DCM), an organic solvent, instead of the IL. The nanostructure obtained at the DCM|W interface is shown in Fig.2c. We obtained burr-like structures in the case with DCM. The results indicate that gold nanofibers are unique structures that are grown peculiarly at the IL|W interface.

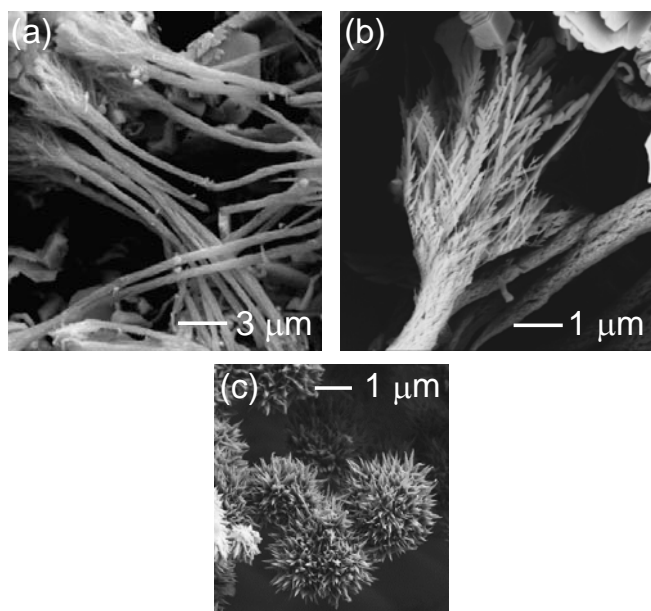


Fig. 2 SEM images (a,b) for the Au nanofibers formed at the IL|W interface and (c) for the Au nanostructures formed at the DCM|W interface.

One of the questions is why such dendritic structures are formed around the tips of the Au nanofibers. To form dendritic nanostructure of Au, previous studies designed chemical species that play a critical role in the reaction. In the case of homogeneous Au reduction in aqueous solutions by a reducing agent,⁵⁹⁻⁶¹ customized cationic surfactants, tetraalkylammonium bromides, were added in the solutions to prepare Au dendrites, inspired by the famous capping reagent CTAB used in Au nanorod synthesis.¹ Electrodeposition at glassy carbon electrode also leads to Au dendrites in the presence of cysteine.⁶² Qin et al. successfully prepared dendritic Au at the interface of Zn and 1-butyl-3-methylimidazolium hexafluorophosphate, an IL, where Zn metal acts as a reducing agent.⁶³ All the above reports used their special chemical species to fulfil the Au dendrite formation.

Therefore, either or both of the presence of TOMA⁺ (tetraalkylammonium cation) and C₄C₄N⁻, the IL ions used in the present study, at the Au surface probably play a crucial role in the dendrite formation in the present study, although the reduction site at the Au surface is likely to be at the W side of the IL|W interface. TOMA⁺ and C₄C₄N⁻ are both surface-active and are expected to be adsorbed at the surface of Au nanostructures which is presumably preferential adsorption at particular crystal faces, as was proposed for CTAB adsorption at the surface of Au nanorods.¹

Another question is why we obtained highly anisotropic 1-D nanostructures at the IL|W interface. The reason can be discussed taking into account the results in previous papers that created Ag nanowires at the O|W interface.⁴⁰⁻⁴² Scholz et al. suggested that an important factor for the 1-D structure formation is the ratio of mass transfer of Ag⁺ ions in W, f_W , to that of reducing agents in O, f_O , toward the Ag surface at the O|W interface.⁴⁰ The reduction of Ag⁺ ion and the oxidation of the reducing agent simultaneously occur but not necessarily at the same place of the Ag surface because Ag nanowires having high electron conductivity can deliver electrons from one surface site to another. If $f_O \ll f_W$, which is achieved by adjusting the ratio of the initial concentrations of both species, the Ag metal at the O|W interface “grows” to the O phase to increase the area of Ag surface and the volume of diffusion zone on the O side, consequently balancing the two mass transfer rates. They actually confirmed that the Ag nanowires were formed when the concentration of Ag⁺ ion in W is significantly higher than that of the reducing agent in O.⁴⁰ This is likely to be the case with the formation of the Au nanofibers. In the present study, the concentration of TPTA in the IL, 40 mmol kg⁻¹, is comparable to (even higher than) the concentration of AuCl₄⁻ in W, 10 mM. Nevertheless, high viscosity of the IL decelerates the mass transfer on the IL side by the factor of 2200 (η_{IL}/η_W where η is viscosity). This imbalance of the mass transfer is reduced by the growth of Au nanofibers into the IL, enlarging the surface area for the oxidation of TPTA.

We also observed Au nanofibers with in-situ dark-field optical microscopy (see ESI for the images). The images show μm-scale bright spots that seems to be mesoscale assembly of Au nanofibers. Such mesoscale assembly was also observed for Au nanoparticles formed at oil-water interface in previous optical microscopy studies.^{64,65} It seems that Au nanofibers remain around the interface in IL and form mesoscale assembly, providing the large reaction surface for the TPTA oxidation.

Finally, the bundle of the Au nanofibers (Fig.2ab) except around the tips seems to be due to the greater ability of ILs to screen electrostatic repulsion than W. ILs are considered as dense “ionic solutions”, having a short Debye length for electrical double layer on the order of 0.1 nm (estimated in the framework of mean-field theory). We speculate that the Au dendrites formed on the W side of the IL|W interface move across the interface to the IL side due to the imbalance of the mass transfer (see the above discussion), where the electrostatic repulsion between the Au surfaces lessens and the dendrites are bundled to the Au nanofibers. The nanofibers are bundled but not aggregated possibly because IL-ions are forming rigid structure at the surface of the nanofibers, preventing the contact of two surfaces.⁴⁵

In conclusions, we prepared dendritic nanofibers of gold by the reduction of Au ion at the IL|W interface. The formation of this novel nanostructures became possible because of several characteristics of ILs and IL-ions: high viscosity, specific surface structure, and high ionic strength. The dendritic nanofibers of gold possess numerous structural defects, high surface area and

narrow gaps inside the nanofibers, appealing to the applications to catalyst and SERS-based sensors. Future studies include the formation of similar nanostructure of other metals such as Ag, Pt, and Pd, and the fine control of the nanofiber structures by changing IL-ions and reducing agents as well as the applications to catalyst and SERS materials, and such studies are in progress in our laboratory.

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