

Electronic Supplementary Information

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

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1 Experimental

The highly hydrophobic IL used in the present study, trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide ([TOMA⁺][C₄C₄N⁻]), was prepared¹ and purified^{2,3} 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).

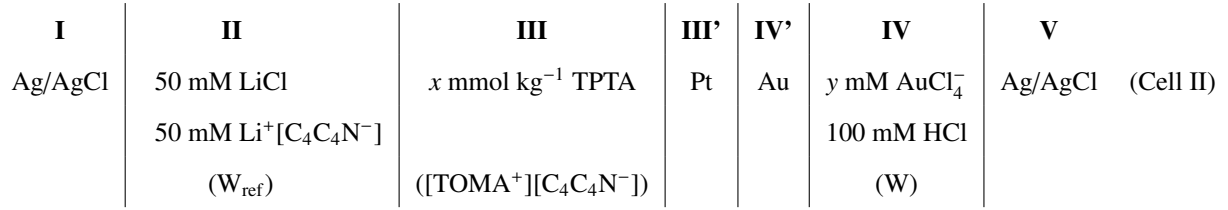
Electrochemical measurements at the IL|W interface were performed using a micropipette to minimize the effect of ohmic drop in IL bulk.^{4,5} A micropipette with a tip inner diameter of 10 μm was filled with W and was immersed in IL to form micro IL|W interface at the tip of the micropipette. The two-electrode electrochemical cell employed is:

I	II	III	IV	V
Ag/AgCl	50 mM LiCl	$x \text{ mmol kg}^{-1}$ TPTA	$y \text{ mM AuCl}_4^-$	Ag/AgCl (Cell I)
	50 mM Li ⁺ [C ₄ C ₄ N ⁻]		100 mM HCl	
	(W _{ref})	([TOMA ⁺][C ₄ C ₄ N ⁻])	(W)	

where M denotes mol dm⁻³. A glass cylinder with the inner diameter of 0.5 mm filled with W_{ref} (phase II) was also immersed in [TOMA⁺][C₄C₄N⁻] as a counter electrode. Ag/AgCl wires were inserted into the micropipette and the glass cylinder. The voltage, E , was applied to the right-hand-side terminal (phase V) with

respect to the left (phase **I**). The current I due to the transfer of cations from W to $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ is taken to be positive.

The above system records current due to the transfer of both of ion and electron across the IL|W interface. In order to analyze only the electron transfer we adopted ECSOW (electron-conductor separating oil|water) system,^{6,7} where liquid-liquid interface is separated by electron conductor to prevent the ion transfer. In the present case for the IL|W interface the electrochemical cell is as follows



In Cell II, we immersed Au wire (phase **IV'**) into W (phase **IV**) filled in a glass bottle and immersed Pt microelectrode with a tip diameter of $10 \mu\text{m}$ (phase **III'**) into $[\text{TOMA}^+][\text{C}_4\text{C}_4\text{N}^-]$ (phase **III**). The Au wire and the Pt microelectrode were electrically connected by a lead wire. Since the area of the Pt-IL interface is several order of magnitudes smaller than the Au|W interface, the recorded current is limited by processes for the electron transfer at Pt|IL interface (mass transfer and redox of $\text{TPTA}^+/\text{TPTA}$). The temperature for the measurements with Cells I and II was controlled at 25.0°C by circulating water in the jacket of the cells from a water bath.

In order to investigate the morphology of the Au nanostructures formed at the IL|W interface, macro IL|W interface was formed in a glass bottle with an inner diameter of 12 mm by filling IL (phase **III**) and W (phase **IV**) in the bottle with $(x,y)=(40,10)$. The sample was left for three days at room temperature. The obtained deposits were collected and suspended in methanol. The suspension was centrifuged and the supernatant was removed. This washing procedure was repeated three time and the deposits were dried in air. The nanostructures on a carbon tape are observed by scanning electron microscope (SEM, ultra-55, Zeiss) equipped with energy dispersive x-ray spectrometer (EDX). The morphology of the Au nanostructures did not change with or without centrifugation.

2 EDX results

The EDX mapping results for the Au dendritic nanofibers on a carbon tape are shown in Fig.S1. The regions where XRF signal of Au was observed are exactly the same as those of the dendritic nanofibers of Au in the SEM images. On the other hand, XRF signal of C is weak at the regions because the nanofibers block the penetration of electron beam to the carbon tape behind the nanofibers. XRF signal of Cl is weak over the whole image area, indicating that there are few Cl element in the nanofibers (and at the surface of the carbon tape).

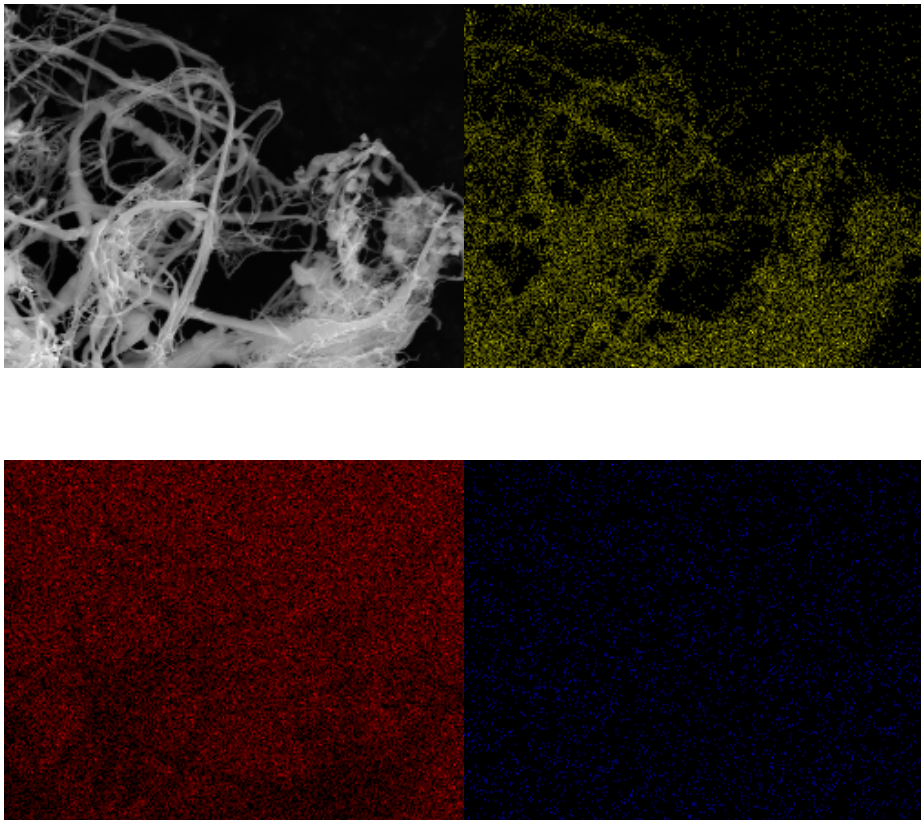


Fig.S1. SEM image (top left) and EDX elemental mapping of Au (top right), C (bottom left), and Cl (bottom right) for Au dendritic nanofibers on the surface of a carbon tape.

3 Optical microscopy results

Fig.S2 shows the microscope images for the IL|W interface at time, t , after the contact of the IL and W phases. One can see bright spots with a size of a few μm and the number of the spots increases with increasing t . The bright spots seems to be mesoscale assembly of Au nanofibers. Background color also changes with time from light green blue ($t = 42$ min) to dark blue ($t = 300$ min). This color results from TPTA⁺ since simple oxidation of TPTA at an electrode also leads to the same color change. Without AuCl₄⁻ in W this background color change does not occur, indicating that the color change is a sign of the spontaneous electron transfer reaction between TPTA and AuCl₄⁻ proceeding over the time scale of hours.

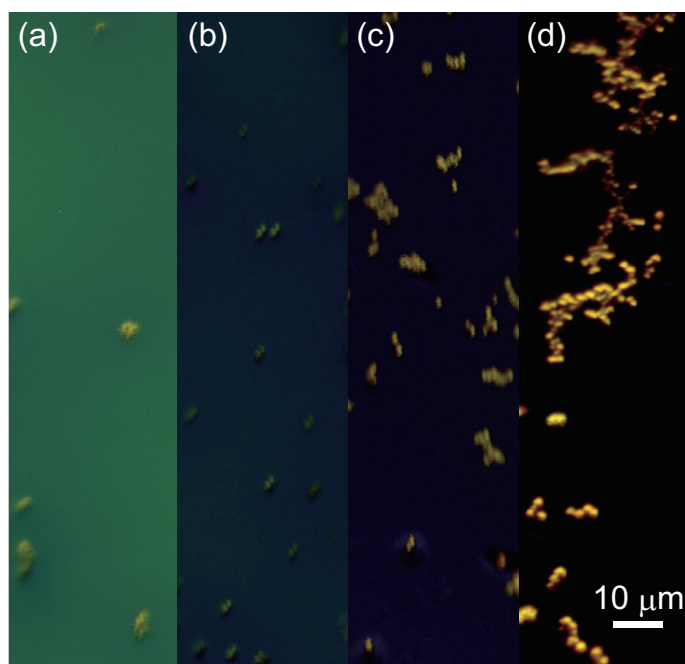


Fig.S2. Microscope images for the interface between IL (phase **III**) and W (phase **IV**) with $(x, y)=(40, 10)$ at time, t , after the contact of the two phases at $t = 0$. (a) $t = 42$, (b) 72, (c) 122, and (d) 300 min.

References

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