

Au nanofibers/CNT 1D/1D composites Formed via Redox Reaction at the Ionic Liquid/Water Interface

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Abstract

Au nanofibers/carbon nanotube (CNT) 1D/1D composites and Janus-type Au/CNT composites have been prepared by utilizing the liquid/liquid interface between water (W) and a hydrophobic ionic liquid (IL) as the redox reaction site. AuCl_4^- in W is reduced at the IL/W interface where CNTs are adsorbed, by a reducing agent in IL, leading to the formation of the Au/CNT composites. The Au/CNT composites are Janus-type in which Au microrouchins and Au nanofibers are deposited on the W side and the IL side of the CNTs on the IL/W interface, respectively. Reversing the order of the CNT adsorption and AuCl_4^- reduction results in the formation of the Au nanofibers/CNT composites, 1D/1D metal/carbon composites.

KEYWORDS: ionic liquid/water interface; anisotropic Au nanostructures; liquid-liquid interface; ITIES; electrodeposition.

Introduction

Au nanostructures show physicochemical properties that are different from the bulk. Au nanostructures dispersed on solid supports have been used as catalysts for selective reduction and oxidation reactions [1][2][3] whose catalytic activity depends on the size and shape of Au nanostructures [4]. Carbon nanotubes (CNTs), which are 1D nanostructure materials, have stability under acid/base conditions and properties that can be tuned by introducing surface functional groups. Catalyst application using Au nanostructures on CNT as a solid support has also been studied [5][6][7].

The oil-water (O-W) two-phase system has been applied to produce metal nanostructures [8][9] and metal/CNT composites [10][11][12][13][14][15], where the reaction can be spatially restricted at the O/W interface by dissolving metal ions in one phase and reducing agents in the other phase. Such reductive metal depositions at the O/W interface proceed spontaneously or with the help of the external control of the interfacial potential difference at the O/W interface, depending on the combination of metal ions and reducing agents. Hydrophobic ionic liquids (ILs) that are immiscible with water [16] can be used instead of oils in the two-phase metal nanostructure synthesis. In addition to being a hydrophobic liquid phase, ILs serve as stabilizers to metal nanostructures [17], by forming ionic multilayers at the interface [18][19][20]. The IL/W interface can be a functional

reaction site, where metal nanostructures [21][22][23] and metal-polymer composites [24] can be produced. Previously we found that Au dendritic nanofibers with a 1D structure are formed via a spontaneous redox reaction at the IL/W interface [25][26][27]. The anisotropic growth of Au is likely to result from the adsorption of IL constituent ions on the Au surface [28] and the difference in viscosity between the two liquids (IL and W) forming the interface [26]. This methodology has been applied to other noble metals [29][30][31][32] and can also be applied to base metals by using the IL/O interface [33].

Extensive studies have been reported on the fabrication of Au nanostructure/CNT composites, however, the Au nanostructures are limited to nanoparticles [7][34][35][36][37][38][39][40][41][42][43], and to the best of our knowledge, no research has been reported on the production of 1D/1D composites of Au nanofibers and CNT in which the 1D structures of two materials are physically and chemically in contact and intertwined. The deposition of Au nanofibers on the CNT surface would lead to the formation of 1D/1D composites, however, such a methodology has not been developed. The success in the IL/W interfacial method to prepare Au nanofibers motivated us to fabricate composites of Au nanofibers and CNT. We recently succeeded in producing 1D/2D composites of Au nanofibers and reduced graphene oxide at the IL/W interface [44], utilizing the physical adsorption of the latter on the interface. In the present study, We fabricated composites of Au and CNT by adsorbing CNT at the IL/W interface by utilizing the fact that CNT can be physically adsorbed at the liquid-liquid interface [45][46]. As a result, 1D/1D composites of Au nanofibers and CNT have been prepared.

Experimental

• Preparation of CNT dispersion

Multi-walled carbon nanotube (MWCNT, diameter 150 nm, length 6 μm) was supplied from Showa Denko (VGCF-H). MWCNT (hereafter will be referred to as CNT) in water was stabilized by carboxymethyl cellulose (CMC) [47]. CNT at a concentration of 0.025 wt% was added to Mill-Q water containing 0.075 wt% CMC (sodium salts, Aldrich), followed by the sonication for 120 minutes [48]. Then, the dispersion was filtered using a glass fiber filter with a particle retention capacity of 0.7 μm to remove CNT aggregates. CNT in the dispersion was observed with a scanning electron microscope (SEM) (Regulus8220, Hitachi). The dispersion was diluted 6-fold and measured using a UV-Vis spectrophotometer (UV-1600PC, Shimadzu) with a 6-fold diluted CMC solution as the reference. In order to confirm the stability of CNT in the dispersion, the UV spectrum was recorded again 2 weeks after the preparation.

• Interfacial preparation of Au/CNT composites (Au reduction followed by CNT adsorption, “IP1”)

For IL, trioctylmethylammonium bis(nonafluorobutanesulfonyl)amide (TOMAC₄C₄N, Fig. S1) was used, which is hydrophobic enough to electrochemically polarize the IL/W interface [25][49]. Tri-p-tolylamine (TPTA, 100 mmol/kg) was dissolved in the IL phase, and an HCl solution (0.1 M) containing AuCl₄⁻ (10 mM) was used as the W phase (pH 0.9). The two-phase system (0.3 mL of IL and 1.2 mL of W) was left for 1 day at room temperature to

prepare Au nanofibers at the interface [25]. Then, the $\text{HCl}/\text{AuCl}_4^-$ aqueous solution, which was the upper phase of the two-phase system, was replaced with a CNT dispersion (0.025 wt%, pH 7.3), and the IL-W two-phase system was left for 2 days while stirring the W phase to accelerate the CNT adsorption onto the interface, otherwise, it is diffusion-limited and slow. The diffusion alone is not efficient to transport CNT, a huge molecule, far from the W bulk to the interface, and the convection by stirring significantly accelerates the mass transport. Even though CMC stabilizes CNTs in the aqueous phase bulk, no hindrance to the adsorption of CNTs to the interface was observed. We call this interfacial preparation of composites “IP1”. After the upper W phase was removed, methanol was added to disperse the composites on the IL surface and to dissolve the IL. Then, the dispersion was centrifuged (CN-2060, Iuchi Seieidou) at 4000 rpm for 15 minutes followed by the removal of the supernatant. This operation removed non-volatile materials (IL and solutes) attached to the composites. This washing operation was performed 5 times with methanol and 5 times with dichloromethane. The washed composites were dried and then observed by SEM, and the composition was analyzed by energy dispersive X-ray analysis (EDX) (Regulus8220, Hitachi).

• **One-phase preparation of Au/CNT composites (“OP”)**

Au nanofibers prepared using the IL/W interfacial method [25] were dispersed in 2 mL of methanol by sonication for 1 min. 0.5 mL of the Au nanofiber dispersion and 2 mL of the CNT dispersion were mixed and stirred vigorously for 30 minutes. We call this one-phase preparation of composites “OP”. The

composites were collected by centrifugation. The structure and composition were analyzed by SEM and EDX.

• Interfacial preparation of Au/CNT composites (CNT adsorption followed by Au reduction, “IP2”)

The procedure was reversed from IP1; after using the CNT dispersion for the W phase, Au was grown on the CNT adsorbed on the IL/W interface by replacing W with an HCl solution containing AuCl_4^- . We call this interfacial preparation of composites “IP2”. The structure and composition of the composites after 1-day reaction were analyzed by SEM and EDX. In order to elucidate the formation mechanism, the composites after 1, 2, and 20-hour reactions were also analyzed. In order to confirm the Au structure on the W side of the CNT adsorbed on the IL/W interface, composites were prepared at the liquid-liquid interface between W and trioctylmethylammonium tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (TOMATFPB, Fig. S1), which is another IL with a melting point (36 °C) higher than room temperature [27][29][50]. At 50 °C, where the IL is a liquid, CNT was adsorbed on the IL/W interface, and then Au was reduced by TPTA and deposited at the interface. After 1-day Au reduction, the two-phase system was cooled down to room temperature. The upper W phase was removed and the composites on the solidified IL were analyzed by SEM and EDX.

The Au nanofiber formation at the IL/W interface is fulfilled by the coupling of electron transfer (ET) that is Au reduction by reducing agent, and ion transfer (IT) that compensates for the charge unbalance caused by ET [25]. IT of AuCl_4^- has been confirmed as a pivotal process to form the Au nanostructures

[27][31][44]. In order to investigate the effect of IT on the composite, we performed another experiment. In this experiment, Li salt of $C_4C_4N^-$, which is a more hydrophobic anion than $AuCl_4^-$ and is more easily transferred to IL, was added into W at 30 mM to prevent the $AuCl_4^-$ transfer from IT to IL [27].

Results and Discussion

• Preparation of CNT dispersion

The SEM image for CNT in the dispersion is shown in Fig. 1a. Each CNT was dissociated, without forming aggregates. The UV spectrum for CNT dispersion is shown in Fig. 1b (red). The absorption peak around 260 nm is assignable to the electronic transition in a dissociated CNT [48], illustrating that CNTs were well dispersed. The UV measurement was performed again 2 weeks later (Fig. 1b, blue). The scattering background decreased, indicating that agglomerates were precipitated. On the other hand, the peak height around 260 nm with respect to the scattering background did not decrease, confirming that the dispersed CNTs are stable for 2 weeks, longer than the time required for the composite formation (3 days in total)

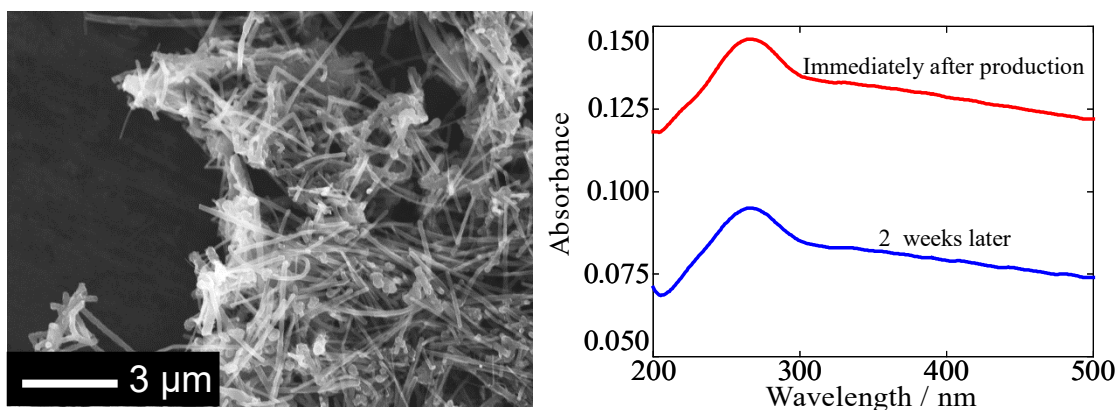
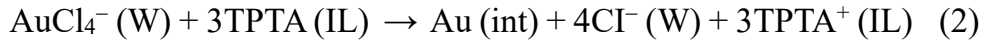
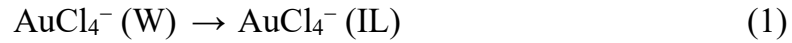


Fig. 1 SEM image of CNTs from the dispersion and UV spectra of CNT dispersion just after the preparation (red) and 2 week later (blue).

• **Interfacial preparation of Au/CNT composites (IP1)**

After reducing AuCl_4^- at the IL/W interface, composites of Au nanofibers and CNTs were produced by adsorbing CNT at the IL/W interface. The SEM/EDX images for Au/CNT composites are shown in Fig. 2. One can see Au nanofibers with thinner diameters from 50 to 100 nm attached to CNT with thicker diameters from 150 to 300 nm. The Au nanofibers are similar to those we previously prepared at the IL/W interface [25]. The Au nanofiber formation at the IL/W interface proceeds via the coupling reaction between IT (Eq. 1) and electron transfer (ET, Eq. 2) [25].



where int is the interface. As mentioned in Introduction, highly anisotropic Au nanostructures are formed at the IL/W interface due to the adsorption of IL-constituting ions on Au [28] and the difference in viscosity between the two liquids forming the interface [26].

In addition to the Au/CNT composites, Au nanofibers (Fig. S2a) and CNTs (Fig. S2b) were also separately observed. This fact suggests that the composites have a heterogeneous Au-on-CNT structure and are also easily split into Au and CNT due to the weak interaction between them.

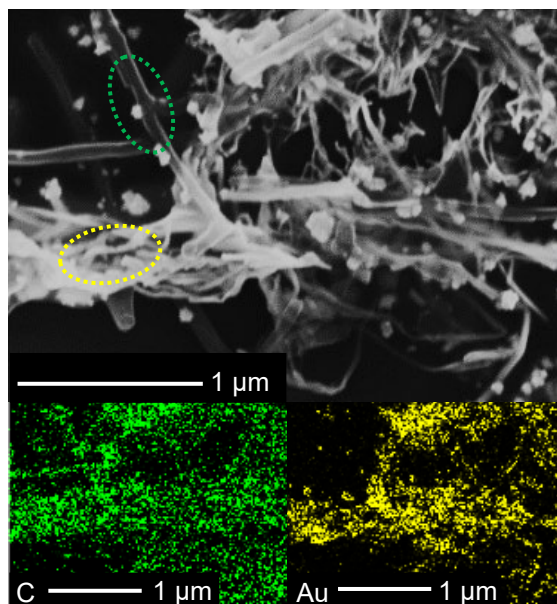


Fig. 2 SEM image and EDX elemental maps of Au nanofiber/CNT composites after 24 h reaction prepared using IP1. The green and yellow circles represent CNT and Au nanofibers, respectively.

• One-phase preparation of Au/CNT composites (OP)

It has been reported that when a Au nanoparticle dispersion is mixed with a CNT dispersion, the composites of Au nanoparticles and CNTs are formed [36]. We adopted the same strategy to make the 1D/1D composite of Au nanofibers and CNTs by mixing a Au nanofiber dispersion, in this case, and a CNT dispersion. The SEM/EDX images for the Au/CNT composites are shown in Fig. 3 and also zoom-out ones in Fig. S3. A structure in which Au nanofibers were attached to and tangled with CNTs was observed. The separation into Au nanofiber and CNT regions was not observed in this case. This fact suggests that stirring in W is enough to make them tangled and form the 1D/1D composites.

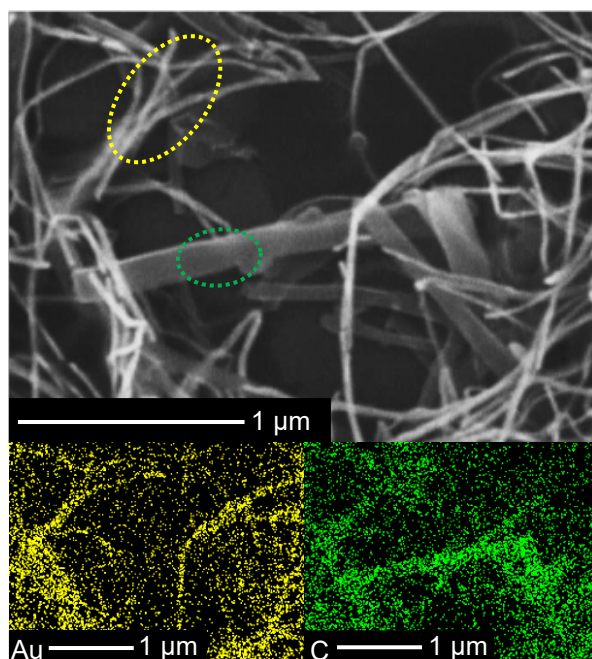


Fig. 3 SEM image and EDX elemental maps of Au nanofiber/CNT composites prepared using OP. The green and yellow circles represent CNT and Au nanofibers, respectively.

• Interfacial preparation of Au/CNT composites (IP2)

In order to fabricate composites with a strong interaction between Au and CNTs, Au was grown on the surface of CNTs adsorbed at the IL/W interface. The SEM image for Au/CNT composites is shown in Fig. 4 and SEM/EDX image for Au/CNT composites is shown in Fig. S4. One can see Au microrouchins, which have radial symmetry and spines [27], and Au nanofibers adhered to CNTs. In our previous study where we synthesized composites of Au and polythiophene at the IL/W interface, we observed a similar structure, in which Au microrouchins and Au nanofibers were attached to polythiophene [27]. A series of analyses revealed that the Janus-type Au/polythiophene composites were realized where Au microrouchins are formed on the W side of polythiophenes on the IL/W interface

and Au nanofibers on the IL side. The similarity between the present CNT and previous polythiophene cases suggests that the present composite of Au and CNT are also Janus-type.

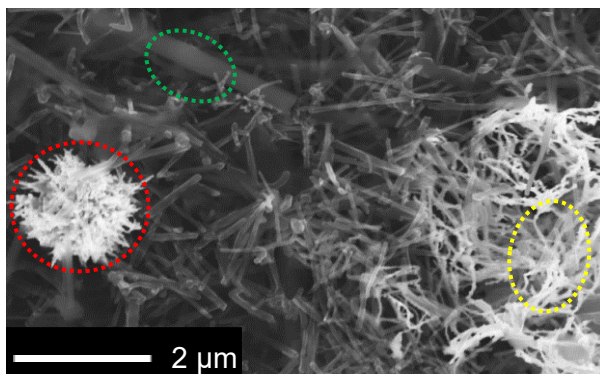


Fig. 4 SEM image of Janus-type composite after 24 h reaction prepared using IP2. The green, red, and yellow circles represent CNT, Au microrouchins, and Au nanofibers, respectively.

Figures 5 and S5 show the SEM images / EDX analysis of composites on a solidified IL, which allows us to investigate the upper W side of the composites. Au microrouchins are observed to be attached to CNT on the solidified IL while Au nanofibers are not confirmed, suggesting that Au nanofibers were attached to the IL side. From these observations, the schematic of the composite is shown in Fig. 8c. The product was found to be Janus-type composites with different Au structures on the IL side (Au nanofibers) and the W side (Au microrouchins).

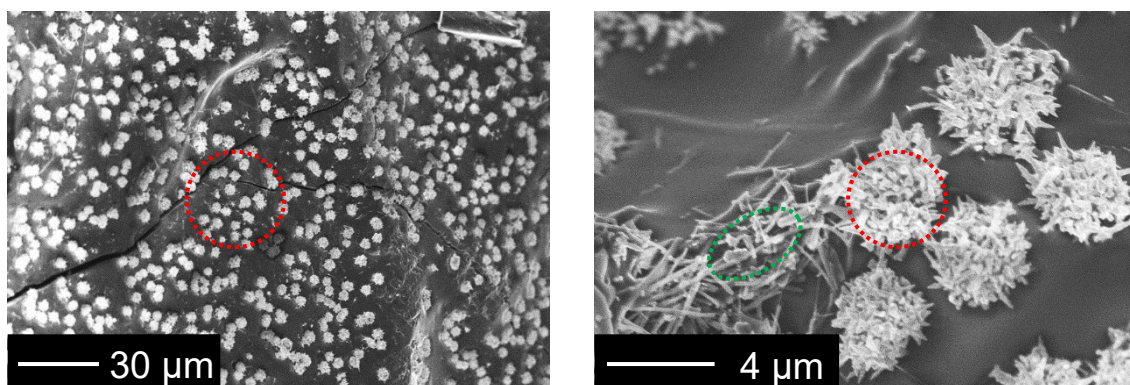


Fig. 5 SEM images on W side of the composites after 24 h reaction prepared using IP2 with TOMATFPB. The green and red circles represent CNT and Au microrouchins, respectively.

In the IL/W interfacial method, metal nanofibers are deposited only when metal precursors (like AuCl_4^-) are transferred from W to IL and then reduced on the IL side [27][29][30][31]. To prevent the IT of AuCl_4^- , $\text{C}_4\text{C}_4\text{N}^-$, which is more hydrophobic than AuCl_4^- and easily transferred to IL, was added into W. Au nanofibers were not deposited as expected, and only Au microrouchins were observed on CNTs (SEM in Fig. 6). This observation reinforces that AuCl_4^- transferred to IL was reduced and deposited as Au nanofiber on the IL side of CNTs.

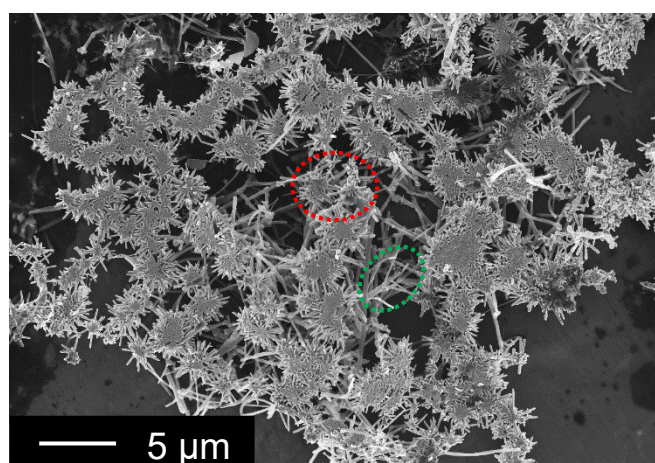


Fig. 6 SEM image of Au microrouchin/CNT composites after 24 h reaction prepared using IP2 with $\text{C}_4\text{C}_4\text{N}^-$ in W. The green and red circles represent CNT and Au microrouchins, respectively.

Figure 7 shows the SEM images to reveal the composite formation process. After 1 hour reaction ($t=1$ h), Au nanoparticles are attached to CNTs (Fig. 7a). At $t=2$ h, the Au nanoparticles were grown to microurchins with dendrites (Fig. 7b). Au nanofibers first appeared at $t=20$ h, resulting in Janus-type composites (Fig. 7c). From these results, we propose the reaction mechanism as follows (Fig. 8). In the first stage (Fig. 8a), CNTs, which are electron conductive [11][51], at the IL/W interface bypass electrons from TPTA (reducing agent) on the IL side to AuCl_4^- on the W side, making Au nanoparticles deposited on the W side of the CNTs. In addition, the IT of AuCl_4^- from W to IL for the charge compensation was coupled with the redox reaction (ET). In the second stage (Fig. 8b), the supply of AuCl_4^- becomes diffusion-limited on the W side of the interface, Au nanoparticles grow dendrites, resulting in Au microurchins. In the third stage (Fig. 8c), AuCl_4^- is almost depleted on the W side but exists on the IL side, reduced to Au nanofibers on the IL side. Two possible reasons why Au nanofibers are obtained on the IL side of the interface are the surface-selective adsorption of IL ions on the Au surface promoting anisotropic growth of Au, and the high viscosity of IL facilitating dendrite growth in a diffusion limiting condition. The reduction potential of AuCl_4^- depends on the solvent [52]. However, in the present study, there will be no potential change between the Au deposition in the W phase and in the IL phase, because even in the latter case, the Cl^- produced via the Au reduction is transferred to the W phase, and the net reaction can still be written as Eq (2).

The reason why Au microurchins are not obtained in IP1 can be explained as follows. First, when Au nanoparticles are deposited at the interface via ET (Eq. 2), IT of AuCl_4^- from W to IL (Eq. 1) for the charge compensation

occurs. By these ET and IT reactions, AuCl_4^- is depleted on the W side, while it is accumulated on the IL side due to the fast supply by IT and sluggish diffusion into the bulk of viscous IL. Therefore, Au grows preferentially on the IL side, and no Au microurchins are formed in IP1. In contrast, in IP2, the Au precipitated on the W side of the CNT is not in contact with the IL, so it can only grow in the W direction, and thus Au microurchins are precipitated. As a result, Janus-type Au/CNT composites have been prepared at the IL/W interface. By adding $\text{C}_4\text{C}_4\text{N}^-$ into the W phase, Au microurchin/CNT composites have been prepared. By shortening the reaction time, 0D/1D composites of Au nanoparticles and CNTs have been prepared.

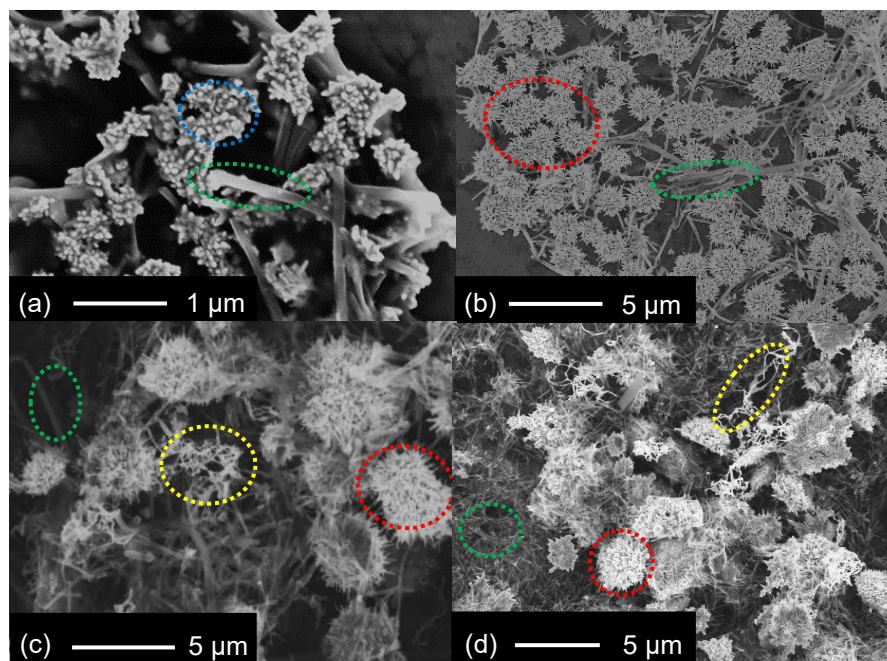


Fig. 7 SEM image of Au/CNT composites after (a) 1, (b) 2, (c) 20 h, and (d) 24 h reaction prepared using IP2. The green, red, yellow, and blue circles represent CNT, Au microurchins, Au nanofibers, and Au nanoparticles, respectively.

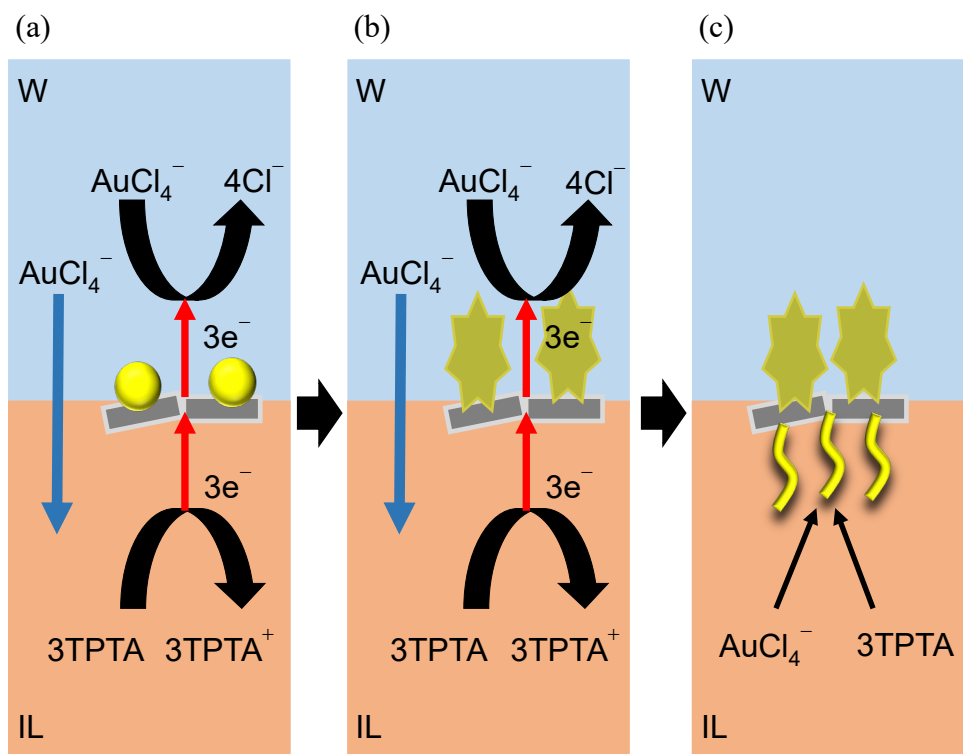


Fig. 8 Composite formation mechanism in IP2.

Conclusions

We have prepared Au/CNT composites of various types by utilizing the IL/W interface as the redox reaction site. AuCl_4^- reduction followed by CNT adsorption at the IL/W interface produced 1D/1D composites of Au nanofibers and CNTs. By reversing the order of the reduction and adsorption, Janus-type composites were produced, in which dendrite-grown Au microrouchins and Au nanofibers were attached to CNTs. By changing the reaction time, composites of Au nanoparticles and CNTs, and those of Au microrouchins and CNTs were also able to be produced.

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Supporting Information

The Supporting Information is available free of charge at ***.

Structure of IL ions; SEM images of composites prepared using IP1; SEM images and EDX elemental maps of composites prepared using OP, IP2, and IP2 with TOMATFPB.

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TOC graphic

