

Formation of Au nanofiber/fullerene nanowhisker 1D/1D composites via reductive deposition at the interface between an ionic liquid and water

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1 Au nanofiber (NF)/fullerene nanowhisker (FNW)
2 1D/1D composites have been prepared at the liquid/liquid
3 interface between an ionic liquid (IL) and water (W). Au NFs
4 have been reductively deposited on the FNWs adsorbed at the
5 IL/W interface via the electron transfer across the interface
6 between AuCl_4^- in W and a reducing agent in IL, coupled
7 with the ion transfer of AuCl_4^- from W to IL.

8 **Keywords:** ionic liquid/water interface | anisotropic Au
9 nanostructures | liquid-liquid interface |
10 ITIES | electrodeposition

11 Metal nanofibers (NFs), which have unique one-
12 dimensional (1D) nanostructures, exhibit physicochemical
13 properties that are different from those of the bulk metal and
14 even metal nanoparticles. They are expected to be applied in
15 a variety of fields as electronic,¹ optical,² electrocatalytic,³
16 and catalytic materials.^{4,5} The 1D/1D composites of metal
17 NFs combined with non-metallic 1D nanostructures have also
18 been reported, such as those with cellulose NFs,⁶⁻⁸ aramid
19 NFs,⁹ and carbon nanotubes (CNTs),¹⁰ which have both
20 conductivity and flexibility, and are expected to be applied to
21 electromagnetic shielding, transparent conductive films and
22 conductive inks.

23 The liquid/liquid interface between oil and water has
24 been utilized as a redox reaction site to fabricate metal
25 nanostructures.^{11,12} By replacing oil with hydrophobic ionic
26 liquid (IL) in the oil-water two-phase system, we found that
27 metal NFs can be fabricated at the IL/W interface.¹³⁻¹⁵ The IL
28 is not just a substitute for oil, rather plays a role as a stabilizer
29 to prevent the aggregation of nanostructures¹⁶ by virtue of the
30 ionic layers spontaneously formed at the growing metal
31 nanostructures.¹⁷⁻¹⁹ The anisotropic growth of metal²⁰ is
32 likely to be induced by such surface ionic structures as well
33 as the viscosity difference between IL and W.²¹

34 This methodology to prepare metal NFs at the IL/W
35 interface can be utilized to fabricate their composites with
36 other nanomaterials. For example, by adopting
37 thiophenetrimer as the reducing agent of AuCl_4^- for their
38 redox reaction at the IL/W interface, Au NF/polythiophene
39 (PT) plate composites were fabricated.²² Au NF/reduced
40 graphene oxide (rGO)²³ and Au NF/CNT¹⁰ composites were
41 prepared by depositing Au NFs on the nanocarbons adsorbed
42 at the IL/W interface. In the present study, we report the
43 fabrication of Au NF/fullerene nanowhisker (FNW)
44 composites, another class of 1D/1D metal/nanocarbon
45 composites, using the IL/W interface method. FNWs are one-
46 dimensional crystals of fullerene molecules bound together
47 by van der Waals forces. One of the characteristics of FNWs
48 is their softness;²⁴ they can be easily processed into a variety
49 of shapes by bundling. Also, FNWs exhibit superconductivity

50 when doped with potassium.²⁵ The FNW composites with Au
51 nanoparticles²⁶⁻²⁸ have been reported for their catalysis
52 applications. A new methodology to form Au/FNW
53 composites of other types, like Au NF/FNW 1D/1D
54 composites, would be valuable to pursue this direction of
55 application further.

56 FNWs with a diameter of about 500 nm were prepared
57 following the method previously reported.²⁹ 4 mL of
58 isopropyl alcohol was added on top of 0.5 mL of a saturated
59 toluene solution of fullerene (nanom purple STL, Frontier
60 Carbon) in a bottle (inner diameter 15 mm) and the liquid-
61 liquid two-phase system was sonicated for 10 seconds. The
62 two-phase system was kept still at 5°C for 24 h during which
63 the two liquids gradually mixed with each other, finally
64 forming one liquid phase with deposited FNWs at the bottom.
65 After removing the supernatant liquid, the FNWs were dried
66 in the bottle in a vacuum box (Sanplatec). The prepared
67 FNWs were observed by scanning electron microscopy
68 (SEM) (Regulus 8220, Hitachi). A SEM image of FNWs is
69 shown in Figure 1. FNWs with a diameter of about 500 nm
70 and a length of about 10 μm were obtained.

71 A hydrophobic IL, triethylmethylammonium
72 bis(nonafluorobutanesulfonyl)amide (TOMAC₄C₄N), was
73 prepared^{30,31} and used as the IL phase. In the IL (0.3 mL)
74 phase, tri-p-tolylamine (TPTA, 100 mmol/kg), a reducing
75 agent, was dissolved. As the W phase, a dispersion of FNWs
76 was prepared by adding 1.6 mL of Mill-Q water to the
77 prepared FNWs in the bottle followed by sonication for 30 s,
78 and it was put on the IL phase. The IL-W two-phase system
79 was kept still for 1 day to adsorb FNWs at the IL/W interface.
80 Then, the dispersion, which was the upper W phase, was
81 replaced with 1.2 mL of HCl solution (0.1 M) containing
82 AuCl_4^- (10 mM), and the IL-W two-phase system was kept
83 still for 1 day to reductively deposit Au on the FNWs at the
84 IL/W interface. The composites on the IL/W interface were
85 dispersed in methanol and transferred to a centrifuge tube.
86 The transferred composites were separated from the liquid by
87 centrifugation at 4000 rpm for 15 min in a centrifuge (CN-
88 1050, AS-ONE) and the supernatant was removed. This
89 washing process was carried out four times with methanol,
90 five times with dichloromethane, and once with methanol.
91 The composites were dried in a vacuum box for 1 day. The
92 structures and compositions of the composites were analyzed
93 by SEM and energy dispersive X-ray analysis (EDX)
94 (Regulus 8220, Hitachi).

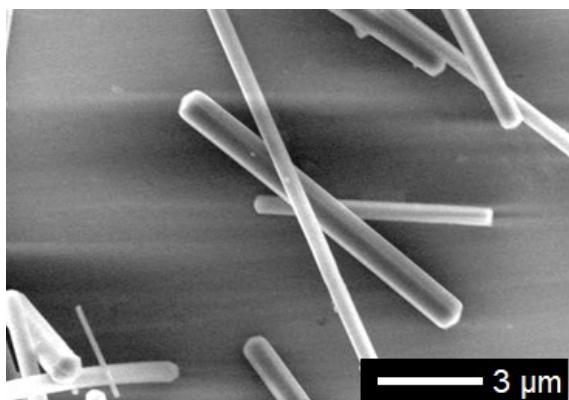


Figure 1. SEM image of FNWs.

The SEM and EDX images of Au NF/FNW composites are shown in Figure 2 and Figure S1, respectively. One can see that Au NFs (50-100 nm diameter³¹) are attached to FNWs (500 nm diameter, see also Figure S1). A control experiment was performed, where fullerene (C60) molecules instead of FNWs were adsorbed on the IL|W interface, and Au was reductively deposited at the IL|W interface (see Supporting Information for details). For this case, composites of Au NFs and C60 aggregates were obtained. These Au NF composites with FNWs and C60 are different from those with PT²¹ and CNT,¹⁰ where Janus-type composites were deposited at the IL|W interface, with different Au structures on the W and IL sides. This structural difference can be explained by the reaction mechanism, which will be described below.

To confirm the formation mechanism of Au NF/FNW composites, another control experiment was performed. The deposition of Au NFs occurs only when the ion transfer (IT) of AuCl_4^- from W to IL occurs and then the transferred AuCl_4^- is reduced on the IL side of the interface.²² To prevent the IT of AuCl_4^- and the subsequent Au NF formation on the IL side of the interface,²² $\text{C}_4\text{C}_4\text{N}^-$ was added in W (30 mM $\text{LiC}_4\text{C}_4\text{N}$), which is more hydrophobic than AuCl_4^- and more

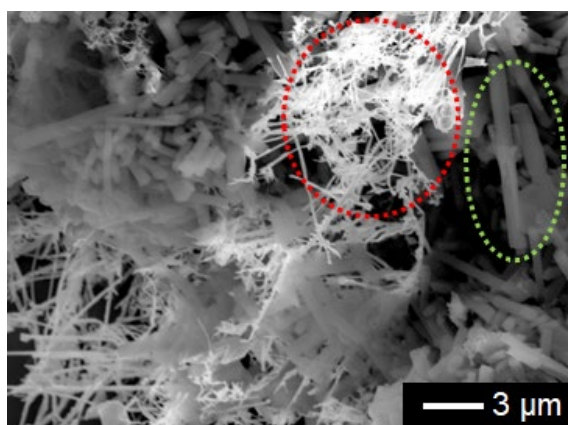


Figure 2. SEM image of Au NF/FNW composites after 24 h reaction. The green and red circles represent FNW and Au NFs, respectively.

thermodynamically favored to transfer to IL. As expected in the SEM image (Figure S2), Au NFs disappeared and Au microrouchins instead are discernible on the FNWs. The formation of Au microrouchins indicates the dendritic growth of Au in a diffusion-limited manner on the W side of the IL|W interface in this $\text{C}_4\text{C}_4\text{N}^-$ -added case.²² In this case, the ET between AuCl_4^- and TPTA starts at the three-phase interface of W, IL, and FNW (see the discussion below and Figure 4a), and the Au nuclei grow toward the W side of the interface because no AuCl_4^- ions are transferred to IL, hampered by the IT of $\text{C}_4\text{C}_4\text{N}^-$. These results indicate that AuCl_4^- ions were transferred to IL and then reduced, forming Au NFs on the IL side of FNWs adsorbed at the IL|W interface.

Figure 3 shows the time evolution of the structure of the Au NF/FNW composites. 1 h after the start of the reaction, short 1D Au were already attached to the FNWs (Figure 3a). In 5 h, the FNWs were covered with Au NFs (Figure 3b). In other words, the growth of Au NFs started immediately after the start of the reaction. This result is in contrast to the case when Au was deposited on the CNTs adsorbed on the IL|W interface.¹⁰ In the CNT case,¹⁰ Au microrouchins were first formed on the W side of the CNTs and then Au NFs appeared 20 h after the start of the reaction.¹⁰

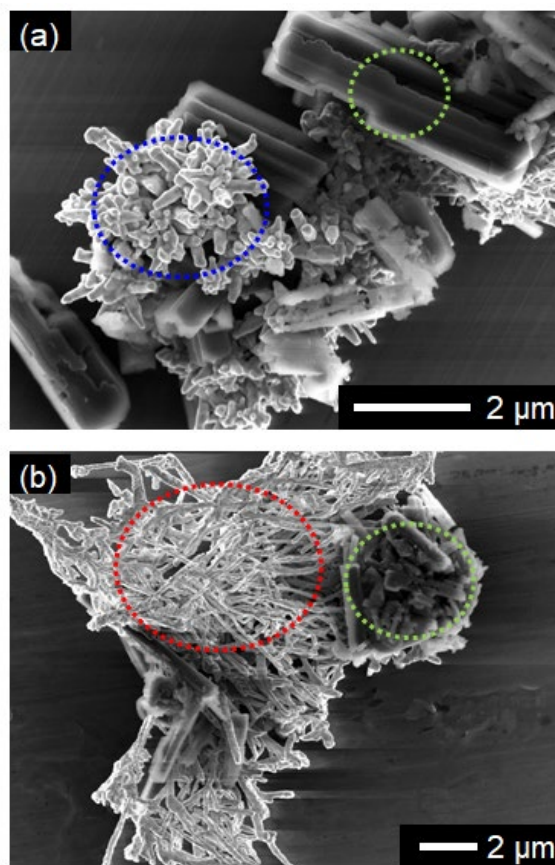


Figure 3. SEM images of Au/FNW composites after (a) 1 and (b) 5 h reaction. The green, blue, and red circles represent FNW, 1D Au, and Au NFs, respectively.

In order to further confirm the orientation of Au NFs, the IL was solidified after the reaction, and the W side of the composites on the surface of the solidified IL was observed by SEM and EDX. This was realized by switching the IL to trioctylmethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TOMATFPB),²² whose melting point (36 °C) is higher than room temperature. The composites were fabricated at 50 °C. It should be noted that Au NFs are formed at the IL|W interface regardless of the difference in IL kind and reaction temperature (Figure S3). Then the IL-W two-phase system was cooled down to room temperature. The upper W phase was removed and the composites on the solidified IL was analyzed. Au particulates attached to FNWs, rather than Au NFs, were observed (Figure S4), suggesting that Au is reductively deposited at the three-phase interface between W, IL, and FNW, and grows toward the IL side of the IL|W interface.

As described above, the structure of the Au NF/FNW composites was different from the CNT counterpart: Janus-type composites with different Au structures on the IL side (Au NFs) and the W side (Au microrouchins) of the CNTs adsorbed at the IL|W interface.¹⁰ This difference can be explained by the conductivity of these nanocarbons; the conductivity of FNWs is significantly low, 10^{-2} S cm⁻¹,³² compared with that of CNTs, 10^4 S cm⁻¹. It is likely that the CNTs at the IL|W interface can bypass electrons from TPTA on the IL side to AuCl₄⁻ on the W side, allowing the Au metal formation on the W side, whereas the FNWs cannot, leading to no Au deposit on the W side of the FNWs, and no Au microrouchins on the Au NF/FNW composites.

The formation mechanism is proposed as follows (Figure 4). First, Au metal is deposited at the three-phase interface of W, IL, and FNW via the electron transfer between TPTA and AuCl₄⁻ and IT of AuCl₄⁻ from W to IL for charge compensation (Figure 4a). Then, the transferred AuCl₄⁻ is reduced on the IL side, and the anisotropic Au growth is induced with the help of both the ordered interfacial ionic structure and the high viscosity in the IL,²¹ leading to the formation of Au NFs (Figure 4b). The IT of liberated Cl⁻ from IL to W also occurs, which is counterbalanced by further IT of AuCl₄⁻. As a result, the composites of Au NFs and FNWs were successfully formed at the IL|W interface.

In summary, the reductive deposition of Au on FNWs after adsorption of FNWs onto the IL|W interface resulted in the spontaneous formation of Au NF/FNW composites at the interface. The formation mechanism of the Au NF/FNW composites and their structure were different from those in the case of CNT,¹⁰ another 1D nanocarbon, which is likely due to their conductivity difference.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.*****.

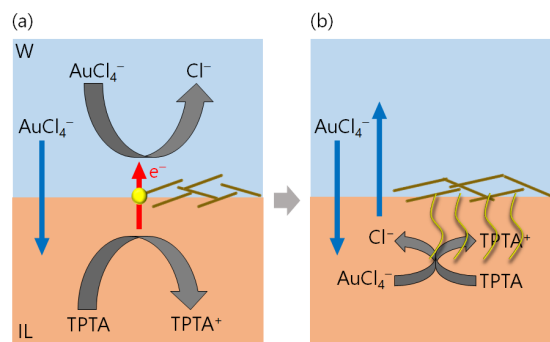


Figure 4. Formation mechanism of Au NF/FNW composites. The blue and red arrows represent the IT and ET across the interface, respectively. The gray arrows are from the reactant to the product of the redox reaction.

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