

Interface-templated synthesis of single-crystalline silver chain-like nanobelts at the liquid-liquid interface between water and redox-active ionic liquid

Yu Zhang,^[a] Naoya Nishi^[a] and Tetsuo Sakka^[a]*

[a] Y. Zhang, N. Nishi, T. Sakka

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering,
Kyoto University.

Kyoto 615-8510, Japan.

E-mail: nishi.naoya.7e@kyoto-u.ac.jp

Abstract

Silver chain-like nanobelts (NBs) have been prepared by a redox-active ionic liquid (RAIL)|water (W) interfacial method with utilizing the soft interface as a template. A highly hydrophobic RAIL (ferrocenylmethyl)dodecyldimethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ([FcMDDA⁺][TFPB⁻]) works as both the reducing agent and the liquid substrate in the RAIL|W interfacial system. The morphology of Ag chain-like NBs, which possesses flat surfaces, sharp corners on the edges, and large aspect ratio, combines the features of one-dimensional (1D) and 2D nanostructures. The formation of Ag chain-like NBs is realized by the linkage of small nanounits through an oriented growth along the RAIL|W interface. The size and shape of the Ag deposited at the RAIL|W interface can be controlled by regulating the concentration of Ag precursor in W, where the higher (lower) concentration of AgNO₃ induces the formation of Ag NBs with smaller (larger) size. The prepared Ag chain-like NBs show good surface enhanced-Raman scattering activity which can be used as the substrate for plasmonic applications.

Key words: Ionic liquid|water interface; ion transfer; electron transfer; electrodeposition; Ag nanobelts.

Introduction

Metal nanostructures have attracted extensive attention in the last decades, due to the fascinating properties which are strikingly in contrast to bulk metals [1-5]. Among all metallic nanomaterials, silver (Ag) is one of the most intriguing ones and is well famed for the highest electrical and thermal conductivities [6-8]. Especially in the field of optical sensing using surface-enhanced Raman scattering (SERS), silver nanostructures are the most widely used material due to the unique plasmonic properties and the relatively low cost [9-12]. One-dimensional (1D) nanostructures are a kind of nanomaterials with at least two dimensions are limited in nanoscale, and whose aspect ratio usually greater than 10. The category of 1D nanostructures includes nanowires [13-16], nanotubes [17], and nanobelts (NBs) [18-21], which have been successfully prepared and applied in the field of catalysis [22], optics [23], electronics [24], and biosensing [25]. Compared with other 1D nanostructures, NBs possess a combination of 1D and 2D morphologies, having flat surfaces, edges, and long aspect ratio simultaneously. Due to these features, NBs possess both advantages of 1D and 2D nanostructures, exhibiting excellent catalytic activity [26], electrical conductivity [27], and inherent thermodynamic stability [28]. Recently, a kind of morphology of chain-like NBs was prepared and drawn more and more interest of researchers. The formation of such kind of morphology is commonly realized by the connection of small nanoplates to form NBs through a lateral growth [29-35]. Therefore, chain-like NBs not only contain the features of NBs but also preserve the sharp corner on the edges which are derived from nanoplates. The introduction of sharp corners to NBs could be meaningful to improve their application performance. Plenty of works have reported that the Ag nanostructures containing sharp corners display significantly enhanced activity or sensitivity in the fields of catalysis or optics, compared with truncated Ag nanostructures [36-39]. By far, the preparation of Ag chain-like nanostructures mostly proceeds in a one-phase solution system,

with the use of surfactants or capping agents to induce the formation of nanoplates, as well as the oriented growth of nanoplates towards NBs [29-33, 35]. Du *et al.* fabricated Ag chain-like nanosheets by using ammonia adsorbed on the {111} facet of Ag, inducing a faster growth rate of other facets to form nanoplates followed by the oriented connection [30]. Kim *et al.* prepared Ag zigzag-shaped nanoplates with the use of cyanuric acid as the capping agent that binds to {111} facet of Ag nanoplates, restricting the vertical growth whereas facilitating the lateral growth of Ag nanoplates to connect with each other [35]. To date, most of the reported Ag chain-like nanostructures are more like nanoplates than NBs due to the large width and small aspect ratio. There still lacks a surfactant-free method to prepare Ag chain-like NBs with a large aspect ratio.

The oil (O)|water (W) interfacial method has been extensively adopted for the preparation of metal nanostructures in decades [40-45]. By separately dissolving the reducing agent and metal precursor in different liquid phases, the O|W interface becomes a selected region where the reduction reaction takes place. Dryfe *et al.* and Hasse *et al.* have applied the O|W interface as the formation site to prepare Ag nanofibers [15, 16, 46]. Recent studies have adopted a new strategy where O is replaced with hydrophobic ionic liquid (IL) in the interfacial method [47, 21, 48-50]. As liquid salts that are entirely composed of ions, ILs possess particular properties that organic solvents do not exhibit. The use of ILs endows the hydrophobic phase with extraordinary functions rather than just as a solvent in the IL|W interfacial system. For instance, the properties of ILs are controllable. The properties of ILs can be adjusted by the elaborate designs of the chemical structures of the cations or anions. Such controllable properties of ILs facilitate the regulation of the interfacial reaction or the growth of metal at the IL|W interface. Yao *et al.* have realized a tunable IL|W interfacial synthesis of Ag films with various morphologies by tailoring the chemical structures of ILs [21, 48, 50]. In our

previous studies, highly hydrophobic ILs were adopted to prepare one-dimensional (1D) metal nanostructures in the IL|W system [47, 51-54]. In one study, the hydrophobicity of the IL was modulated to make interfacial reactions spontaneously taking place [52]. The high viscosity of ILs was confirmed to be one of the factors that induce an anisotropic growth of 1D nanostructures [47, 51-54]. Moreover, it was proved that the aggregation of metal nanostructures formed at the IL|W interface was prevented, which is probably associated with IL ions forming rigid-multilayering structures at the interface [54-59]. Other than the above functions, when an IL contains a redox-active group in the constituting ion, the redox-active IL (RAIL) plays an extra role of the reducing agent for metal precursor. We have confirmed that the interface between W and RAIL can also be applied to prepare metal nanostructures by directly using the hydrophobic phase, i.e. RAIL, as a reducing agent [53, 54].

In the present study, Ag chain-like NBs are spontaneously formed at the interface between water and a highly hydrophobic RAIL (ferrocenylmethyl)dodecyldimethylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ([FcMDDA⁺][TFPB⁻]) [60, 61], which was adopted as the reducing agent and liquid substrate in the system. The formed Ag chain-like NBs possess the features of 1D and 2D nanostructure simultaneously, having sharp corners on the edges, flat surfaces, and a large aspect ratio in one morphology. Time-dependent experiments revealed the formation mechanism, where Ag chain-like NBs are evolved from an oriented growth of small nanounits along the RAIL|W interface. The reduction sites of Ag⁺ are spatially confined at the RAIL|W interface due to the separation of Ag precursor in W and reducing agent in RAIL. Therefore, the RAIL|W interface naturally works as a planar template to induce the formation of flat surfaces of Ag chain-like NBs. The width of Ag chain-like NBs can be easily controlled by the adjustment of the Ag⁺ concentration in W, where the higher (lower)

concentration of Ag^+ induces the formation of Ag chain-like NBs with smaller (larger) width. The present study displays a new mechanism for the formation of 1D nanostructures in the IL|W interfacial system which is significantly distinguished from our previous reports [47, 51-54]. A series of our studies demonstrate that the IL|W interfacial method is a general strategy to effectively induce the formation of 1D nanostructures for a broad range of metal precursors.

Experimental

Synthesis of the RAIL $[\text{FcMDDA}^+][\text{TFPB}^-]$

$[\text{FcMDDA}^+][\text{TFPB}^-]$ was synthesized as previously described [54].

Synthesis of Ag NBs

For a typical synthesis, 2 mL of AgNO_3 (10 mM) solution was gently pipetted onto 0.2 g of RAIL $[\text{FcMDDA}^+][\text{TFPB}^-]$ in a 3 mL glass bottle so that the RAIL|W interface was formed. The interfacial system was kept in a thermostatic bath at 70 °C for 48 h. After the reaction, a grey deposit layer was found at the RAIL|W interface, which was collected through removing the W first, followed by the addition of a mixed solvent (50:50 vol %) of methanol and dichloromethane (DCM) to dissolve the RAIL. The deposit was obtained after repeated washing-centrifugation procedure for 10 times.

Characterization of materials

The prepared Ag chain-like NBs were observed by scanning electron microscope (SEM, SU8220, HITACHI) and a transmission electron microscope (TEM, JEM-2100F, JEOL), respectively. X-ray diffraction (XRD) measurements were performed by a powder X-ray diffractometer (RINT-2500, RIGAKU) equipped with a $\text{Cu K}\alpha$ source (40 kV, 200 mA, $\lambda = 0.154$ nm). Raman scattering spectra were collected using a Raman spectrometer

(LabRAM HR -800, HORIBA Jobin Yvon) equipped with a microscope, 633-nm HeNe laser, and a charge coupled device (CCD) array detector.

Preparation for SERS measurements

4-Aminobenzenethiol (4-ABT) was adopted as the probing molecules for SERS measurements, and the samples were prepared as follows [62]:

- (1) Aqueous dispersion solution of Ag chain-like NBs (5 mg/mL, 10 μ L) was dropped on a glass slide to form a circular film with a diameter of 4 mm, and then dried at room temperature for 2 h.
- (2) 5 μ L of 10^{-7} mol/L aqueous solution of 4-ABT was drop-coated onto the formed Ag film, and then the substrate was dried at room temperature. After the solvent was evaporated (2 hours later), a circular deposit of 4-ABT was formed on Ag film with a diameter of 3 mm and an area of 7.1 mm². The average occupied area per 4-ABT molecule was 2.3×10^{-11} mm². This value is significantly larger than the surface area per 4-ABT for a fully covered monolayer (2.0×10^{-13} mm² [63-65]), and therefore, means the 4-ABT molecules are sparse on the Ag surface in the present study.
- (3) A sample for the normal Raman measurement was prepared by directly dropping a 4-ABT (5 μ L, 10^{-3} mol/L) aqueous solution onto a bare glass slide to form a circular deposit with a diameter of 3 mm.

Results and discussion

The morphology of the deposit at the RAIL|W interface was investigated by SEM, and the results are shown in Fig. 1a. Highly flexible 1D nanostructures with flat surfaces were observed in Fig. 1a, with a thickness around 40 nm and a width around 100 nm (marked with red arrows), showing the morphology features of NBs. TEM image of Ag NBs is shown in Fig. 1b. In contrast to typical NBs with smooth edges, the nanostructures in the present study possess a lot of sharp corners on the edges which marked with red circles

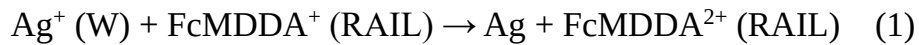
in Fig. 1b, suggesting a chain-like NB morphology. It was reported that triangular and hexagonal nanoplates show the highest specific activity at the corners towards some catalytic reactions, compared with the edges or flat surfaces [66]. Such chain-like NBs in the present study possess sharp corners, flat surfaces, and long aspect ratio simultaneously, which combines the advantages of 1D and 2D morphology together and may show excellent performance in the field of catalysis or optics. A selective area electron diffraction (SEAD) pattern (Fig. 1c) corresponding to the white marked region in Fig. 1b displays a distinct hexagonal symmetry and single-crystalline feature, which confirms the single-crystalline structure of Ag chain-like NBs. XRD analysis was performed to further identify the phase of the Ag chain-like NBs, and the result is shown in Fig. 1d. The diffraction peaks corresponding to the (111), (200), (220), and (311) planes confirm the face-centered cubic (fcc) structure of silver (JCPDS-04-0783).

In order to clarify the formation mechanism for the Ag chain-like NBs, the synthesis system was terminated at the reaction time (t) of 4, 8, 12, 24, 48 h and one week, respectively. The results are shown in Fig. 2. At $t = 4$ h, which is the early stage of the reaction (Fig. 2a), Ag nanounits with a size of around 30 nm are formed and randomly aggregated together without showing 1D feature. Apparently, they were growing three-dimensionally during this period. When the reaction time was prolonged to 8 h (Fig. 2b), aggregated nanoparticles and some 1D nanostructures connected by nanoparticles are observed at the same time with a bigger width of 50 nm. From $t = 8$ to 48 h (Fig. 2b to Fig. 2e), Ag nanounits gradually transform to nanobelts through the lateral connection of the small nanounits. It is noted that the NBs shown in Fig. 2e are horizontally distorted rather than vertically interlaced, as if they are loaded on a planar surface. This implies that the growth of the Ag NBs is realized using a planar surface as the substrate. It could only be exactly the RAIL|W interface in the system where Ag NBs are formed. Based on the morphology evolution from

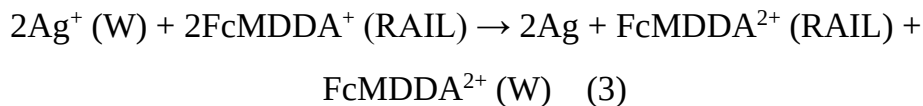
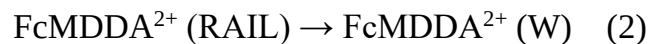
Fig. 2a towards 2e, we can infer that these Ag chain-like NBs are formed by the lateral growth of small nanounits along the RAIL|W interface. This idea was proved by comparing the Ag nanostructures for $t = 8$ h (Fig. 2b) and 48 h (Fig. 1a), showing their thickness remained 40 nm. That is, in the later stage of the reaction, the lateral growth along the RAIL|W interface is dominant and thus induces the linkage of Ag small nanounits to form nanobelts. The result of the reaction time prolonged to one week reinforces the above speculation (Fig. 2f), showing large plate-like structures formed by the overgrowth of Ag NBs, where the edge of each NB can still be distinguished. The morphology transformation with reaction time reveals a lateral growth mechanism along the RAIL|W interface, and the shape of Ag gradually transforms from nanoparticle to NBs, finally evolves to nanoplate by overgrowth.

In our previous studies, we have successfully prepared 1D nanostructures of Au [47, 51], Pt [52], Pd [53], and Pd-Au bimetal [54] by utilizing the IL|W interfacial systems. In those cases, since the metal precursor (i.e. AuCl_4^- , PtCl_4^{2-} or PdCl_4^{2-}) in W is separated from the reducing agent in IL, an interfacial electron transfer (ET) reaction between them will break the charge balance for each liquid phase. Therefore, another charge transfer is required to balance the excess charges brought by ET. Common to the above cases [47, 51-54], the ion transfer (IT) of negatively charged metal precursors from W to IL is coupled with ET and enables the interfacial reactions to occur spontaneously [47-51-54]. However, for the present case, because Ag^+ is a positively charged cation, the IT of Ag^+ from W to IL aggravates the charge unbalance of liquid phases and cannot play a role for neutralizing the excess charges brought by ET. The successful reduction of Ag^+ in the present synthesis indicates another IT has occurred and has been coupled with ET between Ag^+ and FcMDDA^+ . UV-vis measurements were carried out for the W of the synthesis system after 48 h reaction and the results are shown in Fig. S1. A peak around 627 nm was found after 48 h reaction, which is attributable to the

oxidized cation FcMDDA^{2+} [53, 54]. FcMDDA^{2+} is generated by the ET between the Ag precursor and the redox-active cation FcMDDA^+ , as described in eqn 1:



The existence of FcMDDA^{2+} in W after the reaction suggests that the IT of FcMDDA^{2+} from RAIL to W occurred (eqn 2) [53, 54] and played a role for coupling with ET during the reaction period, as shown in the total interfacial reaction (eqn 3):



In our previous studies where metal precursors are negatively charged [41-45], the IT of metal precursors from W to IL not only are coupled with ET but also bring metal sources into IL, making possible the growth of metal towards the IL side of the IL|W interface. The high viscosity of IL induces an anisotropic growth of 1D nanostructures [46, 47, 51-54]. The formation mechanism of Ag chain-like NBs in the present study is apparently distinguished from the above cases, since the IT of Ag^+ from W to RAIL is not favored to take place in the present condition. The growth of Ag towards the RAIL side of the RAIL|W interface is unable to take place, due to the lack of metal sources inside IL. The mechanism that induces the formation of 1D morphology by the high viscosity of IL cannot work for this system. However, thanks to the IT of FcMDDA^{2+} from RAIL to W, the reduction of Ag^+ still occurred. As positively charged cations, Ag^+ ions are likely to be adsorbed at the RAIL|W interface by the

electrostatic attraction with the RAIL-anion TFPB^- , and then reduced by the redox-active cation FcMDDA^+ existing next to the TFPB^- anion at the interface. Consequently, Ag grows at the RAIL|W interface by the continuous supply of Ag^+ from the bulk of W towards the RAIL|W interface.

The concentration dependence of AgNO_3 in the present synthesis system was investigated. Fig. 3 shows the SEM images of the Ag deposited at the RAIL|W interface, where the concentration of AgNO_3 was decreased from 10 mM in the typical condition for the synthesis of Ag chain-like NBs to 5, 2.5, and 1 mM. An apparent increase in the width of chain-like Ag nanostructures can be observed with the decrease in the concentration of AgNO_3 from Fig 3a to 3d. The edge of each Ag triangular or hexagonal plate can be clearly discerned in these Ag nanostructures, indicating that they are formed by the fuse of a lot of plates along their lateral planes. In the RAIL|W interfacial system, the RAIL phase was adopted as a reducing agent with a constant and quite high concentration. The decrease in the concentration of AgNO_3 which is the oxidizing agent in W, would slow down the reaction rate taking place at the RAIL|W interface. Based on the Gibbs-Thomson equation, the low reaction rate facilitates the growth of pre-existing seeds whereas the high reaction rate is in favor of the self-nucleation process [35, 67]. Therefore, the slower reaction rates brought by the lower concentrations of AgNO_3 promote the growth of already existing Ag nuclei to a larger size. Moreover, the coexistence of some irregular Ag nanoparticles in Fig. 3 implies that an Ostwald ripening process occurs and contributes to the formation of Ag chain-like nanostructures with a larger size, finally leading to the above results. The above results demonstrate that the size of the chain-like nanostructures can be easily controlled by adjusting the interfacial reduction rate via the control of the Ag^+ concentration in W.

The morphology of Ag nanostructures in Fig. 3 distinctly presents the plate features with flat surfaces. In most studies, to induce the formation of Ag

nanoplates commonly involves the use of capping agents to selectively adsorb on the specific facets of Ag [67-70]. In the present study, it is reasonable to suspect that the RAIL-ions play the same role as the capping agent, “adsorbed” on the Ag surface. A control experiment was performed to verify the above hypothesis. 5 mL of methanol was added to the reaction system to turn the interfacial system into a one-phase mixture, and then the mixture was reacted at 70 °C for 48 h. The SEM images of the product obtained from the mixture are shown in Fig. 4a and 4b. Unexpectedly, Ag nanorods rather than nanoplates were obtained as the result (Fig. 4a). Besides, the morphology of nanorods shows a penta-twinned feature based on the SEM image in a higher resolution (Fig. 4b). The morphology of these nanorods quite resembles a reported work. Zhang *et al.* prepared cyclic penta-twinned Ag nanorods by mixing silver ions with glucose as a reductant in an aqueous solution at 80 °C without the use of surfactant. The cyclic penta-twinned structures are formed by five crystallites fused along the {111} facets to generate a gapless rod due to the stacking fault and the intrinsic equilibrium structures with the lower energy [71]. Herein, the same reason was regarded to be responsible for the formation of penta-twinned nanorods in our case. However, considering a large amount of RAIL-ions (FcMDDA^+ and TFPB^-) still exist in the one-phase mixture, the failed formation of Ag nanoplates indirectly proved that the RAIL-ions cannot play the role of capping agent to be selectively adsorbed on the specific facet of Ag. Therefore, the formation of the Ag plates in Fig. 3 is likely induced by growing along the flat RAIL|W interface as the template rather than the capping agent effect. The initially formed Ag nanoplates will be stably fixed at the RAIL|W interface because of the lower net surface energy [72]. Such situation only allows the Ag nanoplates laterally in contact with each other. Eventually, the chain-like Ag nanostructures are formed through the connection of the Ag nanoplates.

In order to reveal the role of the RAIL played in the interfacial system

except for the reducing agent, the RAIL $[\text{FcMDDA}^+][\text{TFPB}^-]$ was replaced by a redox-inactive IL trihexyltetradecylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate ($[\text{THTDP}^+][\text{TFPB}^-]$), with ferrocene (Fc, 50 mM) added into the IL as the reducing agent, and the above interfacial system was reacted under the other conditions remained unchanged. The SEM image of the obtained product is shown in Fig. 4c. When using Fc as the reducing agent, a large amount of Ag NBs with non-uniform width were observed. This may be related to the high viscosity of the IL, leading to a slow diffusion of Fc inside IL, and consequently, resulting in the concentration of the reducing agent Fc also non-uniform at the IL|W interface. The non-uniform width of NBs is caused by the non-uniform growth rate of Ag at the different regions of the IL|W interface. However, by using the RAIL $[\text{FcMDDA}^+][\text{TFPB}^-]$ itself as a reducing agent, the slow diffusion rate brought by the high viscosity can be compensated by the high concentration of the redox cation FcMDDA^+ , leading to a stable growth rate for obtaining uniform Ag chain-like NBs at the RAIL|W interface (Fig. 4d). The above results indicate that the use of RAIL $[\text{FcMDDA}^+][\text{TFPB}^-]$ is beneficial for the formation of Ag chain-like NBs with average size.

Based on the above discussion, a possible mechanism for the formation of chain-like Ag NBs can be inferred and the schematic is shown in Fig. 5. Due to the separation of Ag precursor and the reducing agent in W and RAIL, Ag nuclei are spontaneously generated at the RAIL|W interface (Fig. 5a). The negative current of the ET from the redox-active cation FcMDDA^+ to Ag^+ (eqn 1), is balanced with the positive current of the IT of oxidized FcMDDA^{2+} from RAIL to W (eqn 2), so that the interfacial reaction can take place spontaneously. The RAIL|W interface acts as a planar template to induce the formation of small Ag nanounits with flat surface (Fig. 5b). Since Ag nanostructures are adsorbed and fixed at the RAIL|W interface which cannot move vertically, an oriented growth of Ag nanostructures through the lateral direction is promoted

at the RAIL|W interface, finally facilitating the Ag nanostructures connected one by one to form chain-like nanostructures (Fig. 5c). Unlike our previous studies where the formation of 1D metal nanostructures is induced by the high viscosity of IL, in the present case, the formation of 1D structures is realized by the linkage of small units through an oriented lateral growth.

To evaluate the SERS activity for typical Ag chain-like NBs, 4-ABT was adopted as the probing molecules for SERS measurements. Fig. 6 shows Raman spectra for 4-ABT adsorbed on Ag chain-like NBs and bare glass, respectively. Two vibration bands at 1086 cm^{-1} and 1592 cm^{-1} corresponding to C-S and C-C stretching with a_1 -type symmetry [73, 74], can be distinguished for the glass case. These two bands are shifted to 1071 cm^{-1} and 1575 cm^{-1} for the Ag chain-like NBs case with significantly enhanced intensities, which is associated with the electromagnetic and chemical enhancement in SERS. The latter involves the formation of Ag-S bond between the thiol group of 4-ABT and the Ag surface. Moreover, the bands at 1141, 1392, and 1439 cm^{-1} corresponding to $\nu(\text{C-H})$, $\nu(\text{C-C}) + \delta(\text{C-H})$, and $\delta(\text{C-H}) + \nu(\text{C-C})$ with b_2 -type symmetry were clearly observed for the case of Ag chain-like NBs [59, 60]. However, they were hardly distinguished for the case of glass due to the low intensities. Thus, the bands of $\nu(\text{C-S})$ and $\nu(\text{C-C})$ are chosen to calculate the SERS enhancement factor (EF), by comparing the corresponding SERS and the Raman signals of 4-ABT, respectively, as shown in the following eqn:

$$\text{EF} = (I_{\text{SERS}}N_{\text{bulk}})/(I_{\text{bulk}}N_{\text{SERS}})$$

where N_{SERS} and N_{bulk} are the numbers of 4-ABT molecules giving rise to the SERS and Raman signals, while I_{SERS} and I_{bulk} are the corresponding SERS and Raman intensities. EF values are calculated to be 1.4×10^5 for the band of $\nu(\text{C-S})$, and 4.1×10^5 for the band of $\nu(\text{C-C})$ (detail for the calculation is in Supporting Information). The calculated EF values are comparable to some

reference data of Ag nanorods [74] or Ag nanoparticles [75]. In comparison with other reported Ag substrate, the Ag chain-like NBs in the present study are easy to be prepared without the use of any surfactant and show good SERS activity, which can be used for plasmonic applications.

Conclusions

Ag chain-like NBs were successfully prepared via a RAIL|W interfacial method by utilizing the soft interface as a template. The use of RAIL in the interfacial system is important for the present synthesis due to the following reasons: (1) RAIL plays dual roles of the reducing agent and liquid substrate simultaneously; (2) the oxidized FcMDDA²⁺ generated from the ET between Ag and redox cation FcMDDA⁺, spontaneously transferred from RAIL to W during the reaction period, in order to neutralize the excess charges brought by ET; (3) the high concentration of the reducing agent in RAIL is proved to be important to obtain Ag chain-like NBs with average size. Ag nanounits with flat surface are formed first by taking the RAIL|W interface as a planar template, and then linked with each other through the lateral growth, resulting in the final morphology of Ag chain-like NBs having three features of flat surfaces, sharp corners on the edges, and large aspect ratio simultaneously. The size of Ag NBs can be adjusted by the control of the AgNO₃ concentration, where higher (lower) concentration of AgNO₃ favors the formation of Ag NBs with smaller (larger) size.

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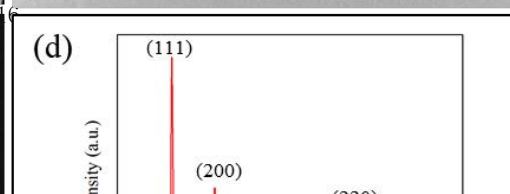
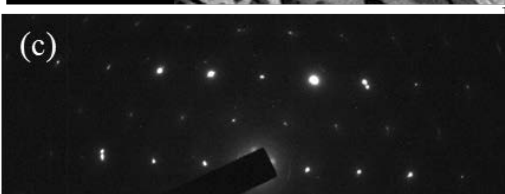
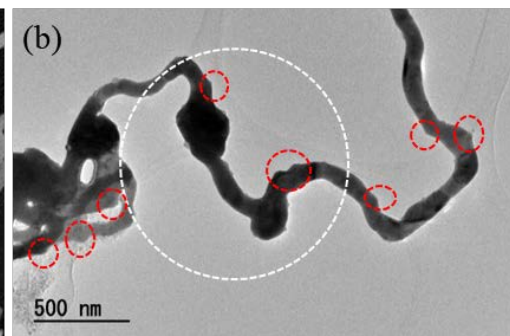
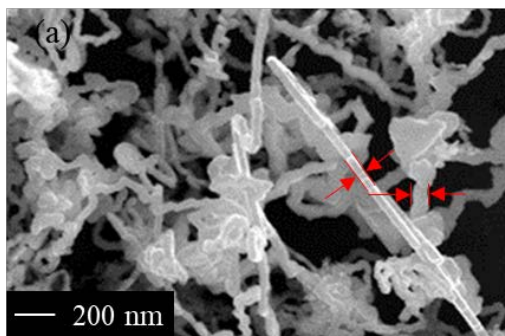


Figure 1 (a) SEM image, (b) TEM image, (c) SAED image, and (d) XRD pattern for Ag NBs.

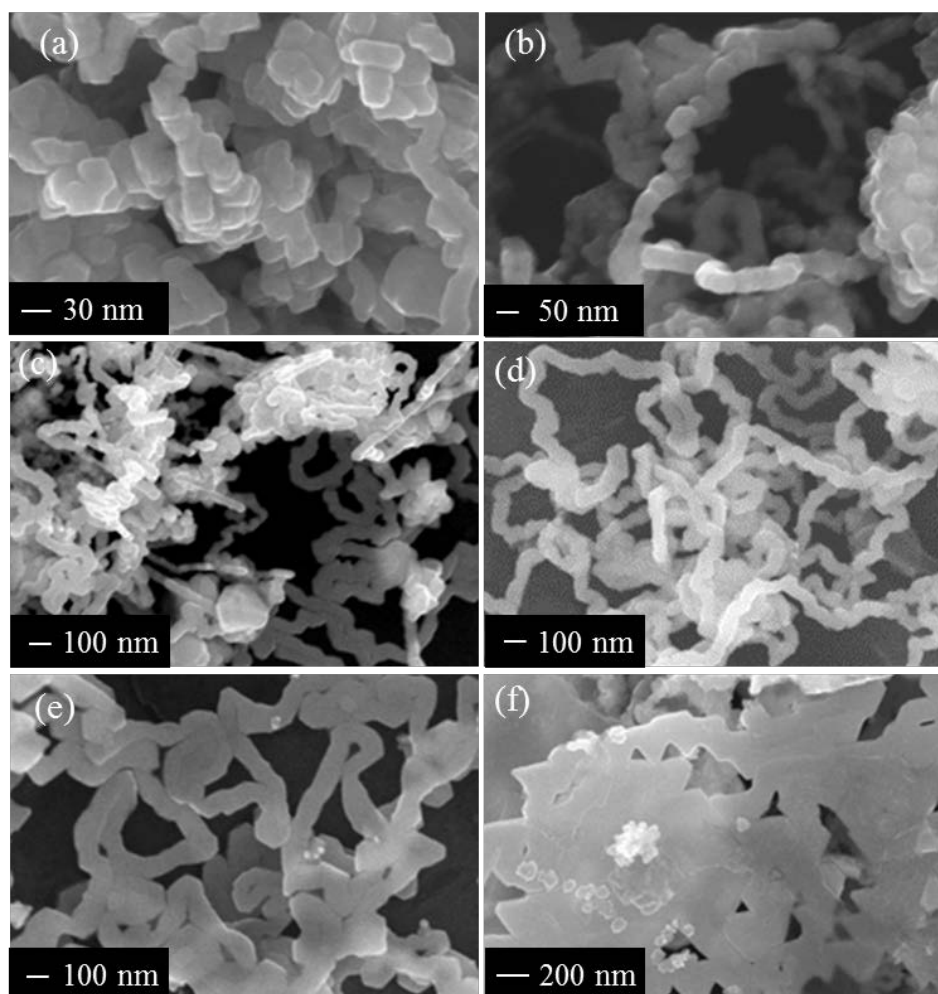


Figure 2 (a) SEM images for Ag NBs obtained by terminating the synthesis at $t = 4$ h (a), 8 h (b), 12 h (c), 24 h (d), 48 h (e), and one week (f).

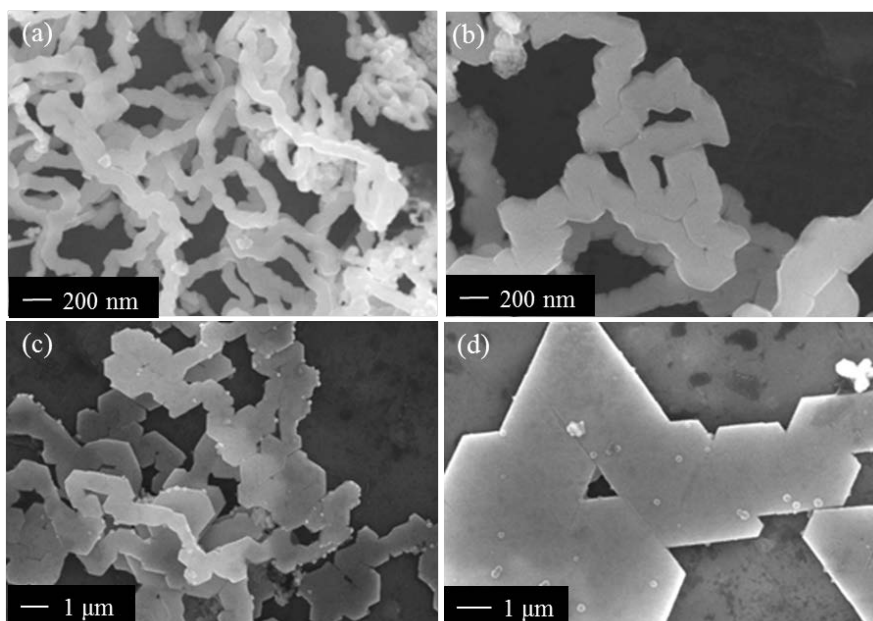


Figure 3 SEM images for Ag NBs obtained from the synthesis where the concentration of AgNO₃ in W was controlled in 10 mM (a), 5 mM (b), 2.5 mM (c), and 1 mM (d).

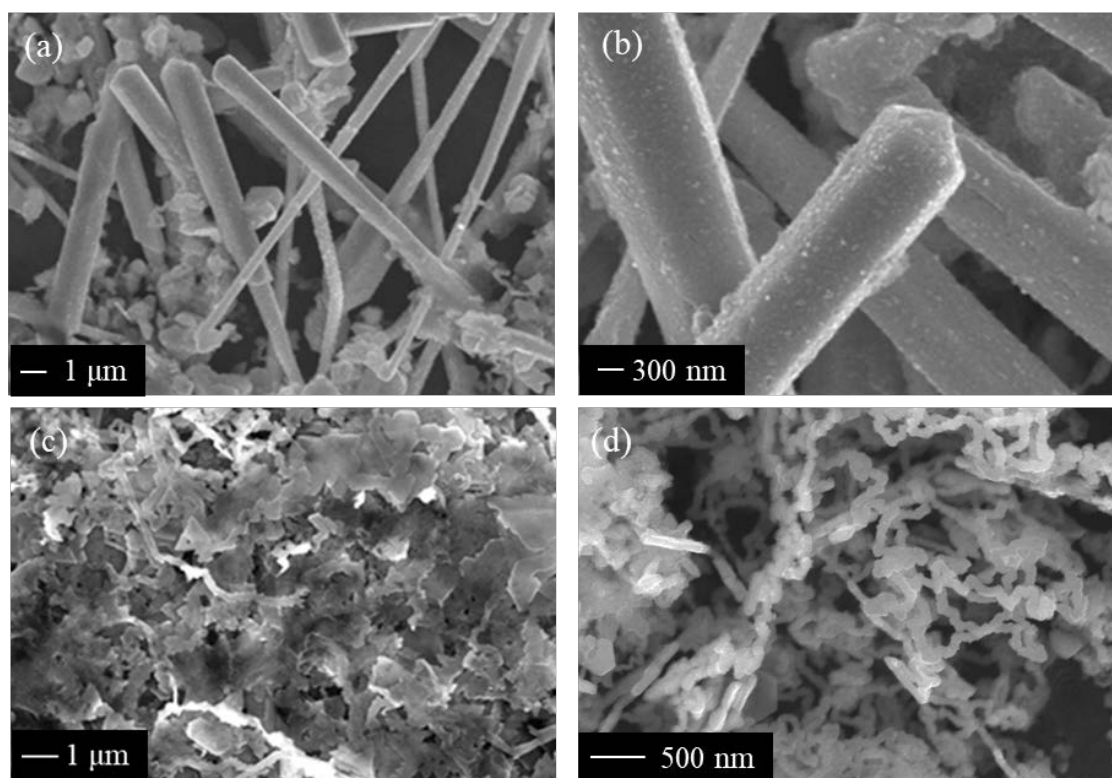


Figure 4 SEM images of Ag nanostructures obtained from the methanol diluted one-phase system (a, b), the IL|W interfacial system with the use of Fc (50 mM) as the reducing agent (c), and the RAIL|W interfacial system (d).

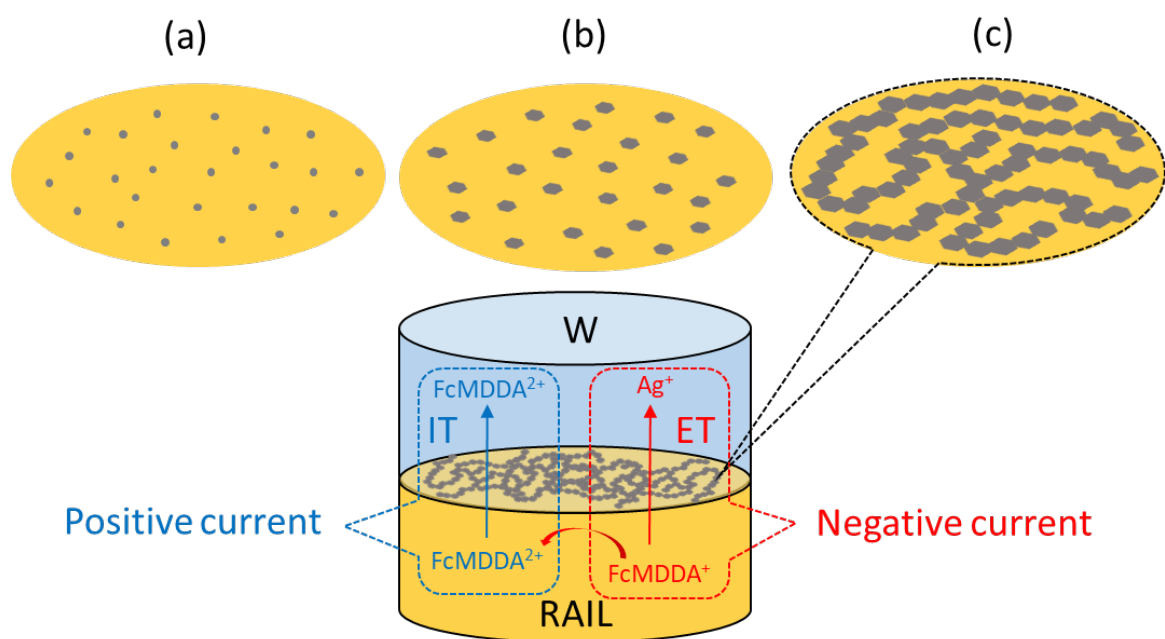


Figure 5 Schematic for the possible mechanism of the formation of Ag chain-like NBs.

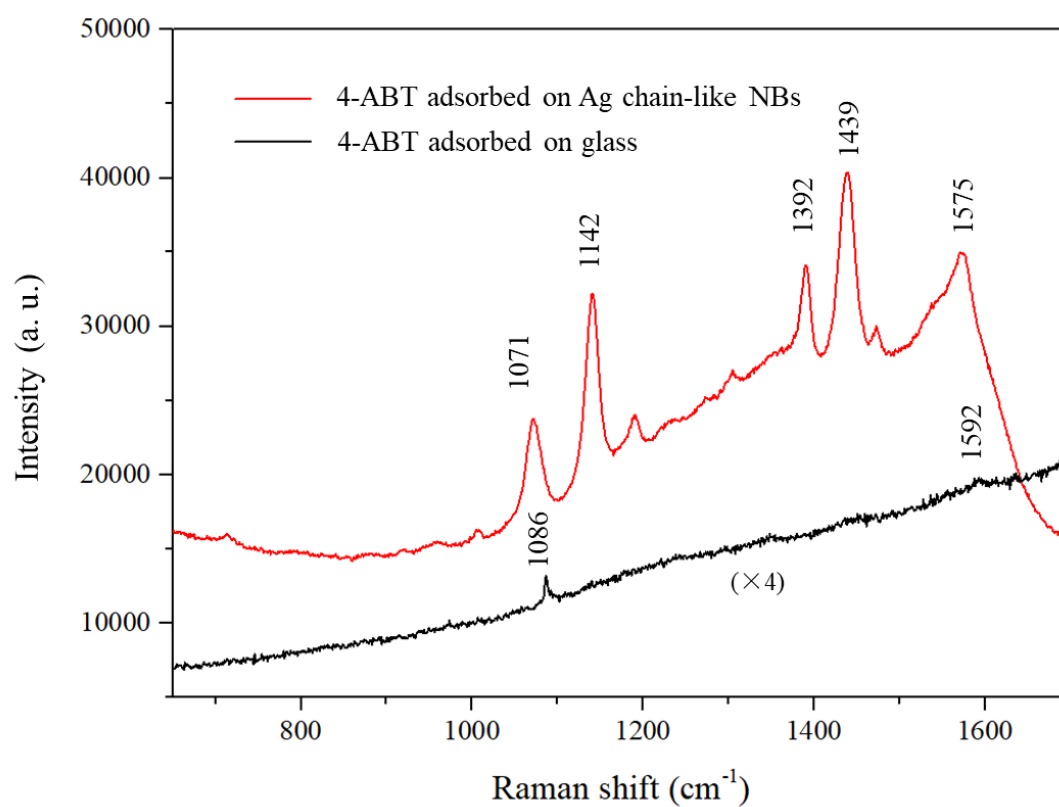
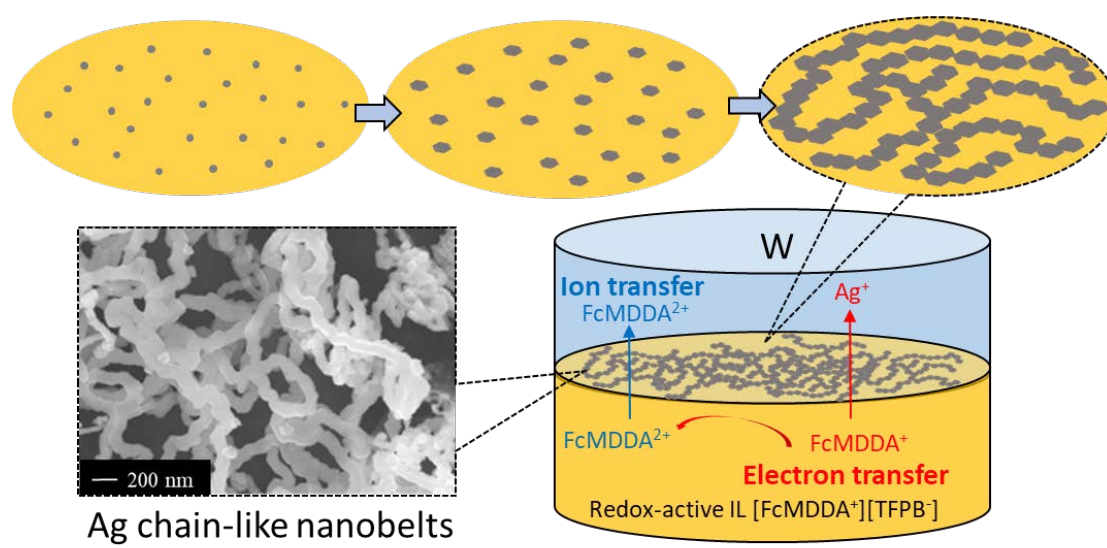


Figure 6 Raman spectra of 4-ABT adsorbed on Ag chain-like NBs (red) and glass (black). Integration time: 10 s.

Graphic abstract



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Highlights

A L-L interface templated strategy for preparing Ag chain-like NBs was developed.

The redox-active IL (RAIL) was adopted as the reducing agent to form the interface with water.

The Ag NBs are formed by an oriented growth along the RAIL|W interface.

The size of Ag NBs can be controlled by regulating the concentration of Ag^+ in W.