Supporting information

A Facile Route to Janus Nanorods via Redox-Assisted Ripening

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Experimental section

Materials

All chemical reagents were used without further purification. Silver nitrate ($AgNO_3$, 99.9%,), L(+)-ascorbic acid (L-AA) and iron chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 98%) were purchased from Sigma-Aldrich. Poly(vinylpyrrolidone) (PVP, Mw=1300000) was purchased from Alfa Aesar. Tetraethyl orthosilicate (TEOS) and hydroquinone (HQ) were purchased from Aladdin. Glyoxal solution (40%, in water) was purchased from Energy-Chemical. Ethylene glycol (AR grade), isopropanol (AR grade), ethanol (AR grade), $NH_3 \cdot H_2O$ (AR grade, 25-28% w/w) were purchased from Sinopharm Chemical Reagent Co., Ltd. Acetone (AR, 99.5%) was purchased from Shanghai Ling Feng Chemical Reagent Co. Ltd. Silver acetate (CH_3COOAg, 99.5%) and silver trifluoroacetate (CF_3COOAg, 98%) were purchased from Macklin. Copper specimen grids (300 mesh) with formvar/carbon support film were purchased from Beijing Zhongjingkeyi Technology Co., Ltd. Deionized water (resistance > 18.2

MΩ•cm^{-1}) was used in all reactions.

Characterization

TEM images were collected from a FEI Talos L120C TEM operated at 100 kV. SEM images were collected on a FEI Quanta 250 FEG STEM operated at 20 kV.

Preparation of TEM Samples

The TEM grids were treated with oxygen plasma in a Harrick plasma cleaner/sterilizer for 60 s to improve the surface hydrophilicity. The sample solution was directly dropped on the hydrophilic face of the TEM grid, followed by dried in air for 30 min.

Synthesis of AgNWs

PVP (0.300 g) and $AgNO_3$ (0.200 g) were dissolved in ethylene glycol (50 mL), and then $FeCl_3.6H_2O$ (0.100 mg) was added. The mixture was stirred at room temperature until $FeCl_3$ was fully dissolved. After that, the mixture was heated at 130 °C with stirring at 600 rpm for 8 h.

Isolation and Purification of AgNWs

The as-synthesized AgNWs solution (1mL) was added in the glass vial with another 5mL acetone. The mixture was shaken well, let stand until a large amount of AgNWs were settled at the bottom, followed by removing the supernatant. This isolation and purification process was repeated twice. The obtained AgNWs were redispersed in water as a stock solution for further use.

Preparation of AgNW@silica

Isopropanol (1 mL), AgNWs stock solution (~4 mg/mL, 400 μL), $NH_3 \cdot H_2O$ (40 μL) and TEOS (2 μL) were added successively into a 4 mL vial under stirring. The purified AgNWs in water (~4 mg/mL, 400 μL) was first added into 4mL vial with another 1mL isopropanol followed by the addition of $NH_3 \cdot H_2O$ (40 μL) and TEOS (2 μL). The resulting solution was magnetic stirred for 30 s to ensure fully mixing. Then the mixture was incubated at room temperature for another 2 h.

Ultrasonic fragmentation of AgNW@silica

The as-synthesized AgNW@silica/water solution was centrifuged at 8000 rpm for 5 minutes and purified in water. Then the product was redispersed in 15 mL water. For sonication, the purified AgNW@silica was added into a 50 mL plastic centrifuge tube, and then sonicated with the 6 mm tip in an ice bath. Ultrasound amplitude of 80% and duration of 120 minutes were applied. All sonication processes were carried out using the Scientz JY92-IIDN ultrasonic homogenizer (900 W, 20 KHz).

Preparation of lollipop structure

After ultrasonic fragmentation, the obtained AgNR@silica solution was centrifuged and washed with ethylene glycol for 2 cycles The purified AgNR@silica was further dispersed in 1 mL ethylene glycol. Then 250 μL $AgNO_3$ (6.4 mg/mL，in glycol) and 200 μL HQ (1 mg/mL，in glycol) were added. The mixture was incubated at 130 ℃ for 6 h, followed by isolated by centrifugation and redispersed in ethanol for storage.

Verify the consumption of reactants in the deaeration process

In order to verify if the decrease in the degree of ripening is from the reduction of $AgNO_3$ by HQ during the deaeration reaction. In the control experiment, the ripening process was first conducted at room temperature, followed by further incubation at 130 ℃ for 6 h. After 20 minutes reaction at room temperature, , only 12 (15%) AgNR@silica grew to the lollipop nanostructures among 76 surveyed, as SEM image shown in Fig. S5. After heat treatment, the ripening was obviously more significant (Fig S6). 20% (24/123) of the AgNR@silica were etched to hollow silica tubes and 73% (78/123) lollipop nanostructures with etched segment of 37% of the total length. Compared with the 130 ℃ ripening on the as-prepared solution, The extent of ripening judging from the hollow nanotube porpulation (from 32% to 20%) is quite significant. But this decrease is much less than the same reaction carried out in the absence of oxygen, in which the percentage of hollow silica tubes can be reduced to 1%. It is also proved deaeration process may lead to the consumption of some reactant, but this consumption was very few. The decrease of etching degree for the ripening in the deaeration process

was not ascribed to the consumption of reactants, but it is the absence of oxidant lead to lower degree of ripening. The rise in the number of lollipops from room temperature to 130 ℃ ripening reaction, also indicated that most $AgNO_3$ was reduced during the heating process.

Supplementary Figures

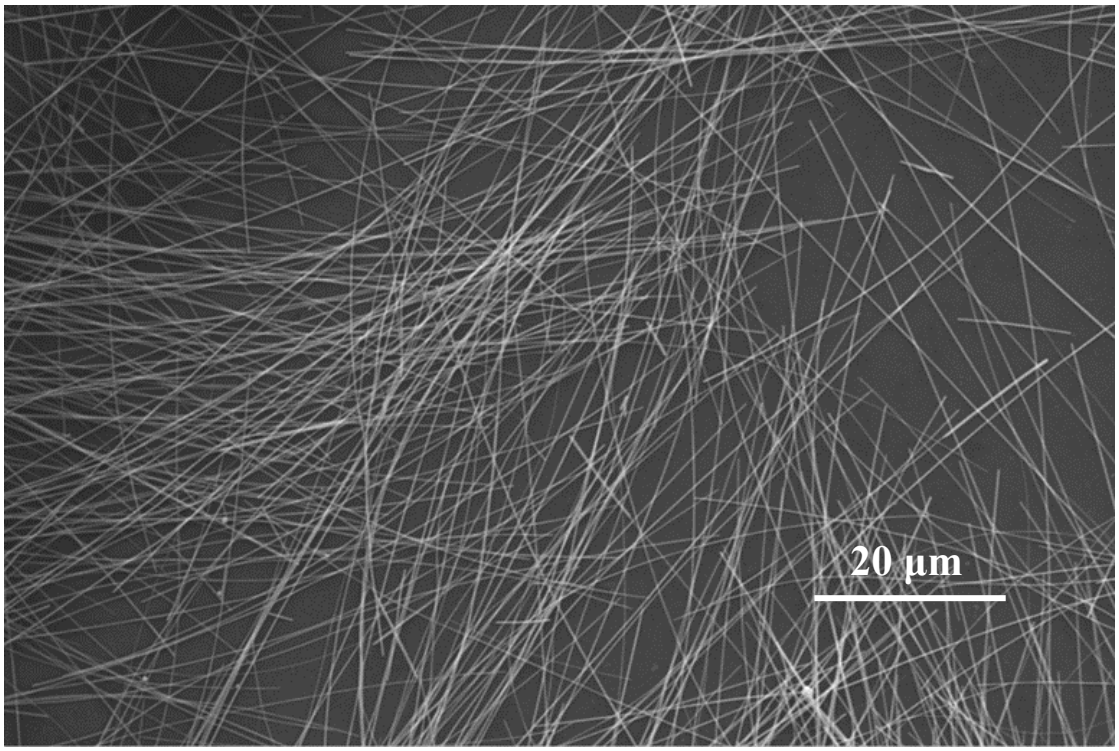

Fig. S1 SEM image of AgNWs.

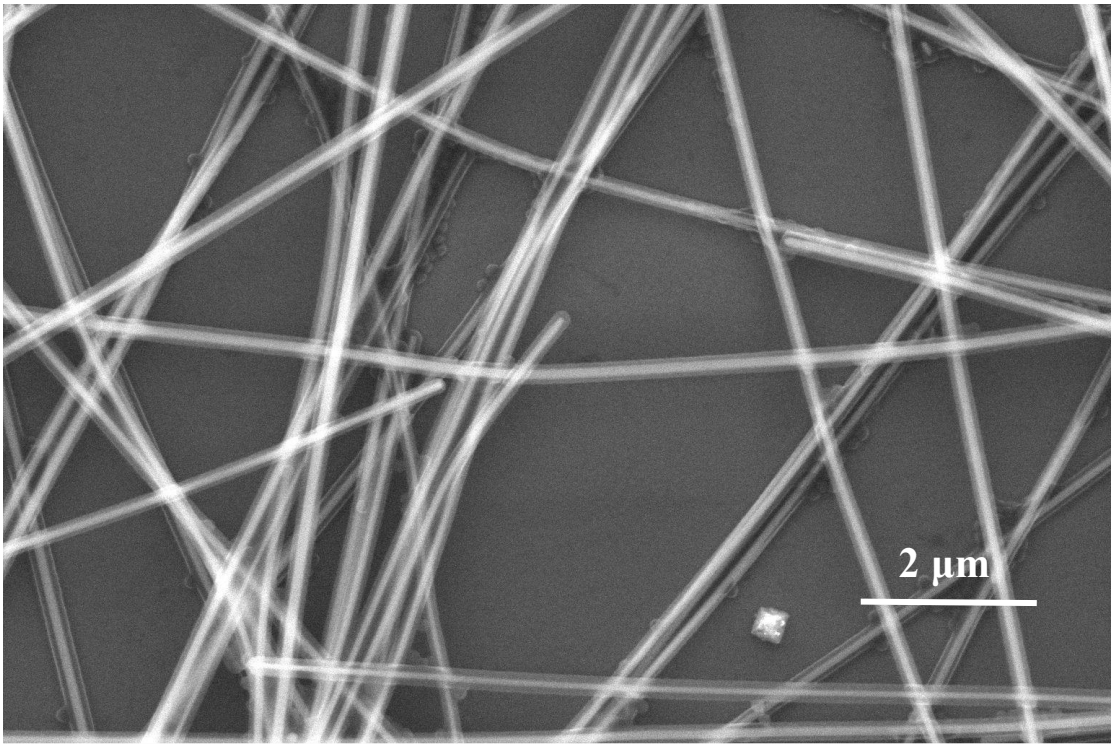

Fig. S2 SEM image of AgNW@silica.

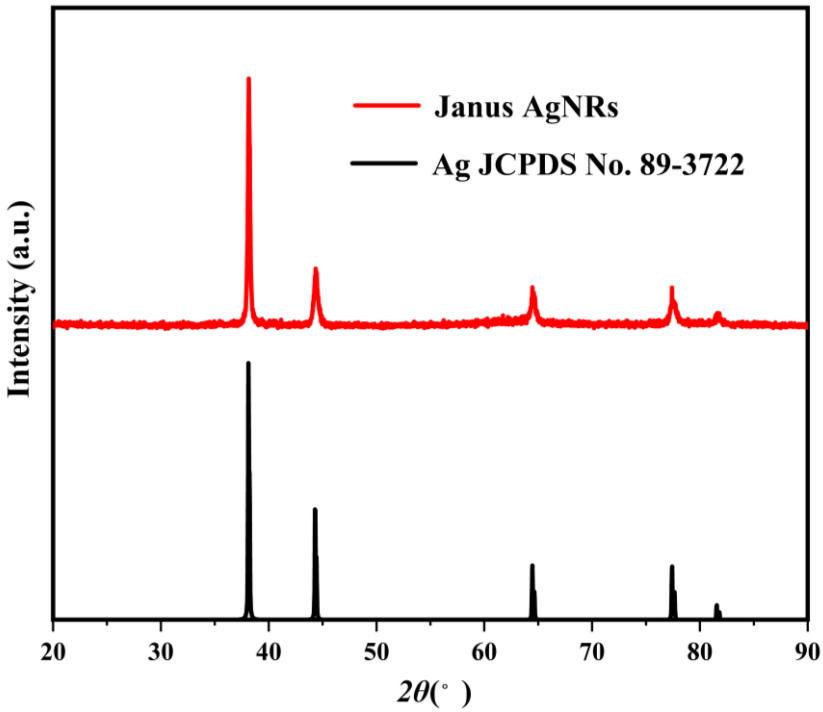

Fig. S3 XRD spectrum of the lollipop without silica.

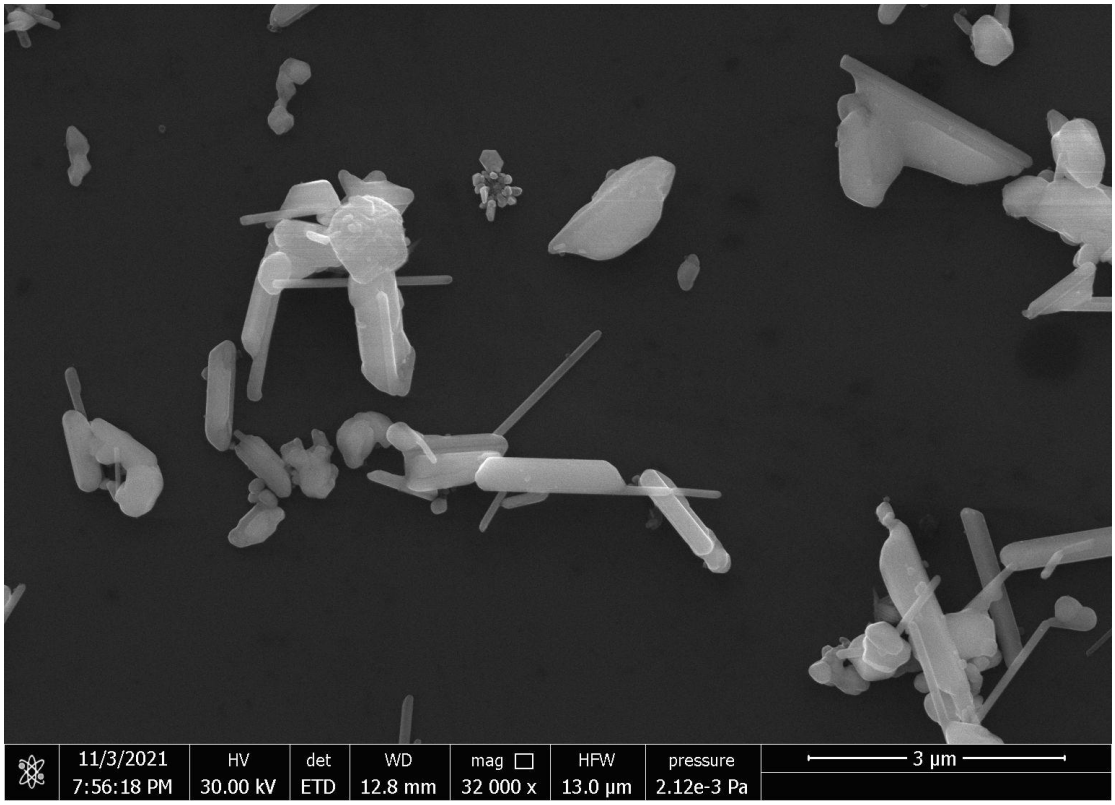

Fig. S4 SEM image of the unprocessed AgNRs after ripening.

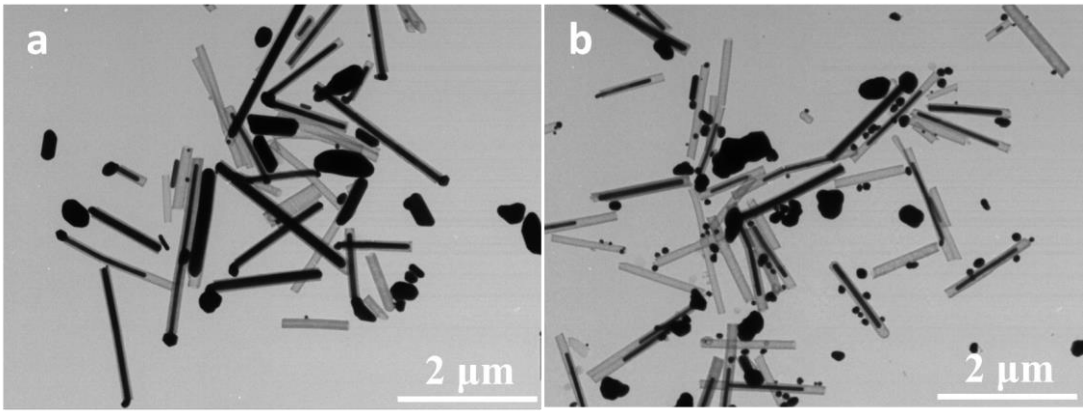

Fig. S5 TEM images of the AgNR@silica after ripening with different silver sources: (a) 6.4 mM CF_3COOAg; (b) 6.4 mM CH_3COOAg.

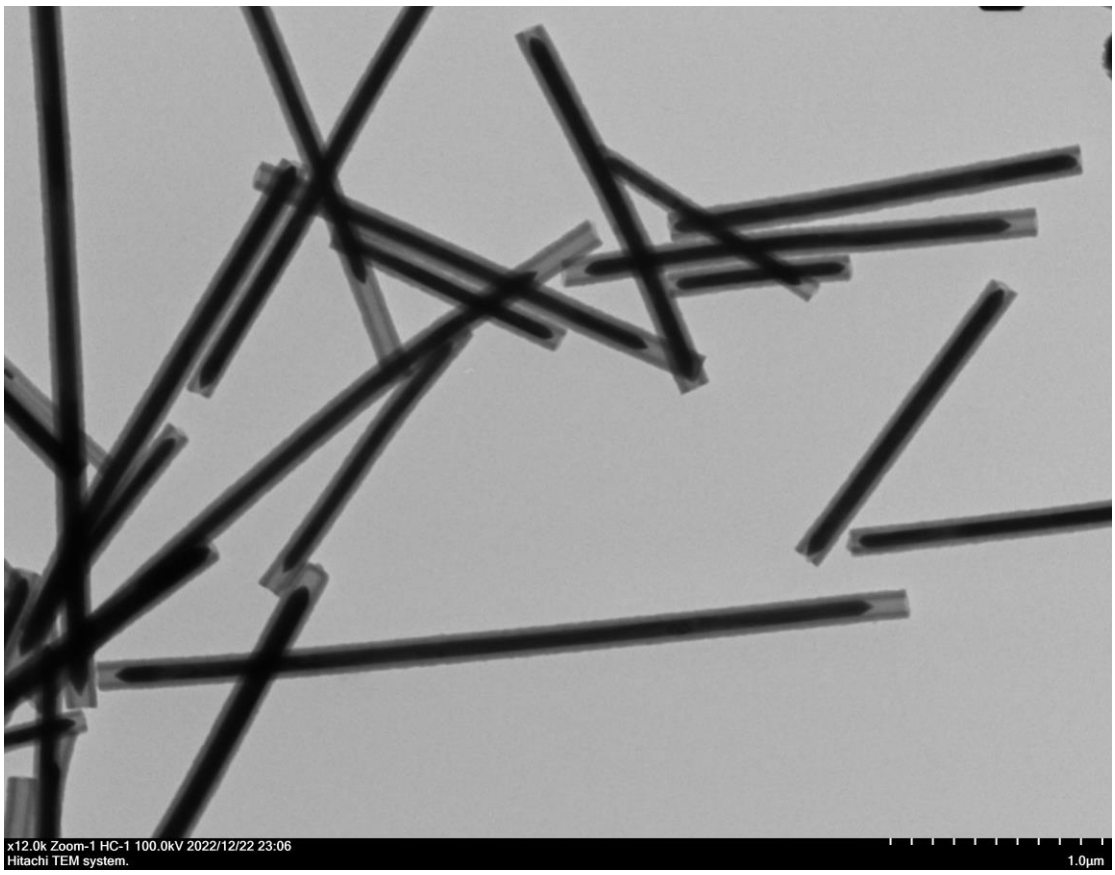

Fig. S6 TEM image of the AgNR@silica with directly adding BQ, in place of Ag^{+}, into the ripening system.

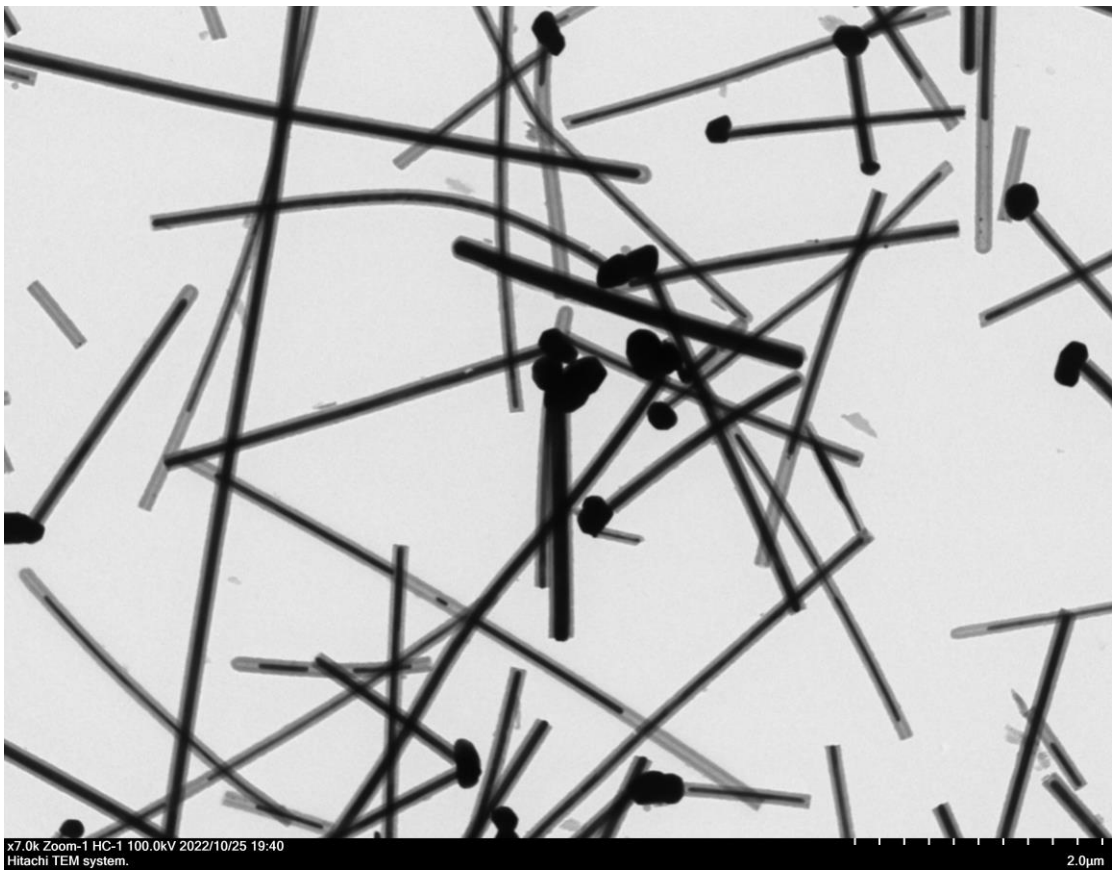

Fig. S7 TEM image of the AgNR@silica and ripening reactant which was heated to 60 ℃ for 6 h in Di-water.

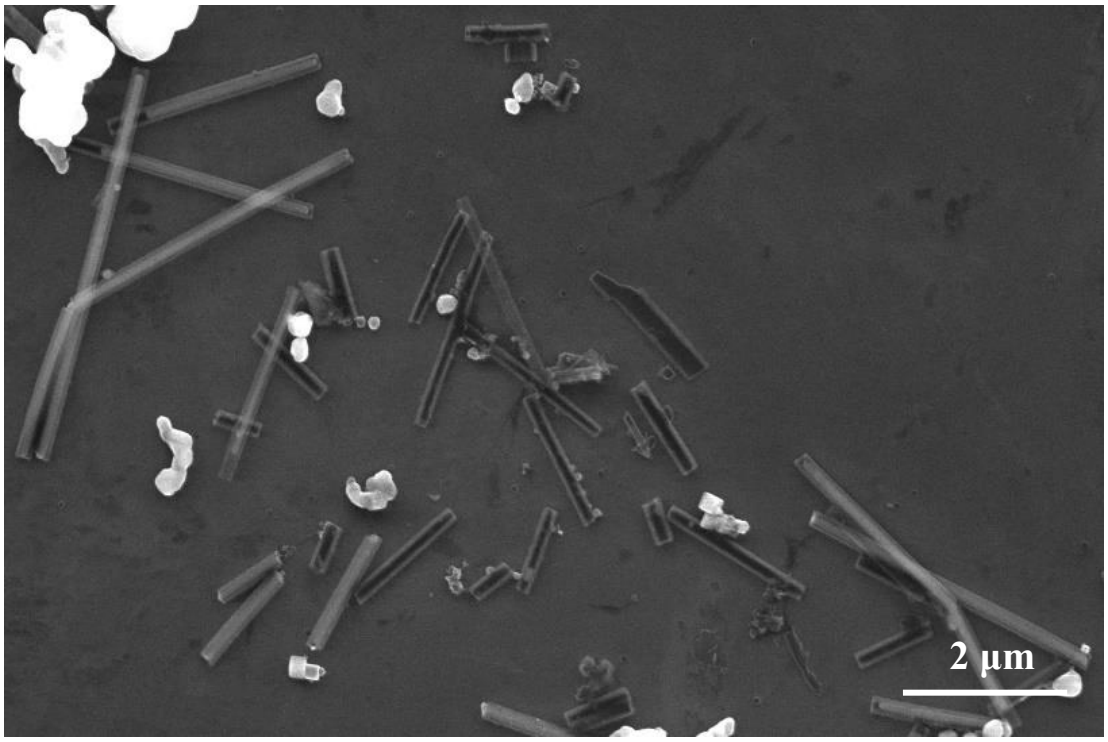

Fig. S8 SEM image of the AgNR@silica after incubated in the anaerobic conditions cycled again in the presence of oxygen.

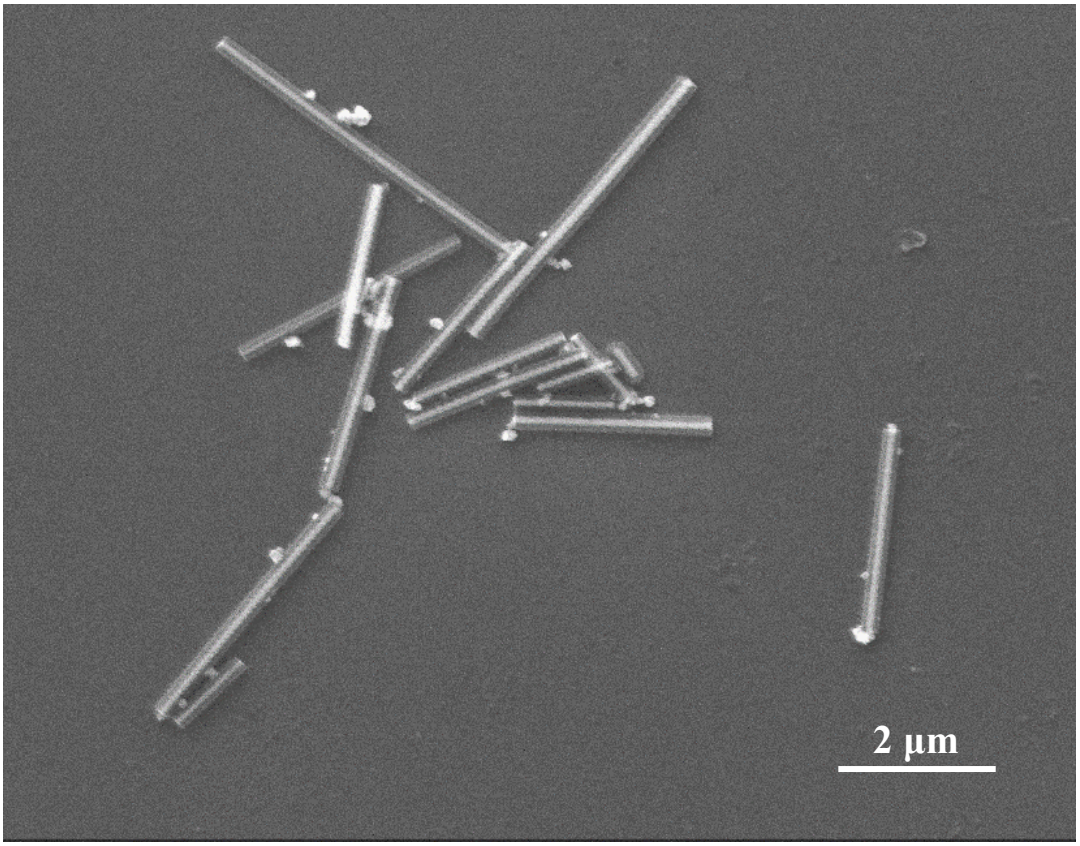

Fig. S9 SEM image of the Ag NR@silica stirred at room temperature for 20 minutes without heating.

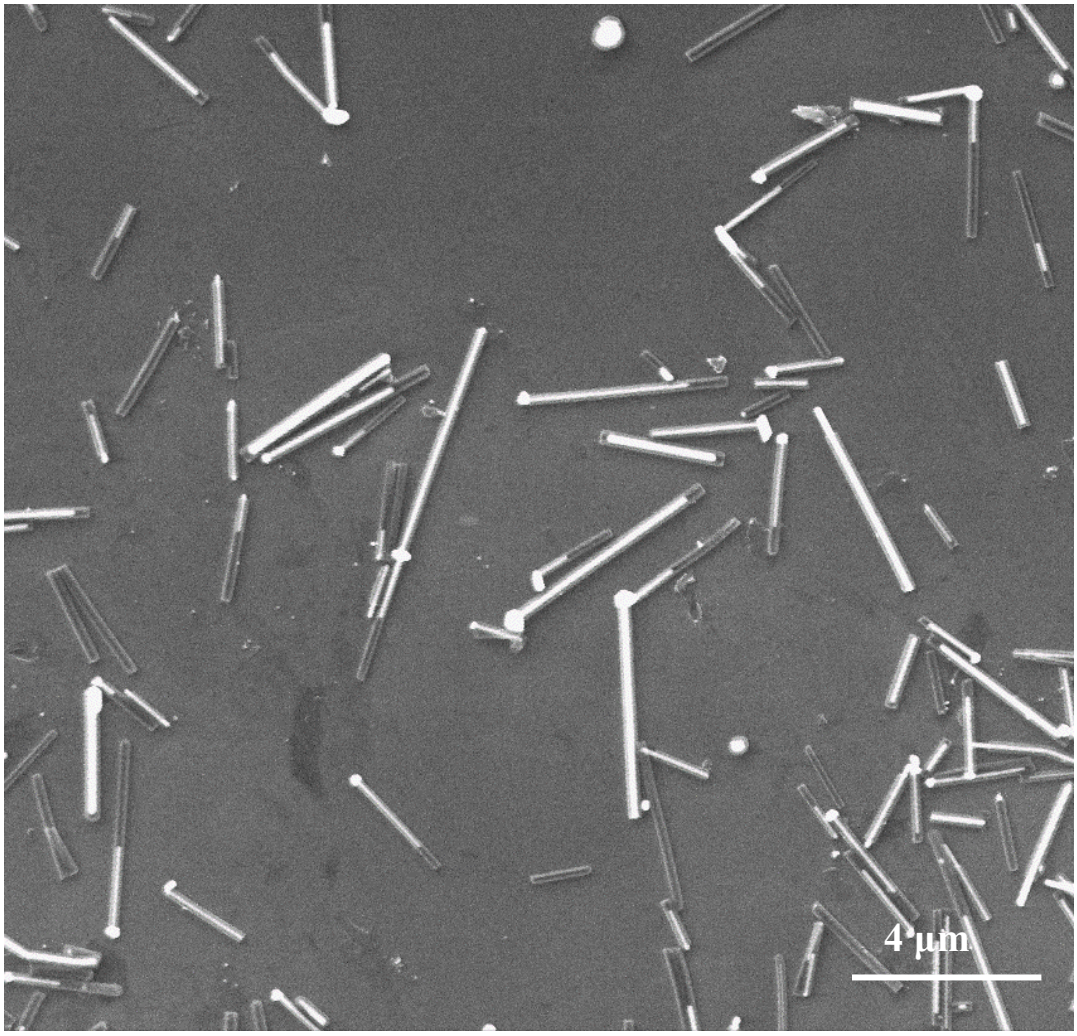

Fig. S10 SEM image of the Fig. S8 sample further heating at 130 °C for 6 h.

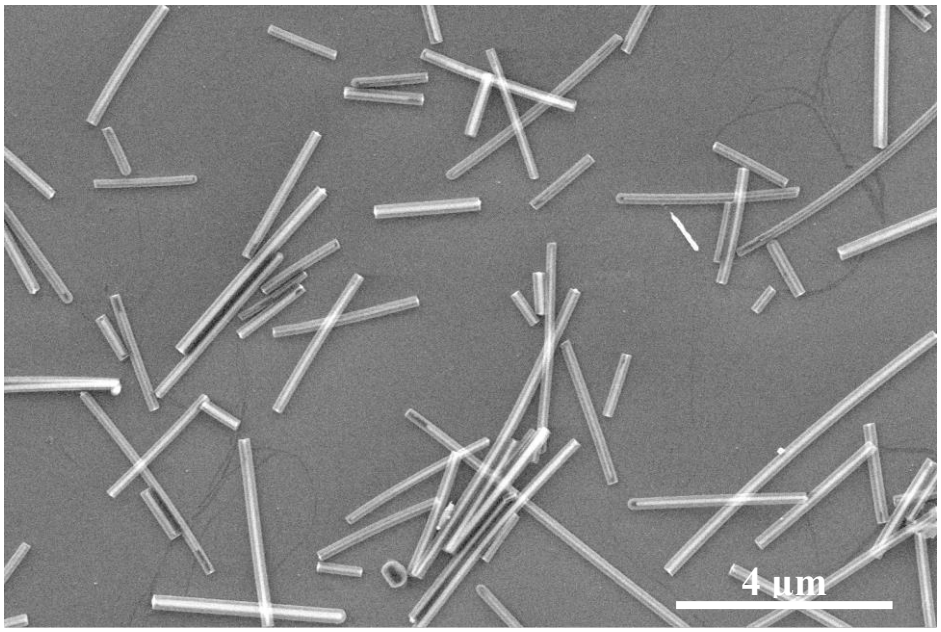

Fig. S11 SEM image of the product that AgNR@silica was directly heated at 130 ℃ in ethylene glycol solution for 6 h, without $AgNO_3$ and hydroquinone added. This result also indicates that having oxygen and AgNR@silica is not enough for the ripening occurence in this system.

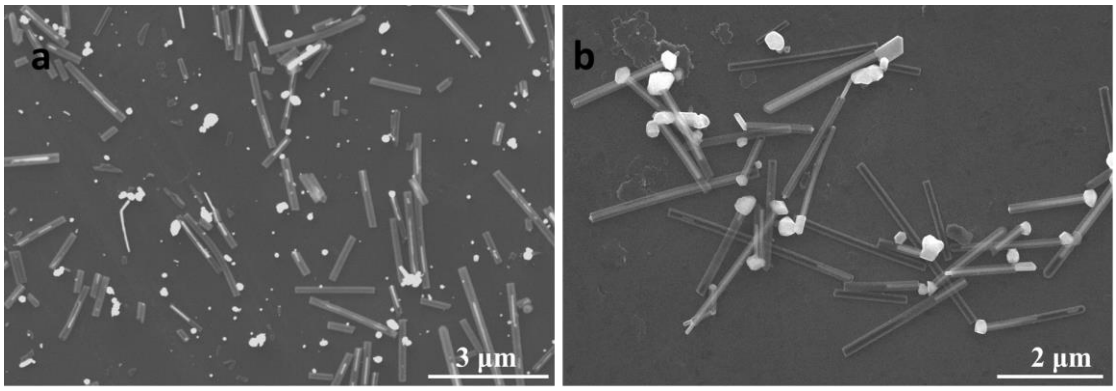

Fig. S12 SEM images of the AgNR@silica after ripening with different reductants: (a) 1.3 mM L-AA; (b) 1.2 M glyoxal.