Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

Synthesis of Substrate-bound Seaweed-like Au Nanowires with Amino Silane Coupling Agents

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Experimental section.

Materials

All chemicals are reagent grade and used as purchased without further purification. 4-mercaptobenzoic acid (4-MBA, 97%), tetraethylorthosilicate (TEOS, 99%) and L-ascorbic acid (99.0%) hexadecyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich; 3-aminopropyltriethoxysilane (APTES, 99%), methanol (99.9%), acetone (AR) and L-arginine (98.0%) were purchased from Aladdin; Sodium citrate tribasicdihydrate (CA, 99.0%), hydrogen tetrachloroaurate(III) trihydrate ($HAuCl_4$, 99.9%, Au 49% on metals basis) were purchased from Alfa Aesar; Acetic acid (AR, 99.5%), cyclohexane (anhydrous, 99.5%) and ethanol (EtOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. 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.

Characterizations

TEM images were collected from a Talos L120C model transmission electron microscope operated at 120 kV. SEM images were collected on a FEI Quanta 250 FEG model. The XRD analysis was carried out on a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. High resolution TEM images were taken from a JEOL 2100F Transmission Electron Microscope operated at 200 kV. And LC-MS were carried out with a Thermo Fisher Scientific – US (MSQ PLUS/U3000) instrument. The mobile phase is acetonitrile and water.

Preparation of TEM Samples

TEM grids were treated with oxygen plasma in a Harrick plasma cleaner/sterilizer for 45 s to improve the surface hydrophilicity. The hydrophilic face of the TEM grid was then placed in contact with the sample solution. A filter paper was used to wick off the excess solution on the TEM grid, which was then dried in air for 30 min.

Pre-treatment of gold-plated silicon wafers

The gold-plated silicon wafers were cut into 0.5cm*0.5cm pieces with a glass knife, then sequentially washed with 10 mL of acetone, ethanol, and deionized water in ultrasonication cleaner, each for 5 min. The cleaned substrates were air dried at room temperature for 30 minutes and stored in deionized water.

Synthesis of the seaweed-like Au nanowires on gold-plated silicon wafers

In a typical synthesis, a piece of gold-plated silicon wafer (about 0.25 cm^2) was first cleaned, and then incubated in an APTES solution (5 mM, H_2O: ethanol = 1:1) for 1 h. After rinsed with water to remove the excess APTES, the wafer was immersed in a growth solution (H_2O: ethanol = 1:1) containing the ligand 4-MBA (550 μM), $HAuCl_4$ (1.7 mM), and L-ascorbic acid (4.1 mM). After 1 h growth, the wafer was retrieved, rinsed with ethanol and dried in air.

Synthesis of Au nanowires on colloidal gold substrates

The colloidal substrates, gold nanoparticles,[1, 2] gold nanorods[3] and gold triangular nanoplates[4] were first synthesized according to the previously reported methods.

Synthesis of Au nanowires on 40 nm Au nanoparticles. 500 μL of as-synthesised 40 nm Au nanoparticles solution was first concentrated by centrifugation to 20 μL (4800 rpm, 8min), and then dispersed into 800 μL of APTES solution (0.005 mM, H_2O: ethanol = 1:1). It is noted that the concentration of the APTES solution must be kept extremely low to prevent the immediate aggregation of Au nanoparticles during the APTES treatment. After 1 h incubation, 300 μL of growth solution containing the 550 μM of 4-MBA, 1.7 mM of $HAuCl_4$ and 4.1 mM of L-ascorbic acid was added into the mixture. The solution was left undisturbed at room temperature for 30 min, and the colour of the solution gradually turned to black. The product was collected by centrifugation (4800 rpm for 5 min) and washed twice with water and ethanol.

Growth of Au nanowires on other colloidal gold substrates followed the same experimental procedure except the concentrated 15 nm Au nanoparticles, nanorods and triangular nanoplates solution were added into the 800 μL of APTES solution.

Synthesis of ultra-long nanowires on gold-plated silicon wafers

Synthesis of Au@silica nanoparticles. The Au@silica nanoparticles were synthesized according to the previously reported method with slight modification.[5] 3 mL of as-synthesized 40 nm Au nanoparticles was concentrated to 6 μL (4800 rpm, 8min) by centrifugation, and then dispersed into 500 μL of H_2O. Under vigorous stirring, 2.5 mL of isopropanol was added, followed by 20 mL of 11-mercaptoundecanoic acid (2 mM, prepared in ethanol). After 5 min mixing, 600 μL of TEOS (8.96 mM, aq) and 90 μL of ammonia (25-28% w/w) were added into the mixture. The mixture was then left to undisturbed at room temperature for 12 h to obtain the Au@silica core-shell nanoparticles.

To grow the ultra-long nanowires on the gold-plated substrate with the Au@silica nanoparticles, the concentrated Au@silica nanoparticles was firstly dispersed into 200-1000 μL APTES (5mM, H_2O: ethanol = 1:1) and mixed with shaking for 10 min. The obtained mixture was used to replacing the APTES solution in the typical growth of the seaweed-like Au nanowires. All the rest procedures were remained the same.

Electrochemical measurements.

All CO_2 experiments were conducted on the electrochemical workstation (CHI 660E) in conventional three-electrode system at room temperature. CO_2 electroreduction was carried out in a customized H-type cell separated by a Nafion 117 membrane with 0.5 M $KHCO_3$ as electrolyte. The substrate covered with nanowires was directly used as the working electrode, with Ag/AgCl as the reference electrode and platinum wire electrode as the counter electrode. The electrolyte solution was purged with pure N_2 or CO_2 for at least 30 min until saturation before the electrochemical measurements. The polarization curves were obtained with a scanning rate of 10 mV/s from 0.2 V vs. RHE to -0.87 V vs. RHE. The electrode stability was tested by chronoamperometry method at a constant potential of −0.5 V vs. RHE for 1000s by maintaining a constant CO_2 flow rate.

Supplementary Figures

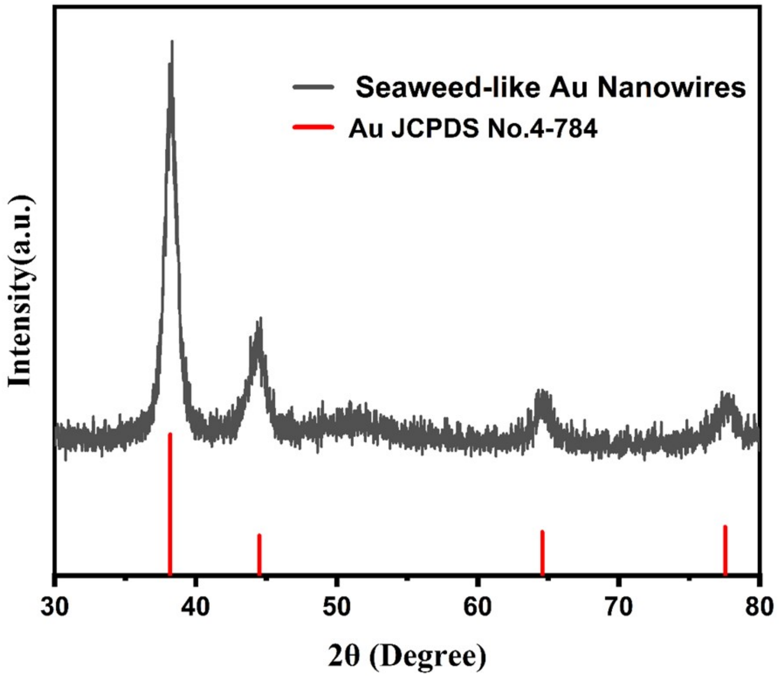

Fig. S1.The XRD spectrum of the as-prepared seaweed-like Au nanowires.

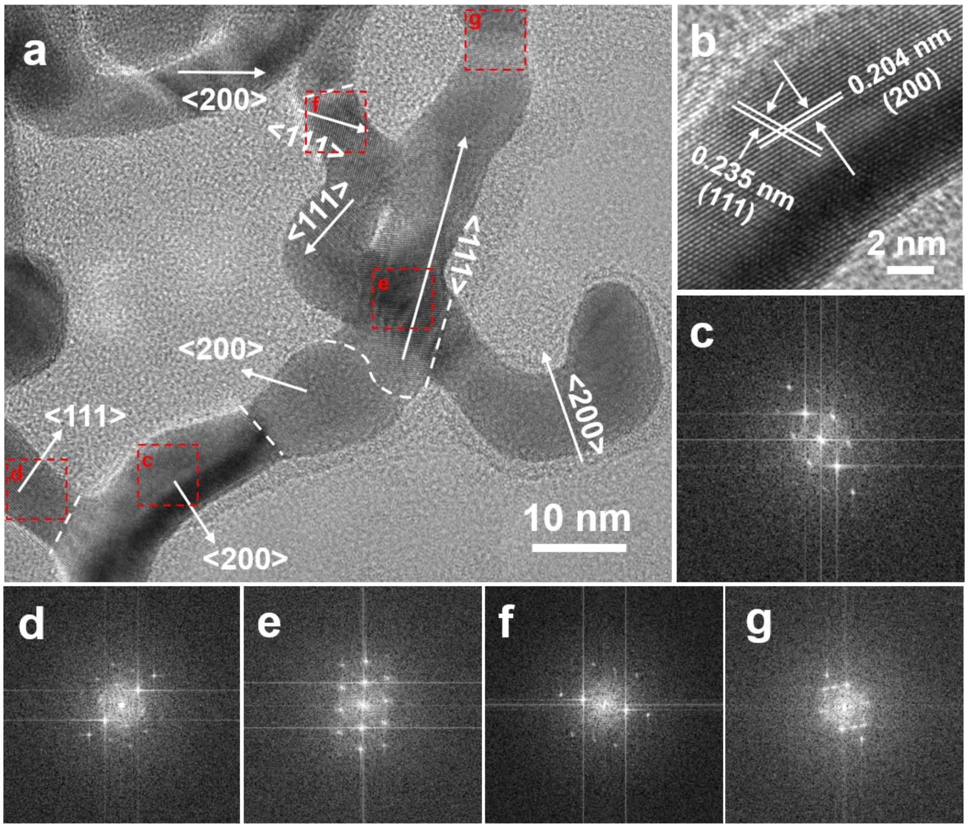

Fig. S2. HRTEM images of (a) the seaweed-like Au nanowires scratched from the substrate, (b) a typical crystalline segment with the (111) and (200) facets labelled. (c-g) Fourier transformation patterns of the selected areas in (a). The diverse patterns indicated the various orientations of the crystalline grains in the polycrystalline nanowire.

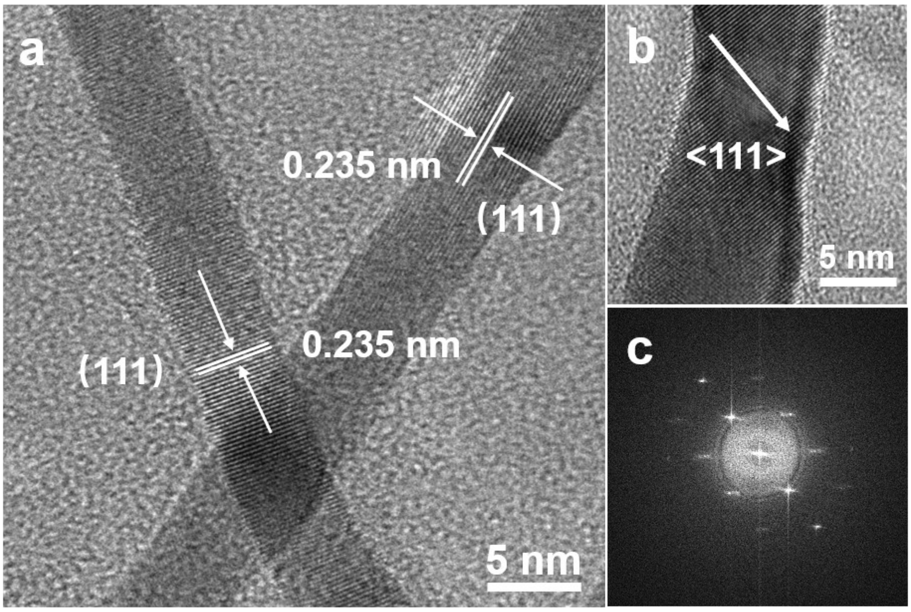

Fig. S3. HRTEM images of (a) the straight Au nanowires scratched from the substrate, (b) a typical crystalline segment with the <111> direction labelled. (c) Fourier transformation pattern of (b).

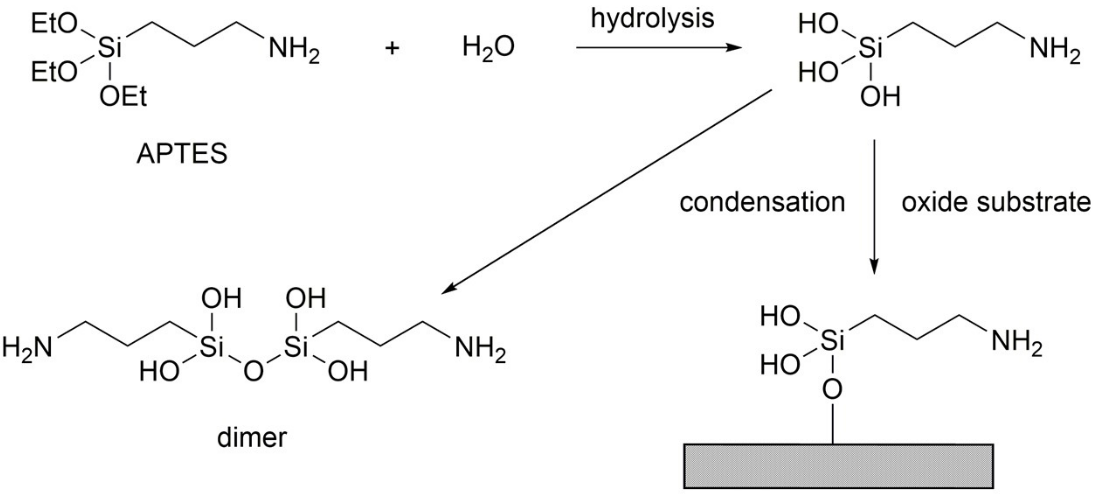

Fig. S4. The hydrolysis and condensation process of APTES.

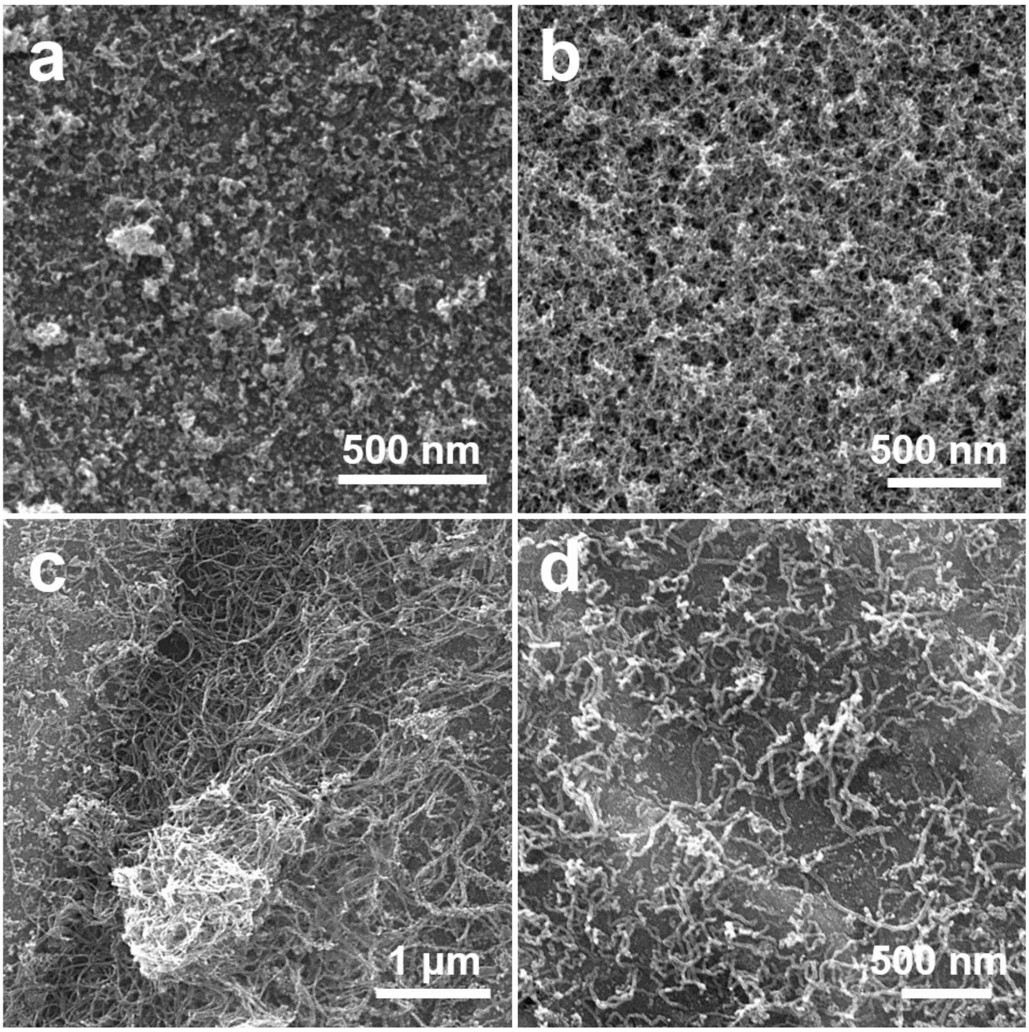

Fig. S5.SEM images of the Au nanowires and nanostructures formed by replacing the APTES treatment with (a) tetraethylorthosilicate, (b) 3-aminopropyltrimethoxysilane, (c) octadecylamine and (d) ethylenediamine.

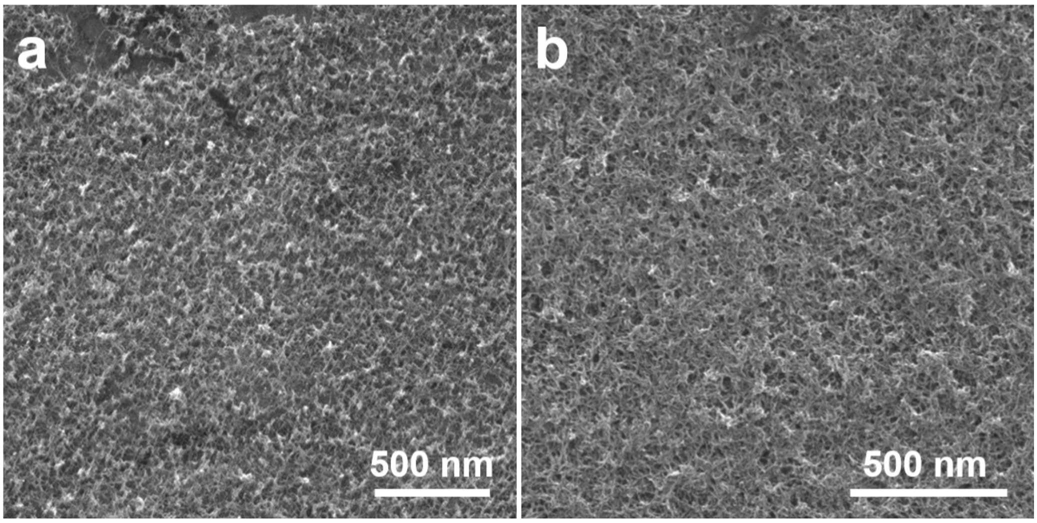

Fig. S6.SEM images of the Au nanowires formed by replacing the APTES treatment with (a) pentafluorophenyl-triethoxysilane and (b) 3-cyanopropyltriethoxysilane.

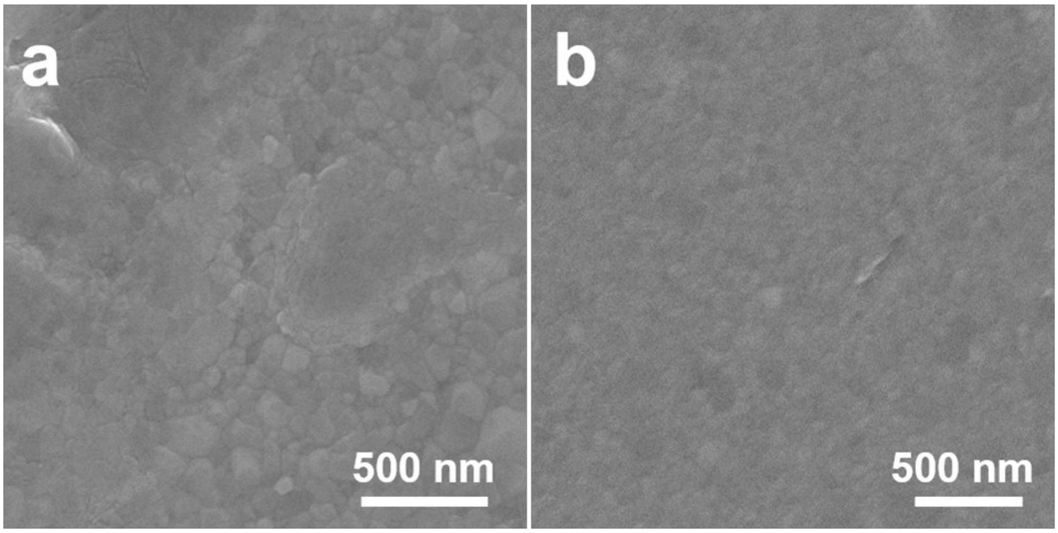

Fig. S7. SEM images of gold-plated silicon wafer (a) before and (b) after incubating in APTES (5 mM) for 1 h.

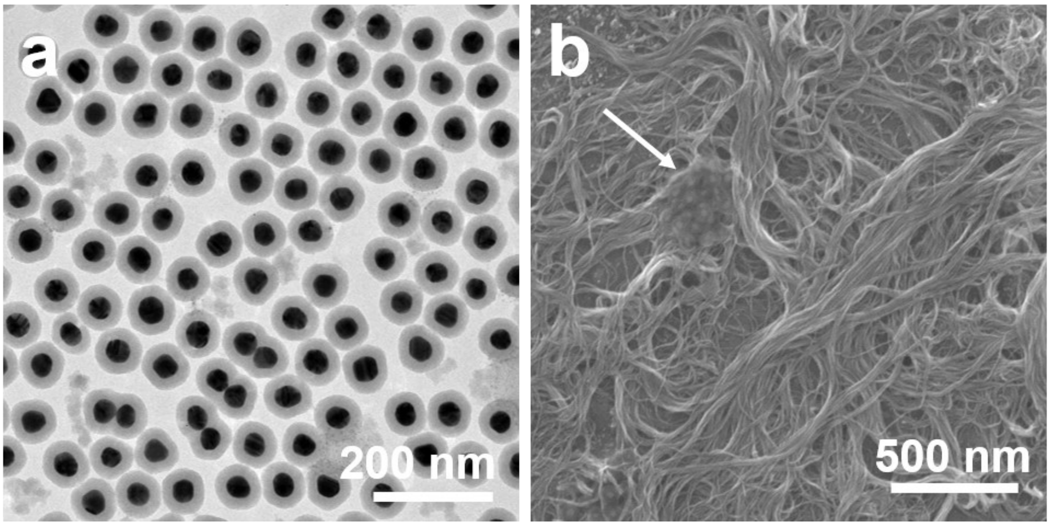

Fig. S8. (a) TEM image of the typical Au@silica nanoparticles and (b) SEM image of the ultra-long Au nanowires formed on gold-plated silicon wafer with the APTES-modified Au@silica nanoparticles. The white arrow indicates the Au@silica nanoparticles.

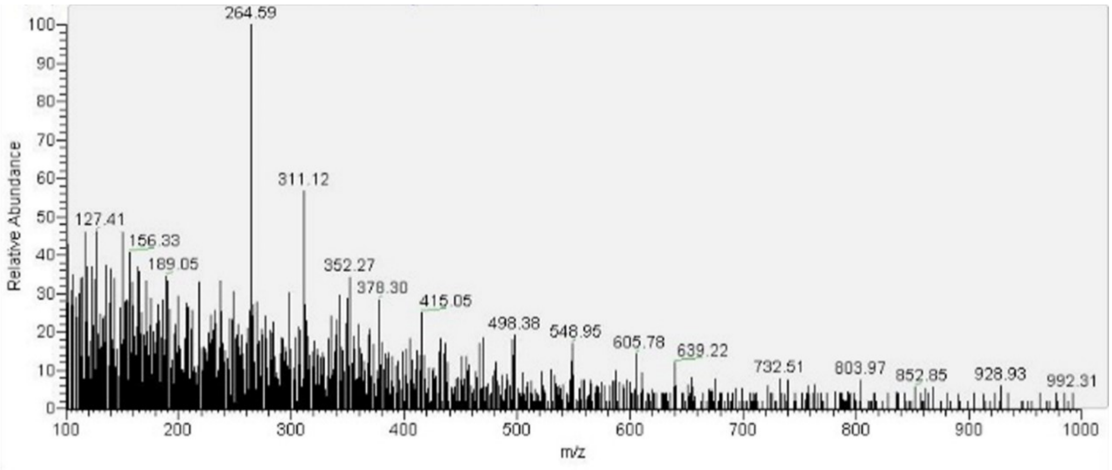

Fig. S9. Liquid chromatography-mass spectrometry (LC-MS) analysis of the species formed by incubating APTES in ethanol for 2 h. MS(m/z): The partial hydrolyzed product calculated for $C_7H_{21}NO_3Si$: [M + CH_3OH + K] $^+$ 264.37; Found 264.59. The dimerization product calculated for $C_6H_{32}N_2O_5Si_2$: [M + CH_3OH + Na] $^+$ 311.74; Found 311.12.

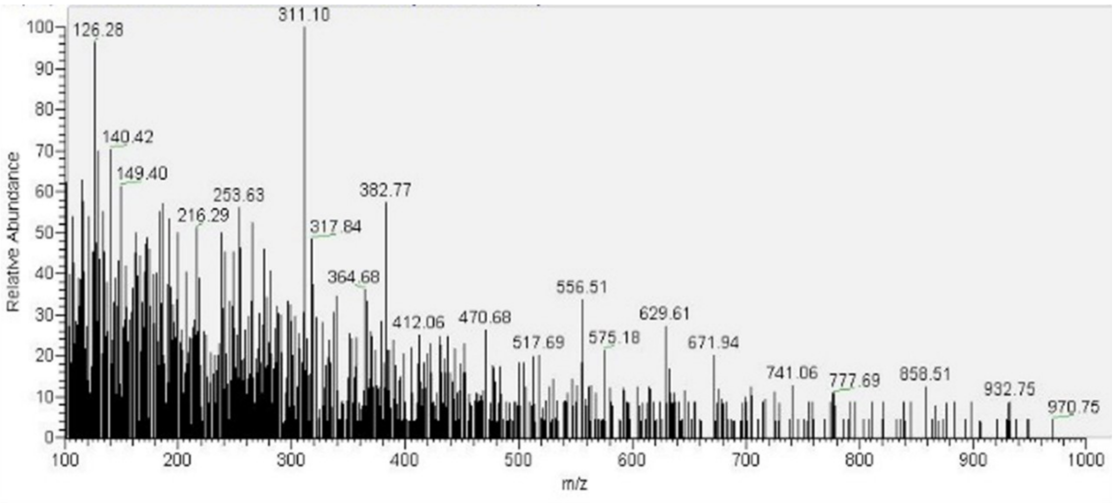

Fig. S10. Liquid chromatography-mass spectrometry (LC-MS) analysis of the species formed by incubating APTES in H_2O/ethanol mixed solvent (v/v =1:1) for 2 h. The dimerization products calculated for $C_6H_{32}N_2O_5Si_2$: [M + CH_3OH + Na] $^+$ 311.74; Found 311.10. Calculated for $C_{12}H_{38}N_2O_5Si_2$: [M + CH_3CN + H] $^+$ 382.74; Found 382.77.

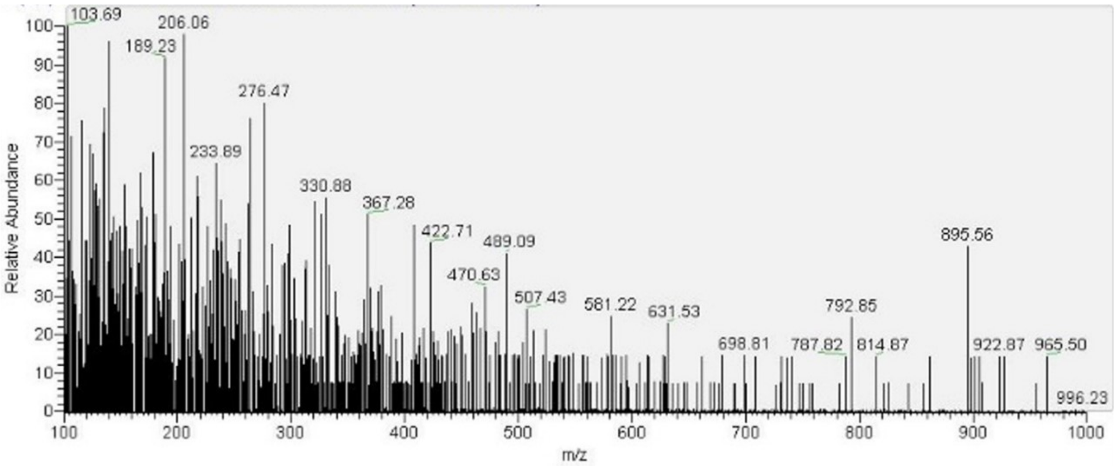

Fig. S11. Liquid chromatography-mass spectrometry (LC-MS) analysis of the species formed by incubating APTES in water for 2 h. One heptamer calculated for $C_{21}H_{107}N_7O_{15}Si_7$: $[M + CH_3CN + H]^+$ 895.59; Found 895.56.

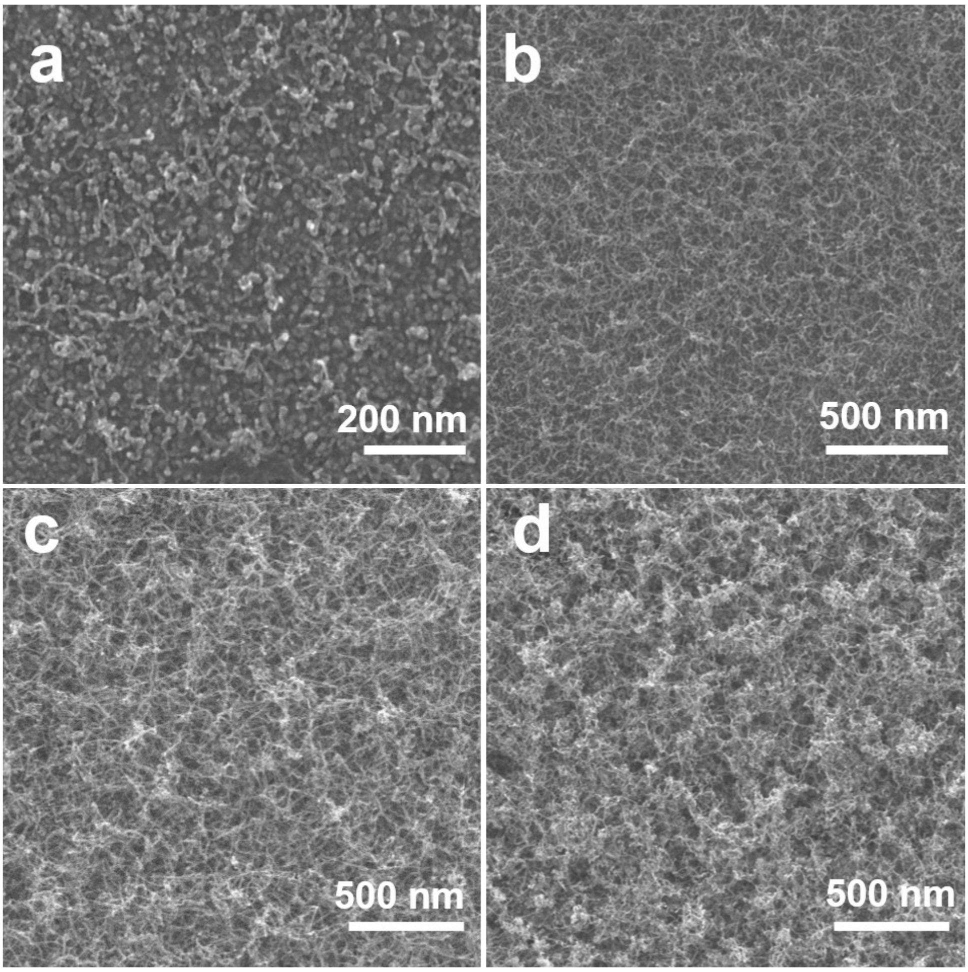

Fig. S12. SEM images of the Au nanowires formed by hydrolyzing the APTES in (a) pure ethanol, (b) H_2O: ethanol = 1:2, (c) H_2O: ethanol = 3:2 and (d) H_2O: ethanol = 9:1 mixed solvent.

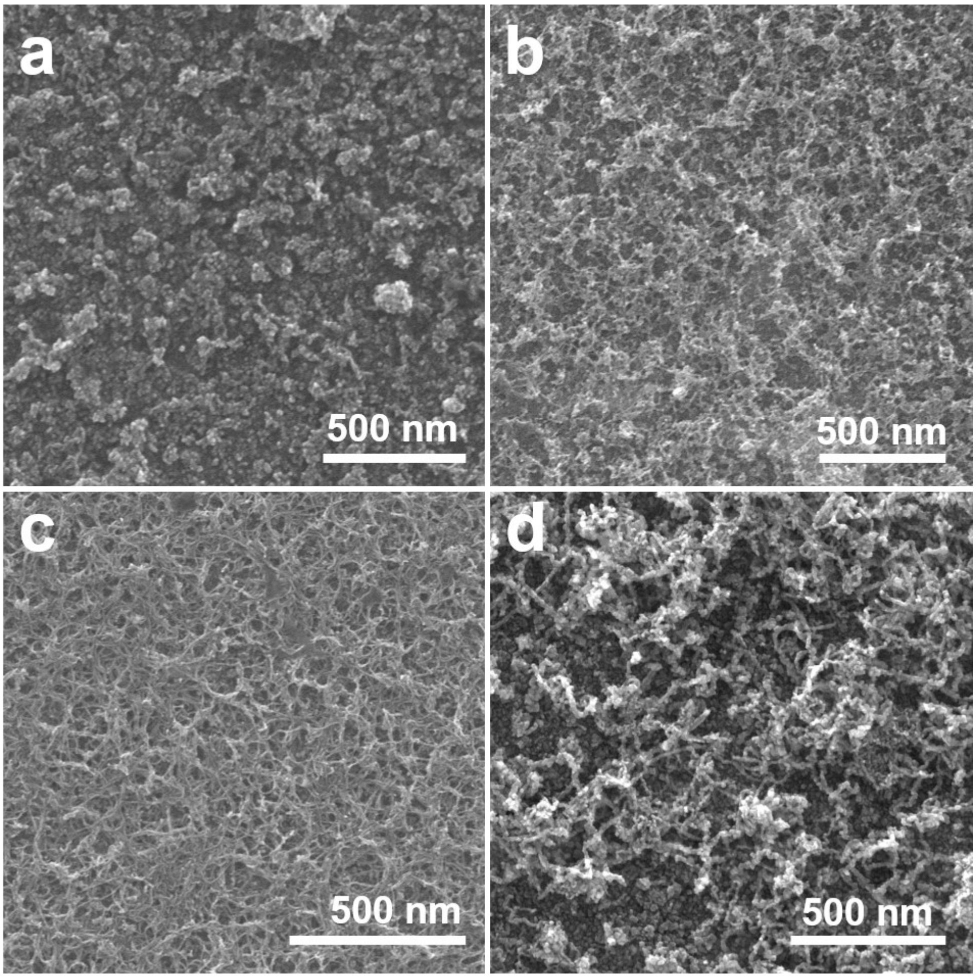

Fig. S13. SEM images of the Au nanowires formed by treating the substrate with (a) 5 μM, (b) 50 μM and (c) 5 mM of APTES solution; and (d) adjusting the pH of the APTES solution to 3.

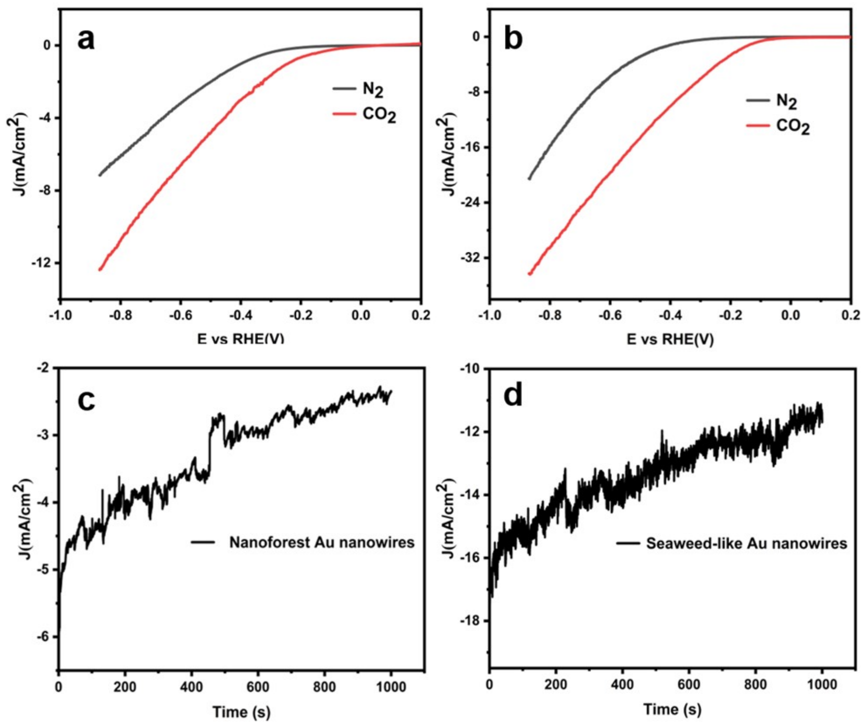

Fig. S14. Linear sweep voltammetric curves of (a) Au nanoforest and (b) seaweed-like Au nanowires in CO_2-saturated 0.5 M $KHCO_3$ solution. chronoamperometry result of (c) Au nanoforest and (d) seaweed-like Au nanowires at -0.5V vs RHE in CO_2-saturated 0.5 M $KHCO_3$ solution, the activity decay for Au nanoforest and seaweed-like nanowires is ~58.2% and ~37.8%, respectively.

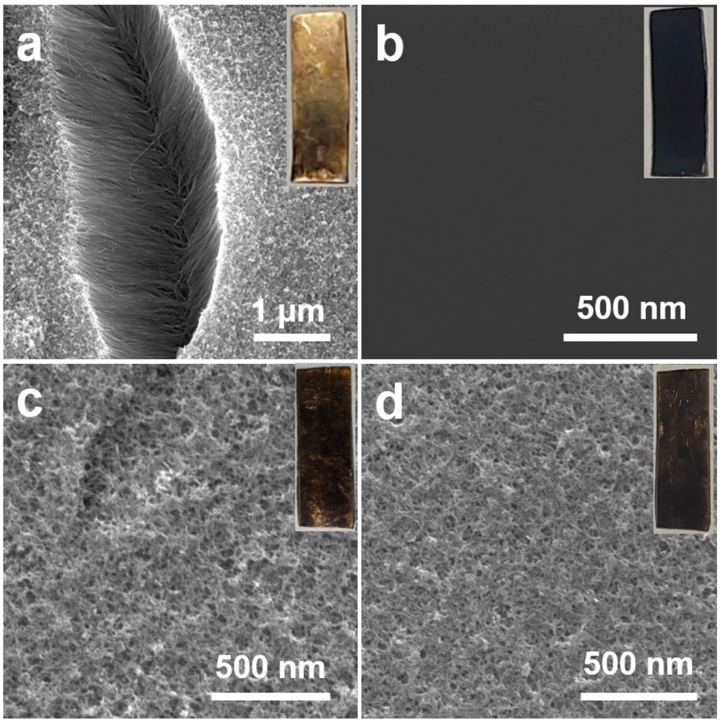

Fig. S15. SEM images and the corresponding digital graphs of the Au nanoforest and seaweed-like Au nanowires before and after stability test. (a-b) nanoforest (a) before and (b) after the stability test; (c-d) seaweed-like nanowires (c) before and (d) after the stability test.

References

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