

Supporting Information for:

Use of Triton X-114 as a Weak Capping Agent for One-Pot Aqueous Phase Synthesis of Ultrathin Noble Metal Nanowires and a Primary Study of Their Electrocatalytic Activity

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Figure S2. TEM Images of Synthesized Au, Pt and Pd Nanowire and Their Size Distribution.

Figure S3. TEM and HRTEM Image of Au NWs.

Figure S4. ^1H NMR Spectra of TX-114 and TX114/Pt NWs.

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Table S1. NMR data.

Table S2. Surface energies of low index facets of Au, Pd and Pt.

Table S3. Effects of Surfactants Species on the Preparation of Au NWs. Typical TEM Images of the Au Nanostructures Prepared by Using Different Surfactants under the Same Conditions as that Used for Preparing Au NWs with TX-114.

Table S4. Voltammetric Characteristics of Alcohols Oxidation on Glassy Carbon Electrodes Modified with Different NWs. The Scan Rate was 50 mV/s.

Materials and Chemicals

Triton N-101(reduced), Triton X-45, Triton X-114, Triton X-165 (70% in H₂O), Triton X-405 (70% in H₂O), Triton X-705 (70% in H₂O), heptaethylene glycol monododecyl ether, Pluronic P-123 (MW ~5, 800) and HClO₄ (70% in H₂O) were purchased from Sigma-Aldrich. Triton X-114 (TX-114) was purchased from Acros Organics (Geel, Belgium). Pluronic F-123 was obtained from BSAF (Ludwigshafen, Germany). PEG-400, -2000 and -6000 were purchased from Xilong Chemical Industry (Guangdong, China). Chloroauric acid (HAuCl₄), chloroplatinic acid (H₂PtCl₆), palladium chloride (PdCl₂), palladium nitrate (Pd(NO₃)₂), ethanol (ultra pure), and H₂SO₄ were supplied by Sinopharm Chemical Reagent Co. (Beijing, China). KOH was obtained from Alfa (Aesar, USA). KBH₄ was purchased from Jinke Chemical Research Institute (Tianjin, China). All the chemical are at least analytic grade, and Milli-Q water was used throughout.

Experiment

Synthesis of NWs

In a typical synthesis (*Figure S1*), proper amount of ice-colded 0.1 M KBH₄ solution was quickly injected into an ice-colded aqueous mixture of metal precursor (HAuCl₄, H₂PtCl₆ or Pd(NO₃)₂) and TX-114 placed in a septum sealed 50 mL conical flask under vigorous stirring, giving a 50 mL solution with 1 mM metal precursor, 0.5 g/L TX-114, as well as respective KBH₄ concentrations of 6, 4 and 2 mM in the preparation of Au, Pt and Pd NWs. After further stirring the mixture for 10 s at 0 °C, another 25 mg TX-114 was introduced into the flask to give a final concentration of 1.0 g/L TX-114. The obtained mixture was stirred for a few seconds and transported to a 10 mL long tapered centrifuge tube. The mixture was heated to ~35 °C and centrifuged at 1000 rpm for 10 min, the as-prepared NWs were separated into the TX-114-rich phase which was ready for use and long-term storage.

For large-scale synthesis of these NWs, the same experimental procedure as above was used except that the quantities of reagents were enlarged 10 times accordingly and the mixing stirring time after addition of KBH₄ was increased from 10 s to 1 min.

All glassware used in the preparation of colloidal nanoparticles was cleaned with freshly prepared aqua regia (*handle with care!*) and rinsed thoroughly with Milli-Q water

Transmission Electron Microscopy (TEM) and High-Resolution Transmission Electron Microscopy (HRTEM)

TEM was carried out with H-7500 (Hitachi, Japan) at 80 kV, while HRTEM was conducted on JEM-2100F (JEOL, Japan) at 200KV. The species were prepared by loading 5 μ L aliquots of the aqueous sample onto ultra-thin amorphous carbon film-coated copper grid sample holders. Excess water was removed quickly with filter paper. The size distribution of the nanoparticles and nanowires were estimated using Image-Pro plus software and Gaussian fitting. At least 100 particles or 100 sites were counted from multi-picture in each case.

UV-vis Spectrum

The UV-vis spectrum was recorded with a Beckerman Nucleic Acid/Protein Analyzer (Du 800, Beckman Coulter, Beckman, USA).

NMR spectroscopy

NMR spectra were recorded on a BRUKER ADVANCED 400 (Bruker, USA) spectrometer at 400 MHz (^1H). Chemical shifts are given in ppm relative to *DMSO-d*₆.

Electrode Preparation

A precise volume of concentrated nanowire or commercial catalyst dispersions was deposited on the polished surface of a glassy carbon electrode (3 mm i.d.). After drying in air, 3 μ L of 5 % (w/v) Nafion solution (DE 530CS, DuPont) was dipped on the surface and let to dry in the air at room temperature again. The same suspension was used for ICP-MS (Agilent 7500ce, USA) determination of the loaded amount of Au, Pd and Pt on the electrode. Quantification of NWs was conducted by measuring the metal content with ICP-MS after dissolution with aqua regia.

Cyclic Voltammetry Measurement

Electrochemical measurements were performed with a CHI 630C electrochemical analyzer (CHI Instruments, Chenhua Co., Shanghai, China). All measurements were conducted at 293K in a three-electrode cell, which includes a Ag/AgCl electrode (saturated KCl) as reference electrode, a platinum wire as counter electrode, and a modified glassy carbon (GC) electrode (3 mm in diameter) as working electrode. The methanol or ethanol electrooxidation experiments were measured in 1 M ethanol/ 1 M KOH for Pd NWs and Pd/ C catalyst, 1 M methanol/ 0.5M H₂SO₄ for Pt NWs and Pt/ C catalyst, and 0.1 M ethanol/ 0.1 M KOH for Au NWs, respectively. The scan rate was 50 mV/s, and N₂ was bubbled for 30 min prior to starting the experiments.

Results and Discussion

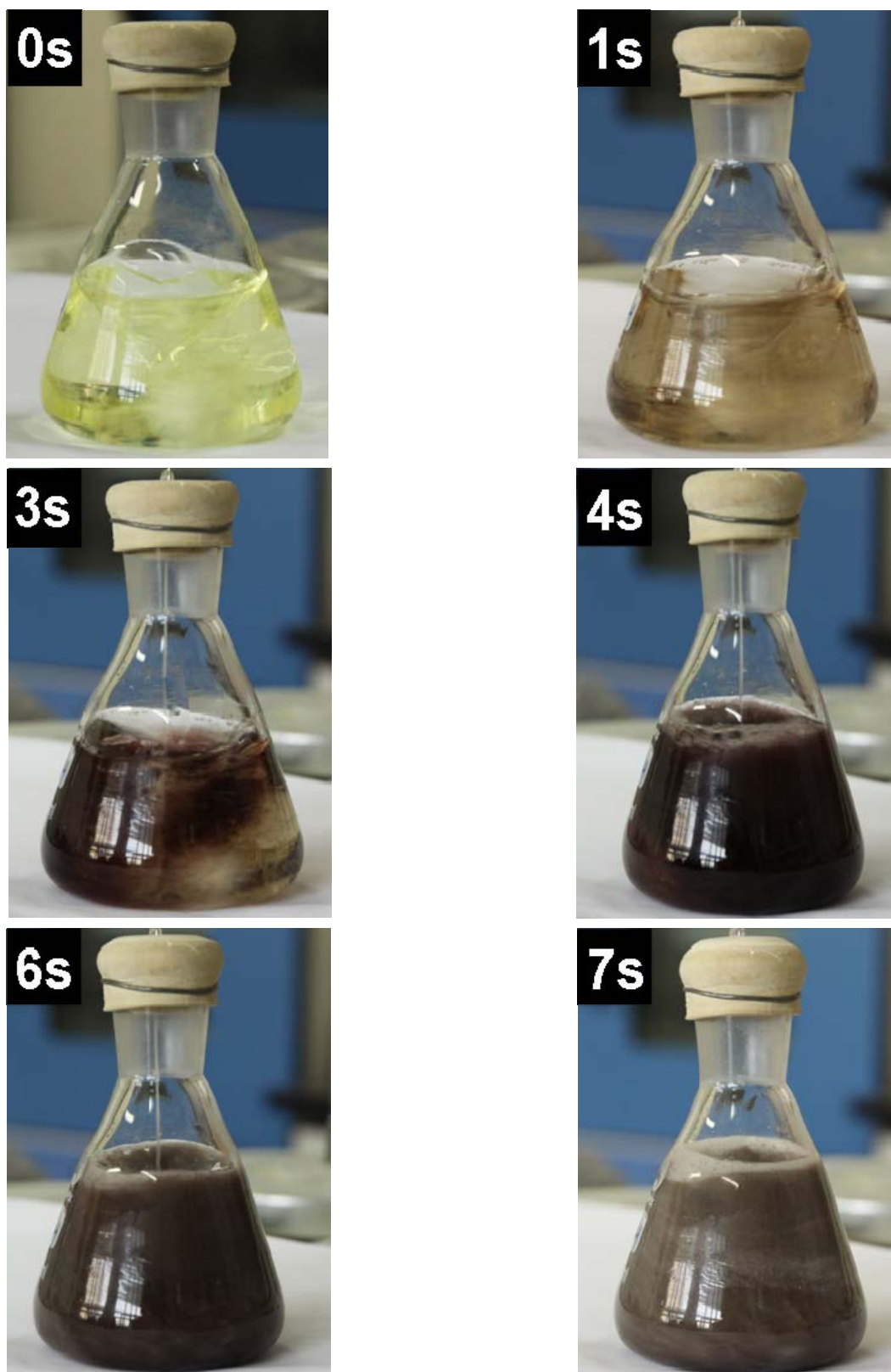


Figure S1. The photographs of color evolution of the synthesis solution from 0 to 7 second in the preparation of Au NWs. The solution color changed from light yellow (0 s, the color of HAuCl_4), brown (1 s, the color of Au cluster), red (3-4 s, the color of Au nanoparticle), dark pink (6-7 s, the color of Au NW).

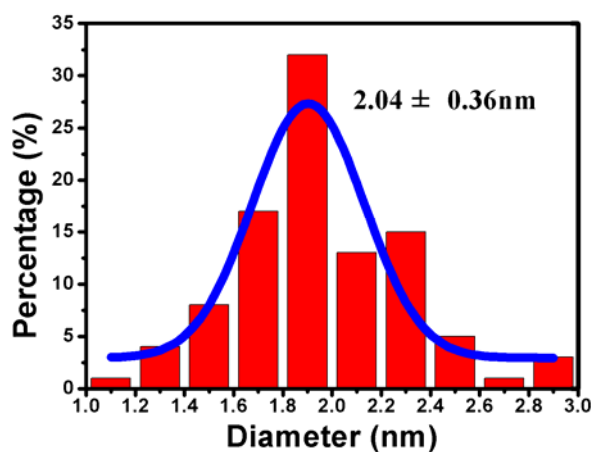
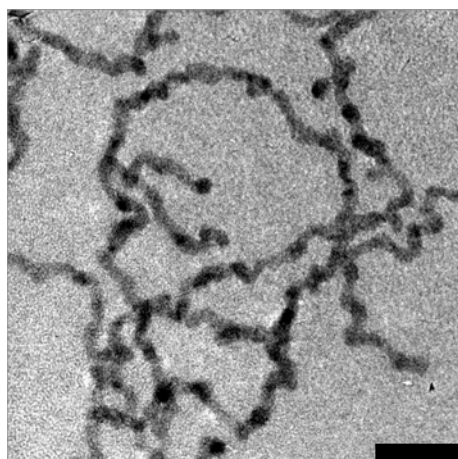
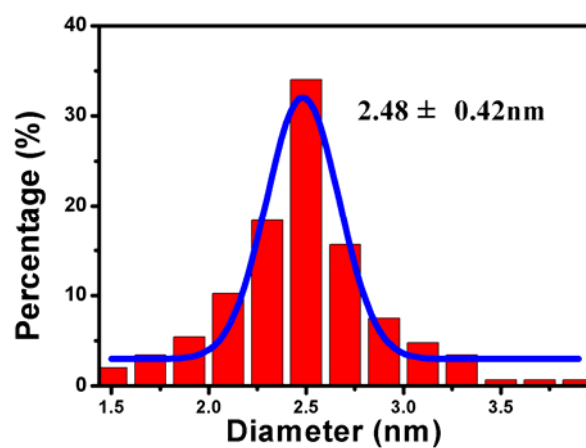
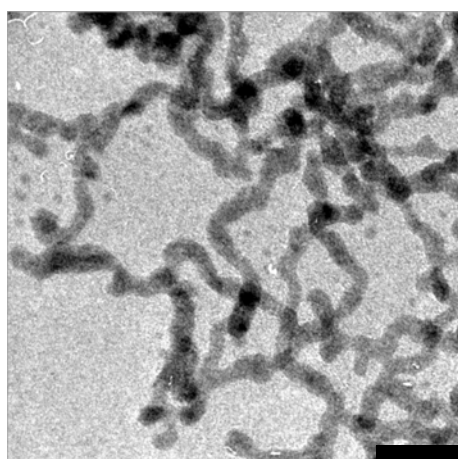
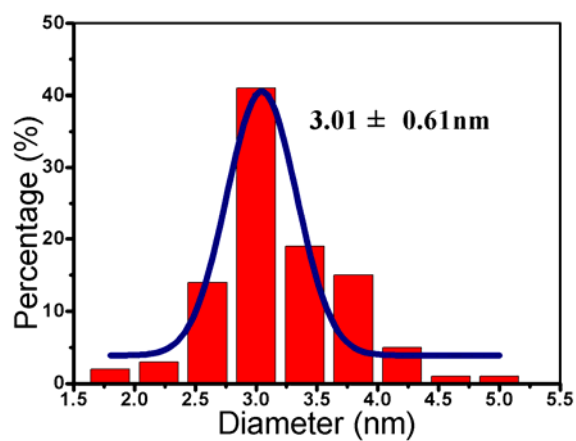
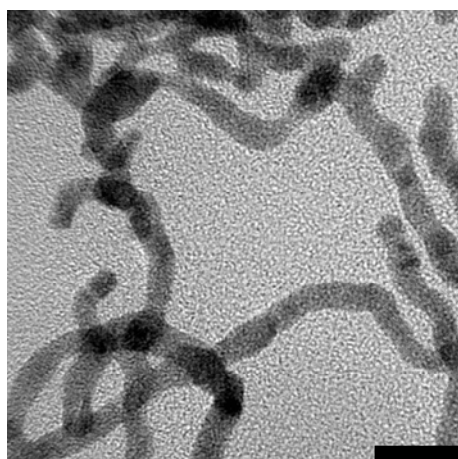


Figure S2. High resolution TEM images (left, Scale Bar is 10 nm) and size distribution (right) of the synthesized Au (upper), Pd (middle) and Pt (lower) NWs.

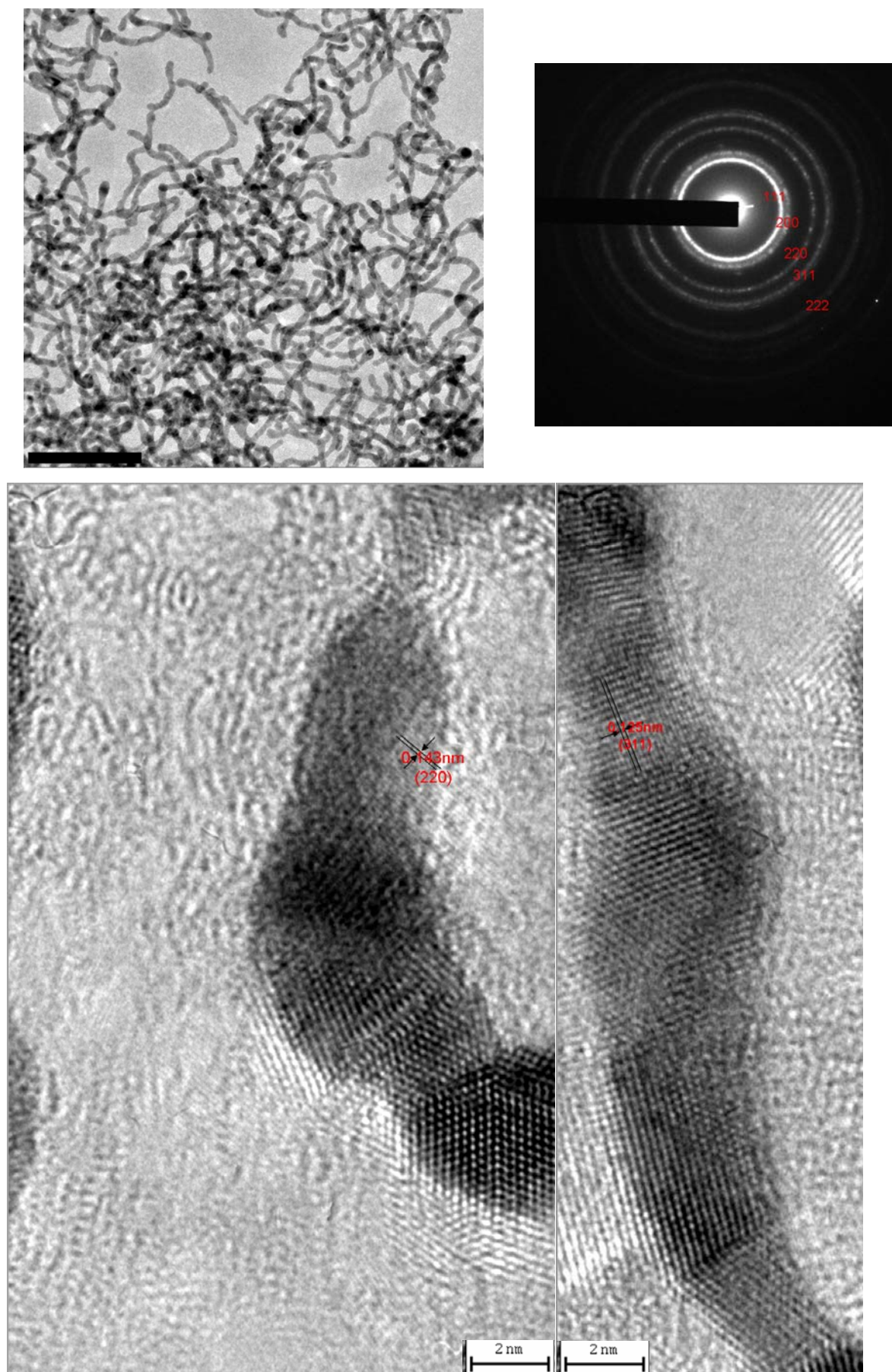


Figure S3. TEM (left upper) and its corresponding SAED patterns (left lower) and HRTEM (right) image of Au NWs. Some lattice planes can be identified as {220} and {311} facets.

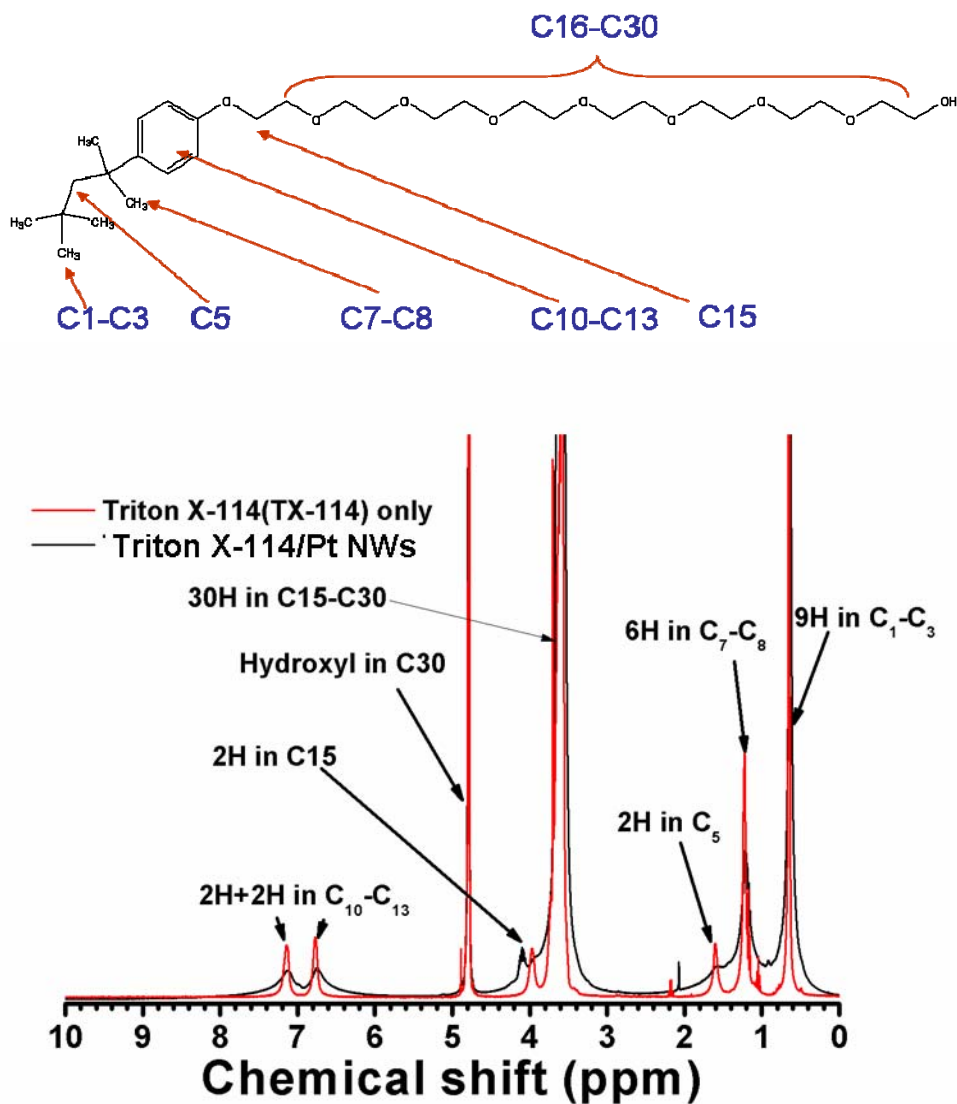


Figure S4. ^1H NMR spectra of TX-114, and TX-114/Pt NWs.

Table S1. The chemical shift and full width at half maximum (FWHM) of hydrogen atoms in TX-114

	Chemical Shift (ppm)	Carbon Number	FWHM (TX-114 only)	FWHM (TX-114 with Pt NWs)
A	0.64	Methyl (C1-C3, 9H)	6.8	16.8
B	1.223	Methyl (C7-C8, 4H)	15.6	51
C	1.601	Methylene (C5, 2H)	21	48
D	6.745	Phenyl (C10-C11, 2H)	24	108
E	7.121	Phenyl (C12-C13, 2H)	28	116
F	3.957/4.080	Methylene (C15, 2H)	32.8	31.2
G	3.52-3.70/3.56-3.66	Methylene (C16-C30, 30H)	-	-
H	4.788	Hydroxyl (C28, 1H)	3	8

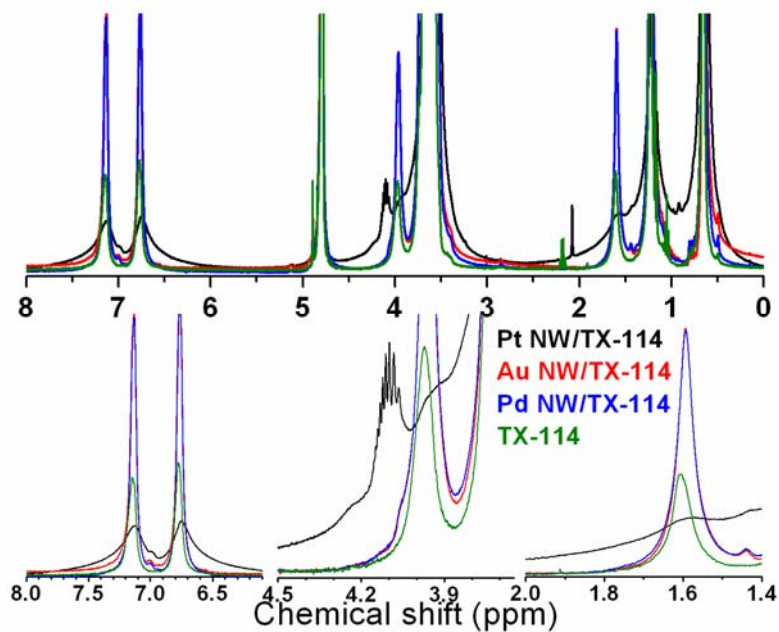


Figure S5. ^1H NMR spectra of TX-114, Pt NWs/TX-114, Pd NWs/TX-114 and Au NWs/TX-114.

Table S2 Surface energies of the low index facets of Au, Pd and Pt.

Cited from L. Vitos, A. V. Ruban, H. L. Skriver, J. Kollar, *Surf. Sci.* 1998, **411**, 186.

Metal	facet	Surface energy (ev/atom)
Au	(111)	0.611
	(100)	0.895
	(110)	1.321
Pd	(111)	0.824
	(100)	1.152
	(110)	1.559
Pt	(111)	1.004
	(100)	1.378
	(110)	2.009

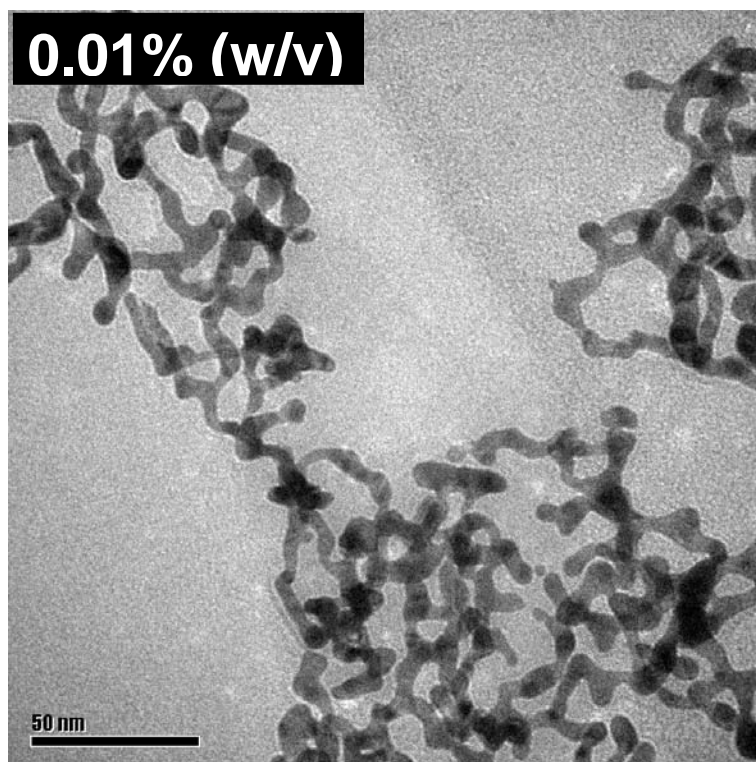


Figure S6. TEM images of Au NWs synthesized with concentration of TX-114 (0.01%, w/v) lower than its critical micelle concentration (0.012%, w/v).

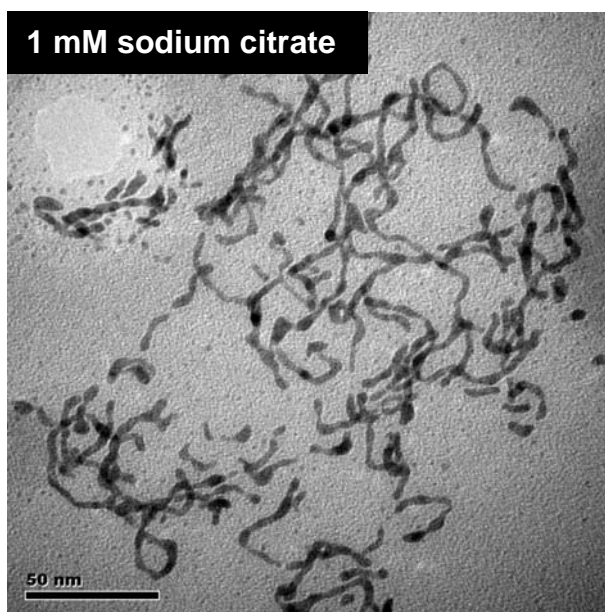
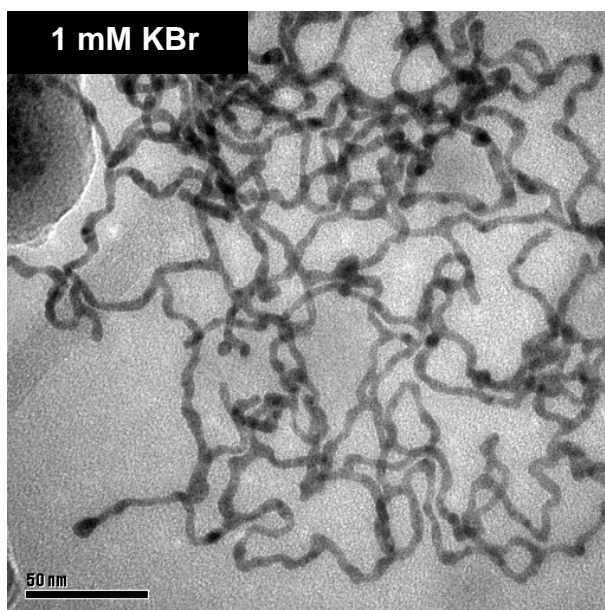
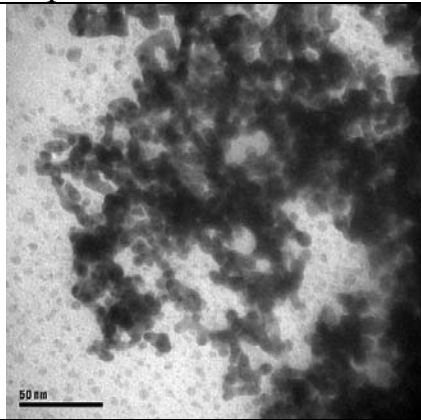
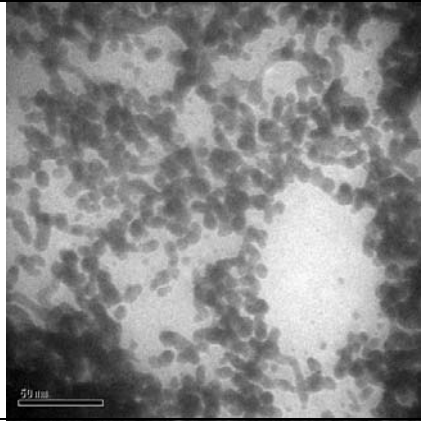
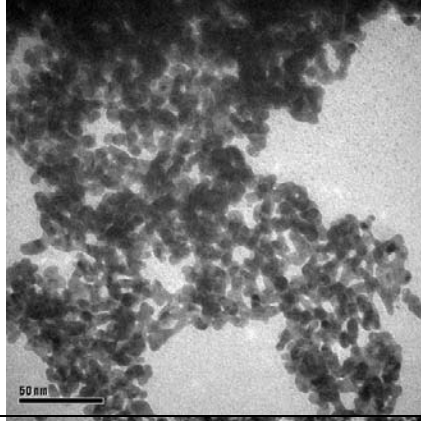
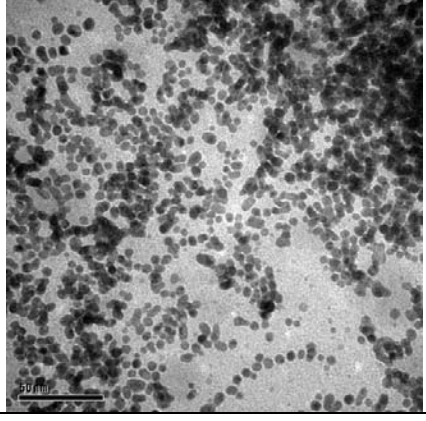
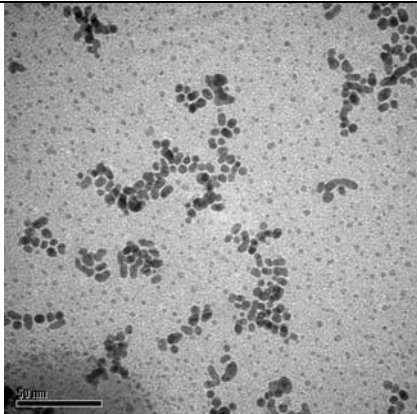
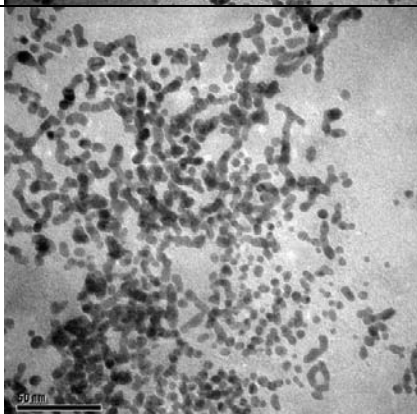
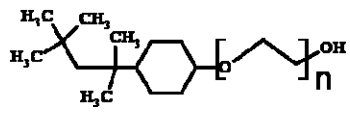
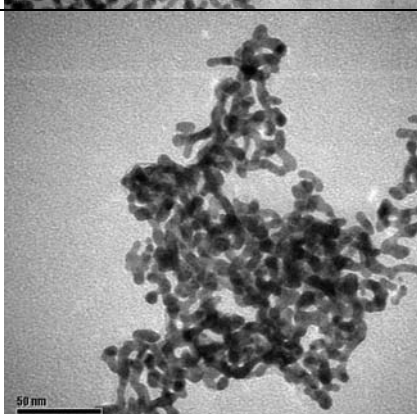
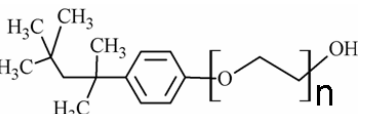
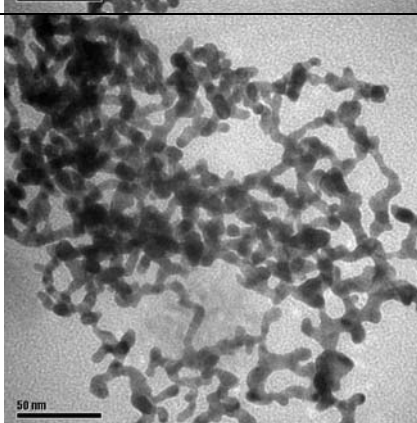
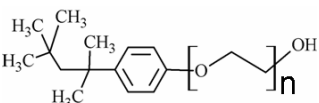
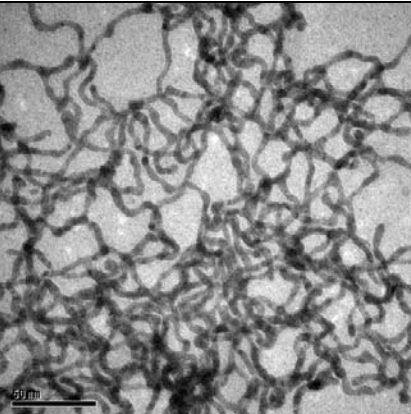
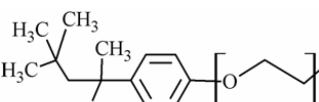
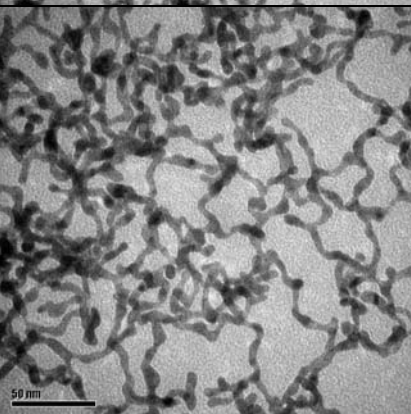
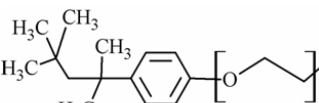
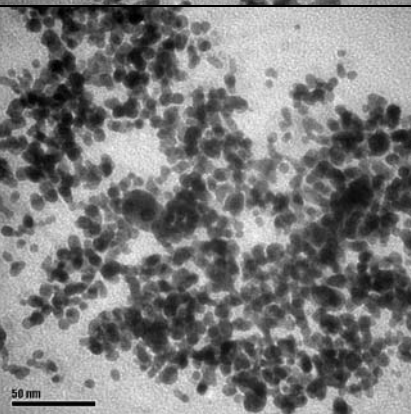
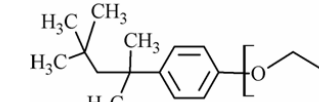
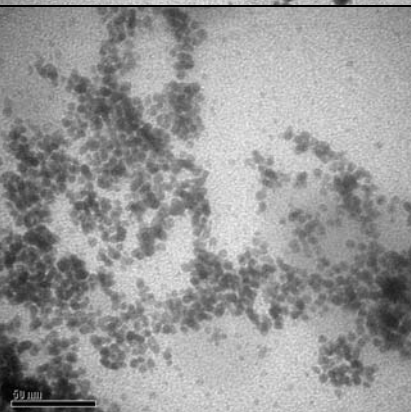


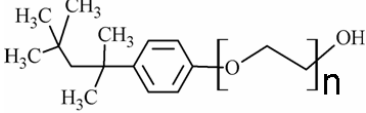
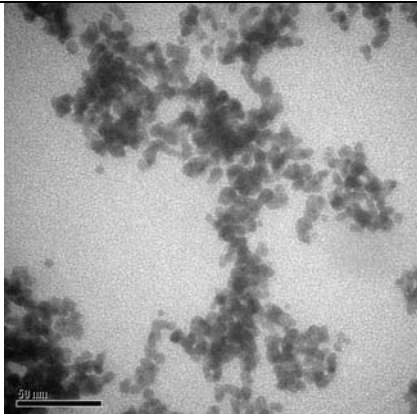
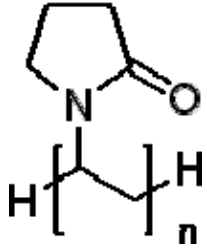
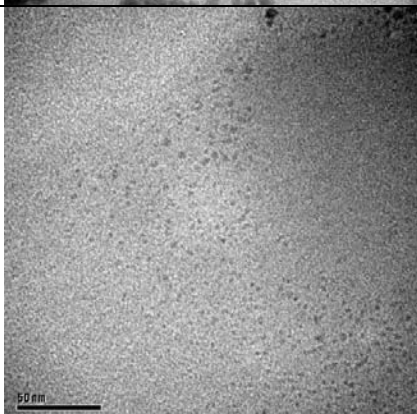
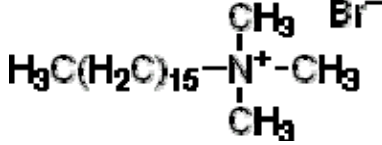
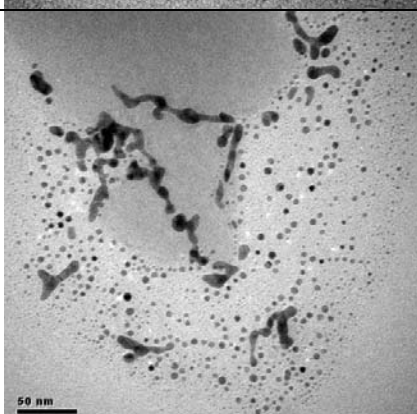
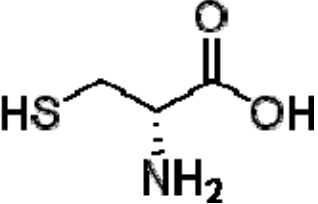
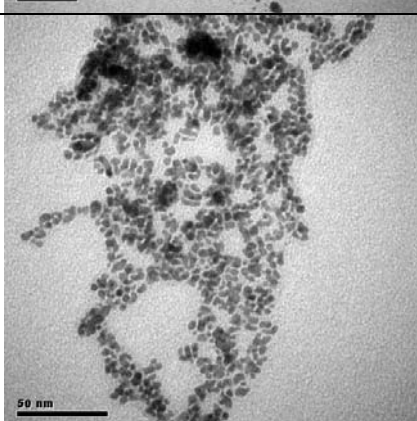
Figure S7. Effect of KBr and Sodium Citrate on the final morphology of the as-synthesized Au nanostructures.

Table S3. Effects of surfactants species on the preparation of Au NWs. Typical TEM images of the Au nanostructures prepared by using different surfactants under the same conditions as that used for preparing Au NWs with TX-114.

Surfactant/stabilizer	Surfactant structure	Experimental result
PEG400	$\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ MW \approx 400	
PEG2000	$\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ MW \approx 2000	
PEG6000	$\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$ MW \approx 6000	
Pluronic P-123	$\text{PEO}_{96}\text{PPO}_{70}\text{PEO}_{96}$ MW \approx 5800	

<p>F-127</p>	<p>PEO₁₀₀PPO₆₅PEO₁₀₀</p>	
<p>Heptaethylene glycol monododecyl ether</p>	<p>C₁₂H₂₅(OCH₂CH₂)₇OH</p>	
<p>Triton N-101</p>	 <p>n = 9~10</p>	
<p>Triton X-45</p>	 <p>n ≈ 4.5</p>	

<p>Triton X-114</p>	<p> $n \approx 7.5$</p>	
<p>Triton X-100</p>	<p> $n \approx 9.5$</p>	
<p>Triton X-165</p>	<p> $n \approx 16$</p>	
<p>Triton X-405</p>	<p> $n \approx 35$</p>	

<p>Triton X-705</p>	 <p>$n \approx 55$</p>	
<p>Polyvinylpyrrolidone (PVP)</p>		
<p>Hexadecyltrimethylamm onium bromide (CTAB)</p>		
<p>Cysteine</p>		

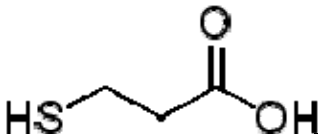
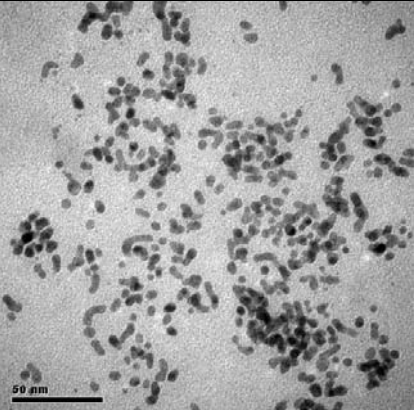
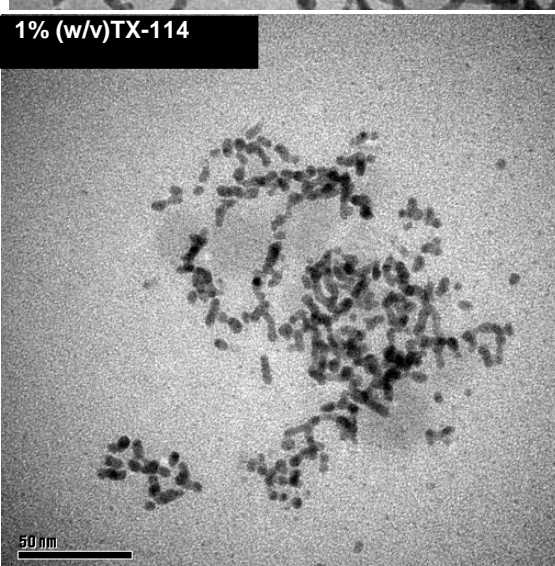
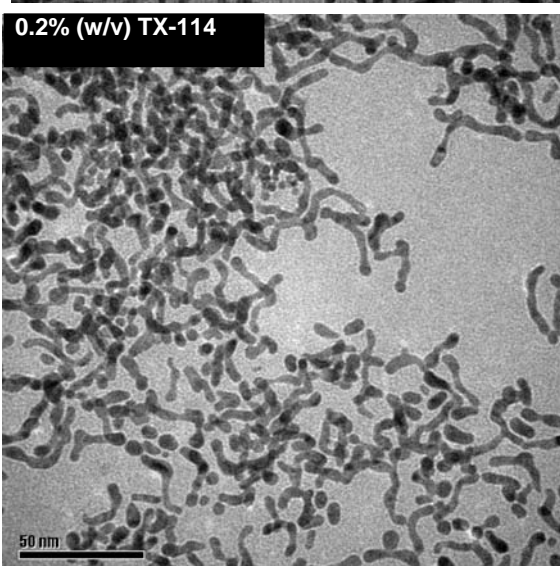
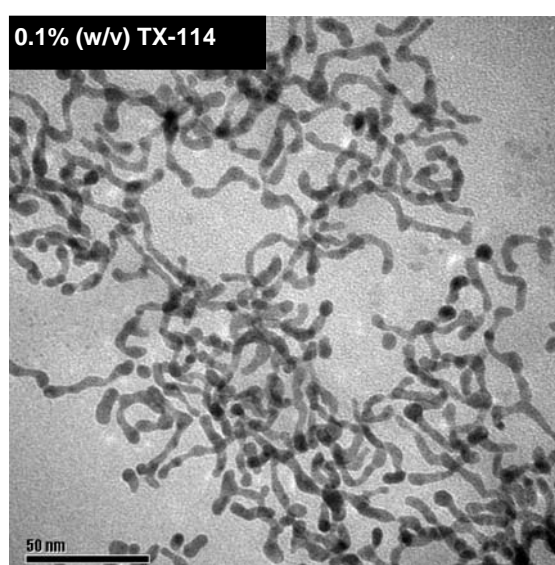
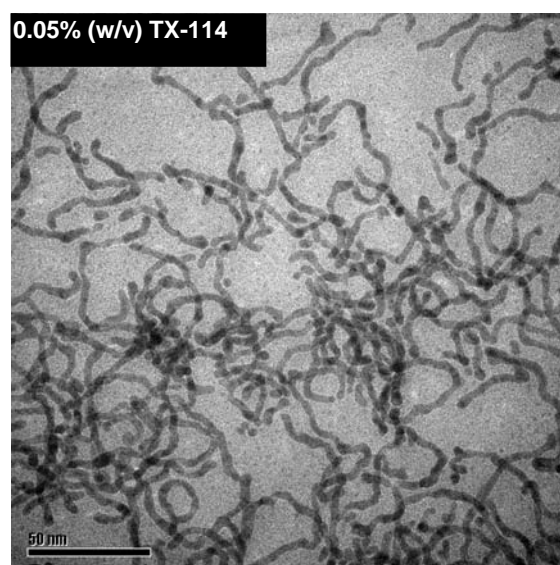
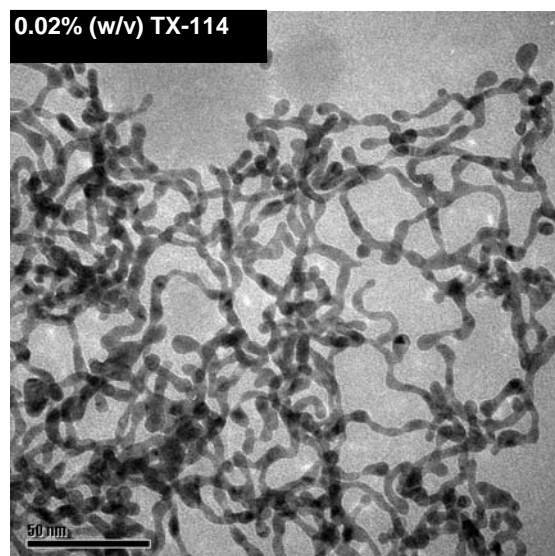
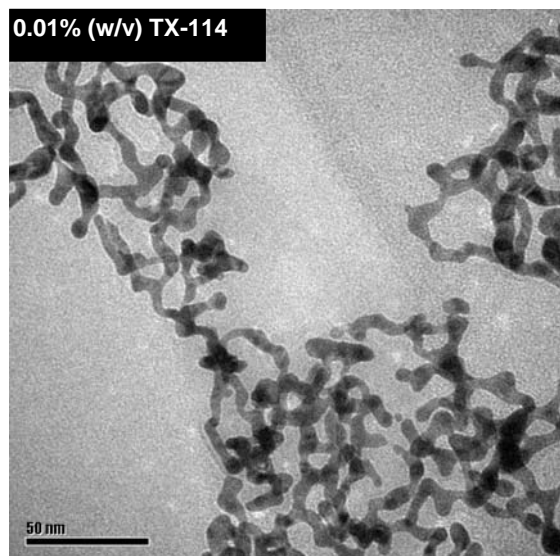
<p>Mercaptopropionic acid (MPA)</p>	 <chem>SCCC(=O)O</chem>	 <p>50 nm</p>
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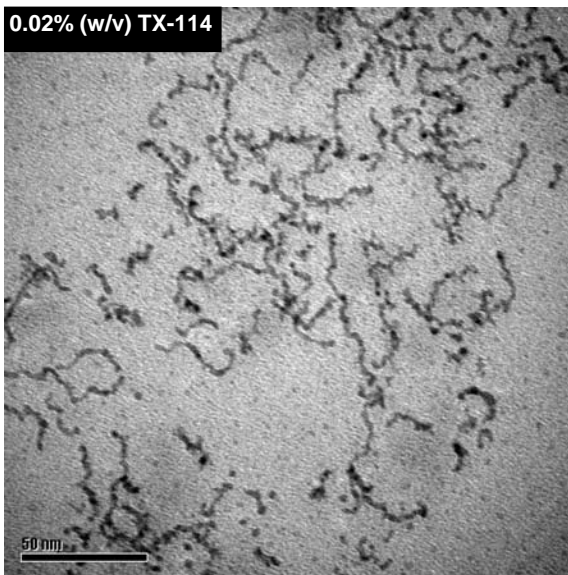
Figure S8. Effect of TX-114 concentration on the morphology of as-prepared nanostructure.

Au nanostructure

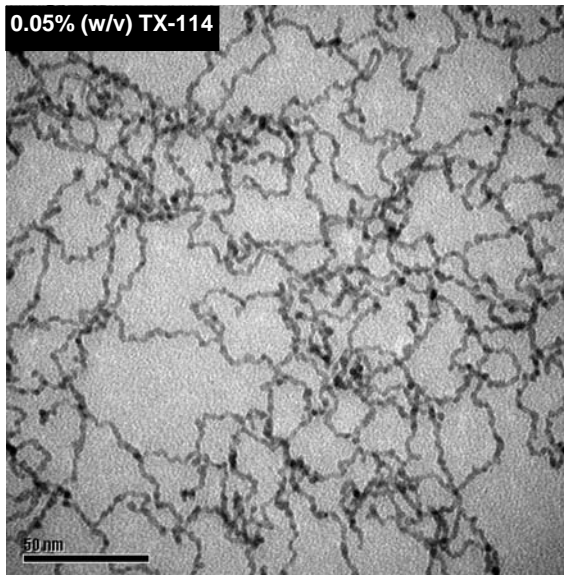


Pt Nanostructure

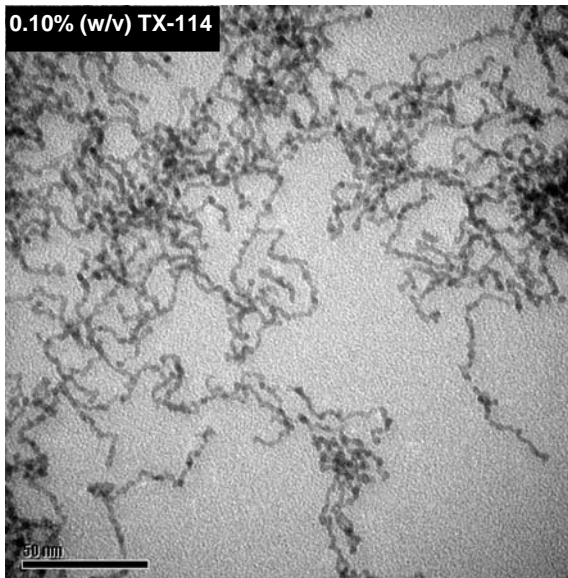
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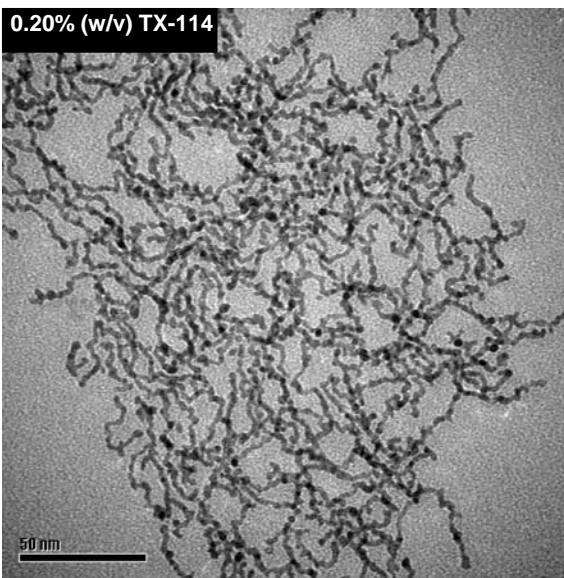
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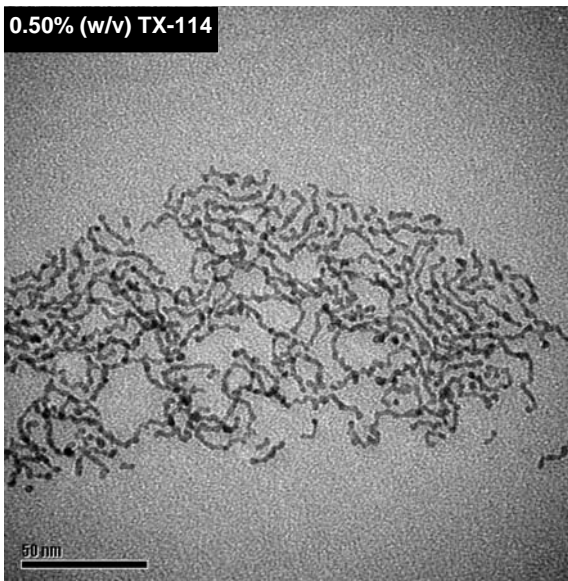
0.10% (w/v) TX-114



0.20% (w/v) TX-114



0.50% (w/v) TX-114



1% (w/v) TX-114

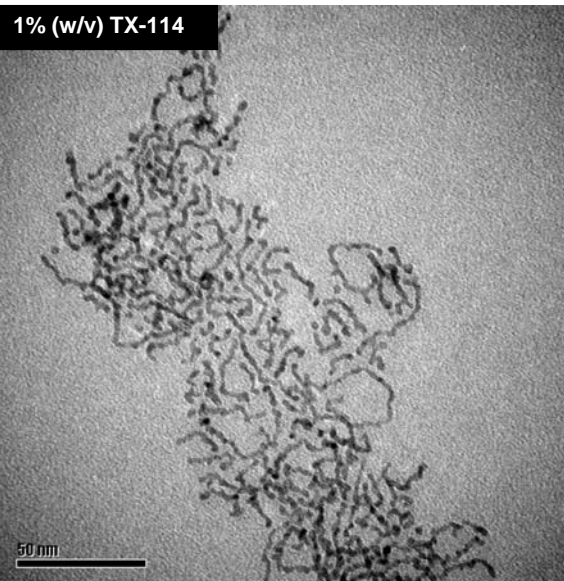
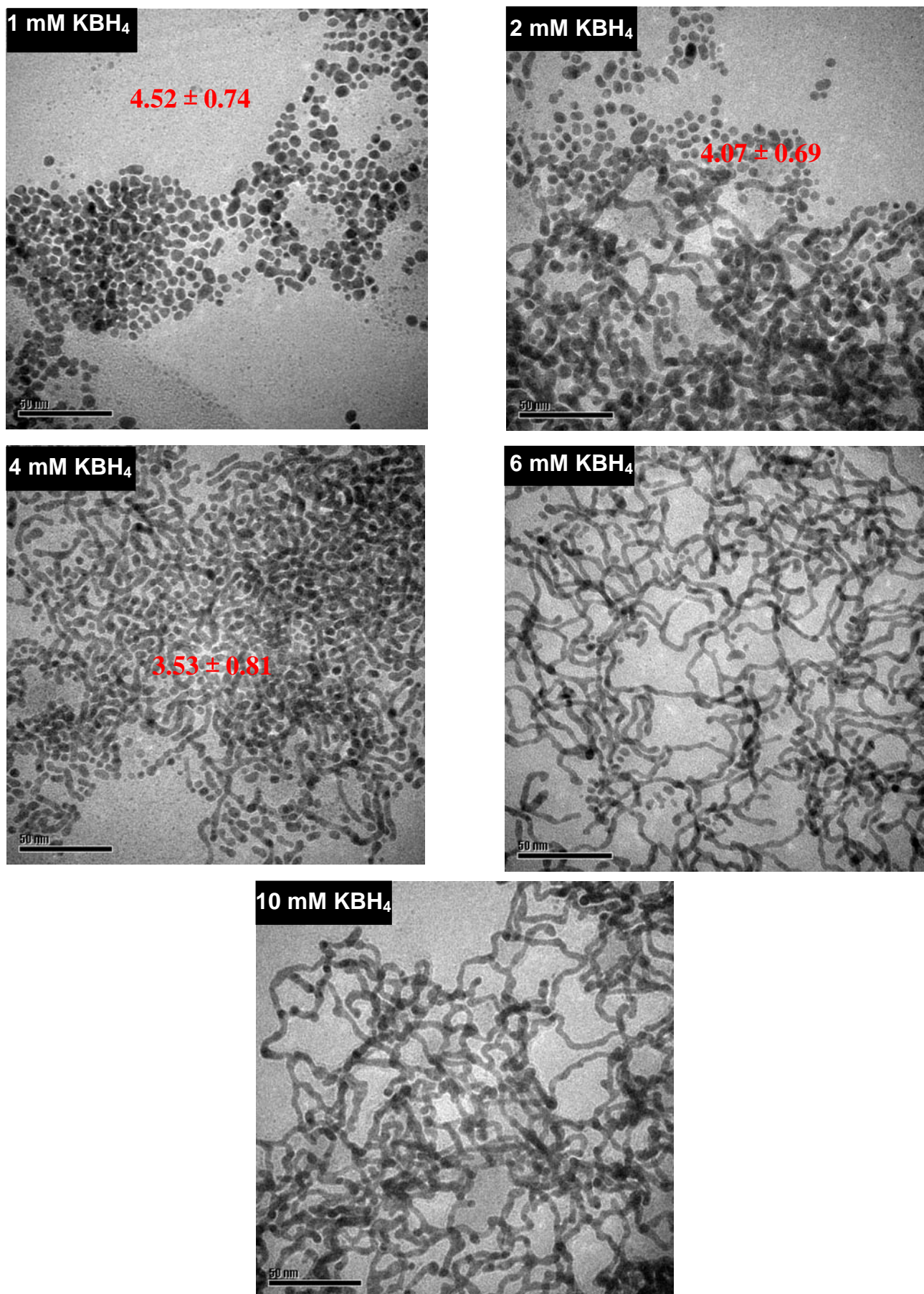
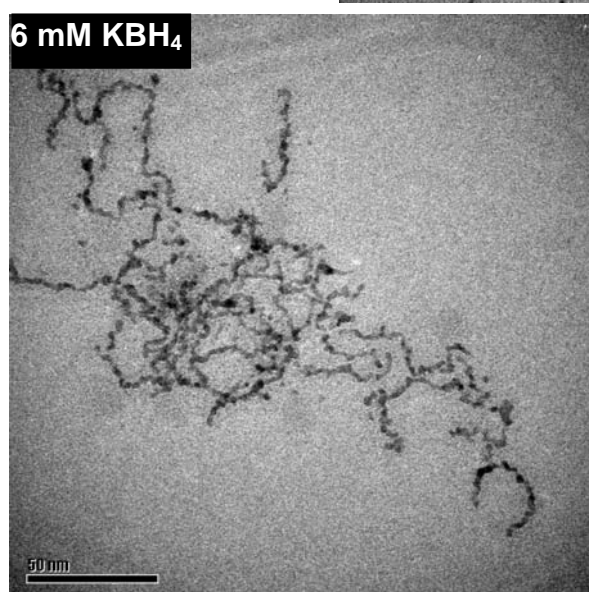
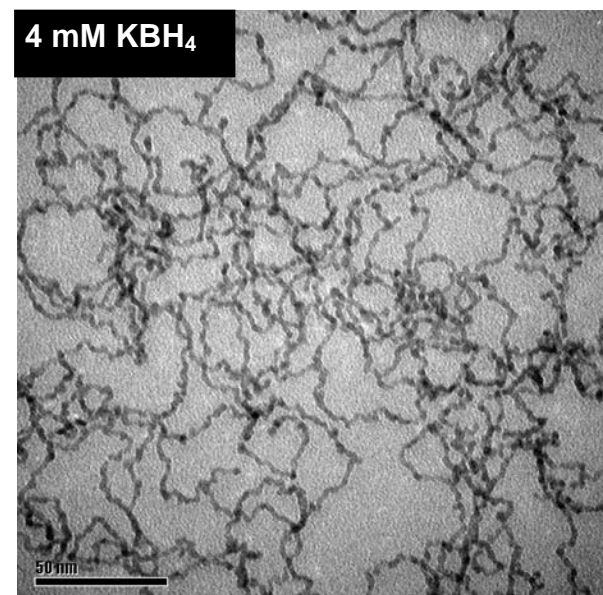
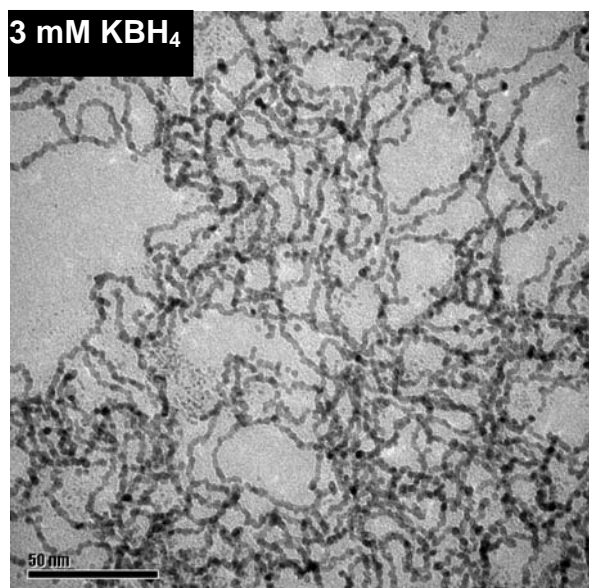
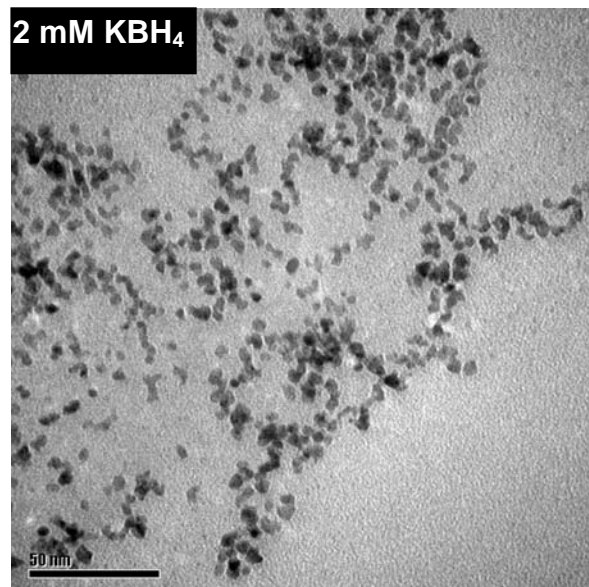
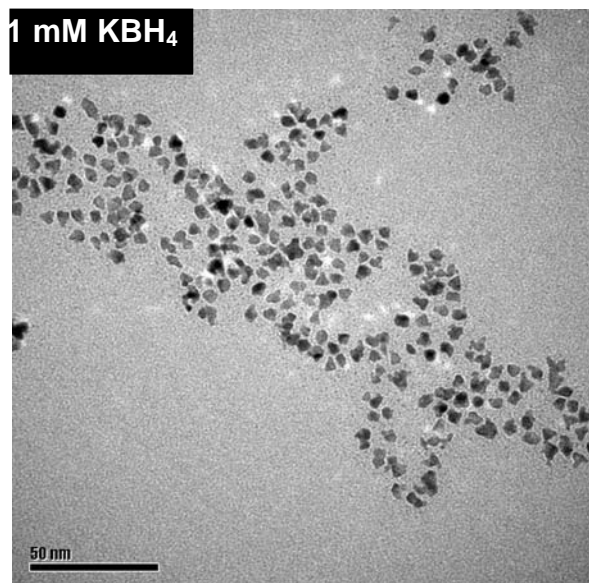


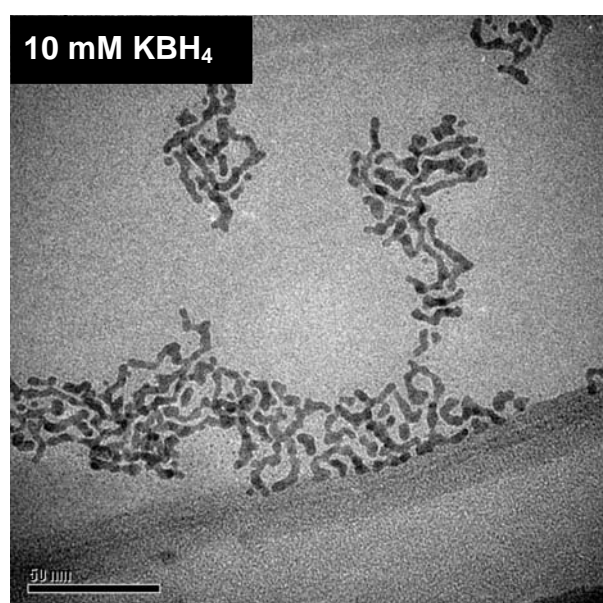
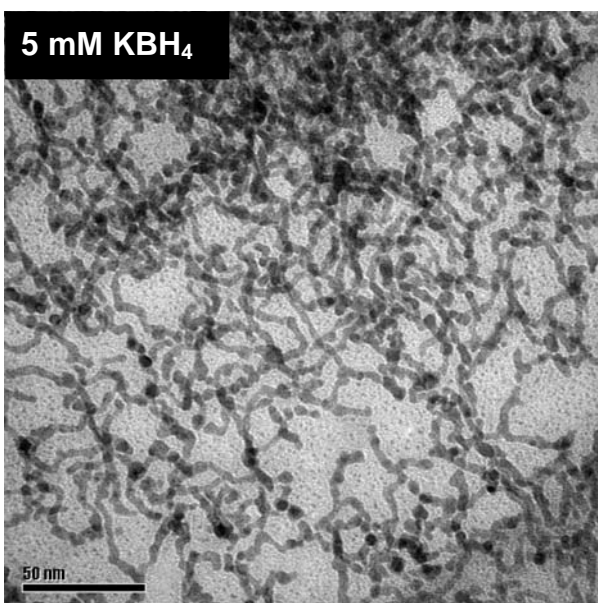
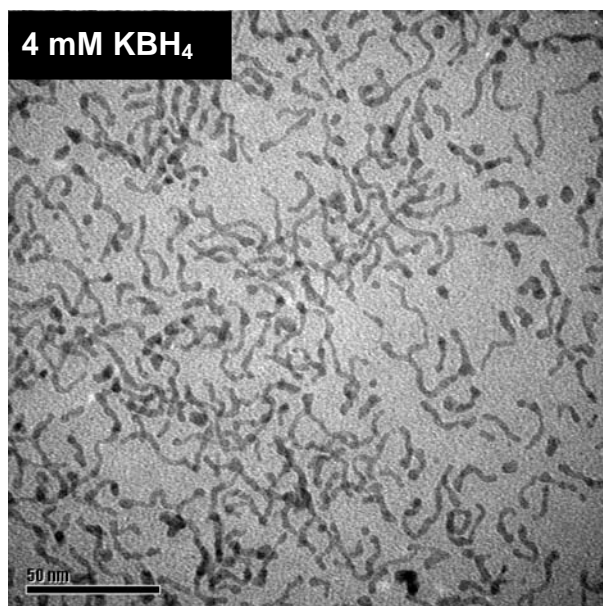
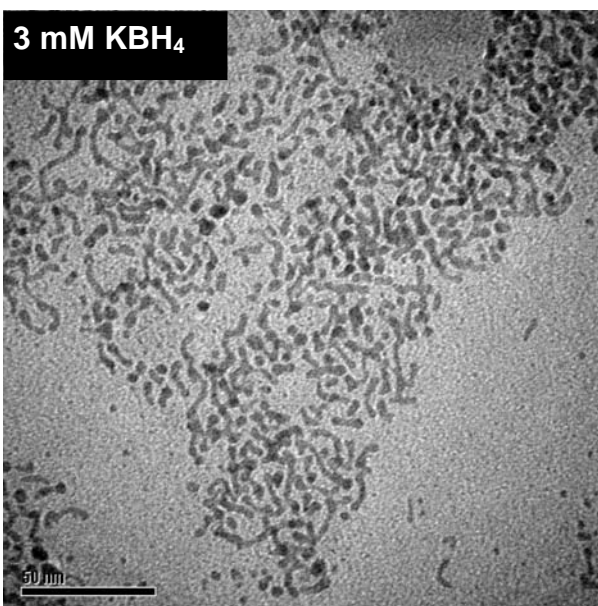
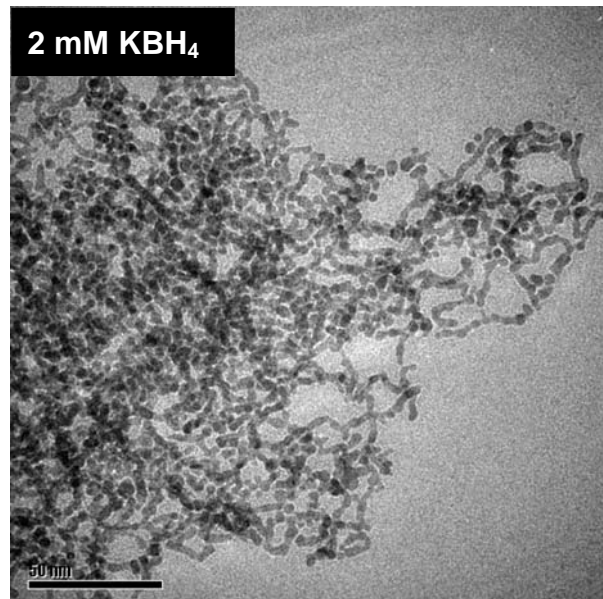
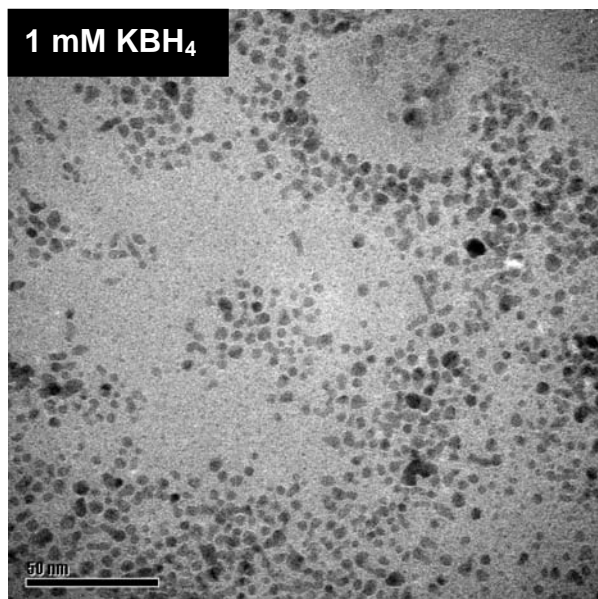
Figure S9. Effect KBH_4 concentration on the morphology of the ss-prepared nanostructure.
Au nanostructure



Pt nanostructure



Pd nanostructure (H_2PdCl_4 as precursor)



Pd nanostructure (Pd (NO₃)₂ as precursor)

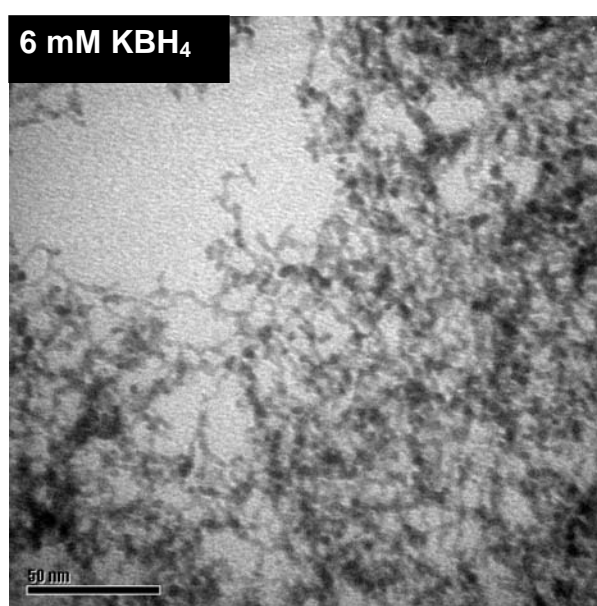
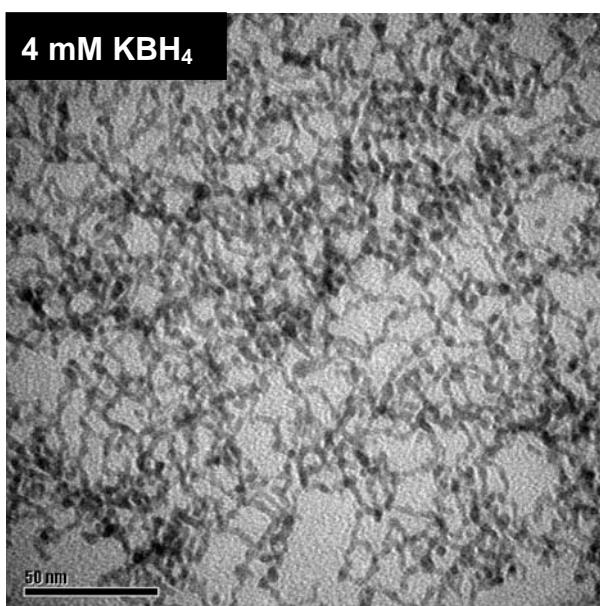
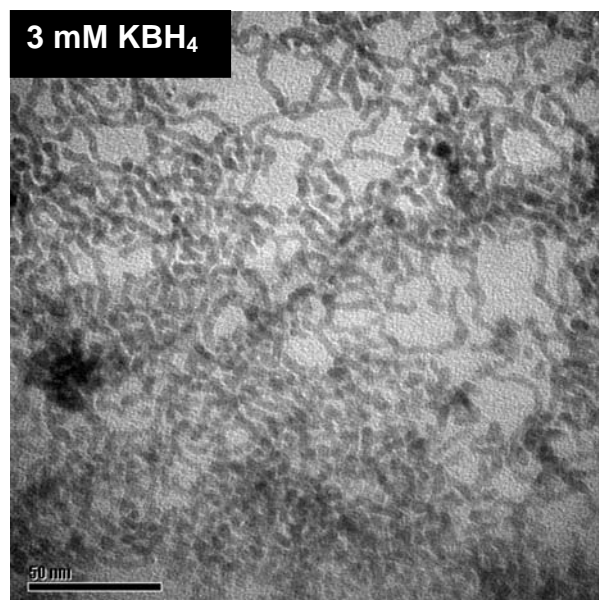
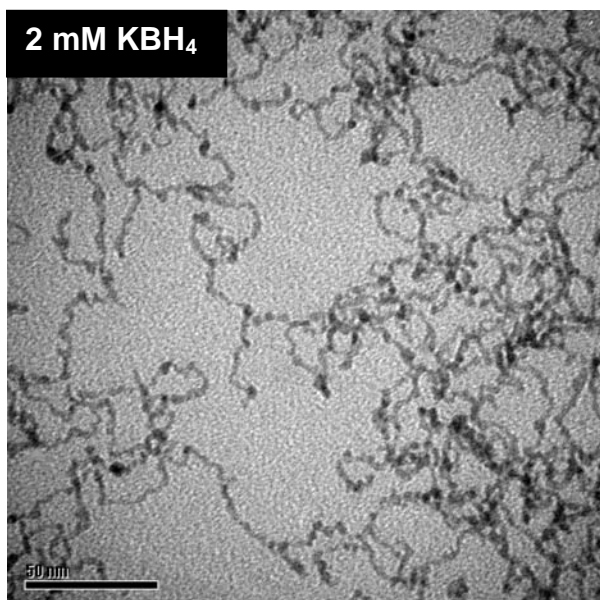
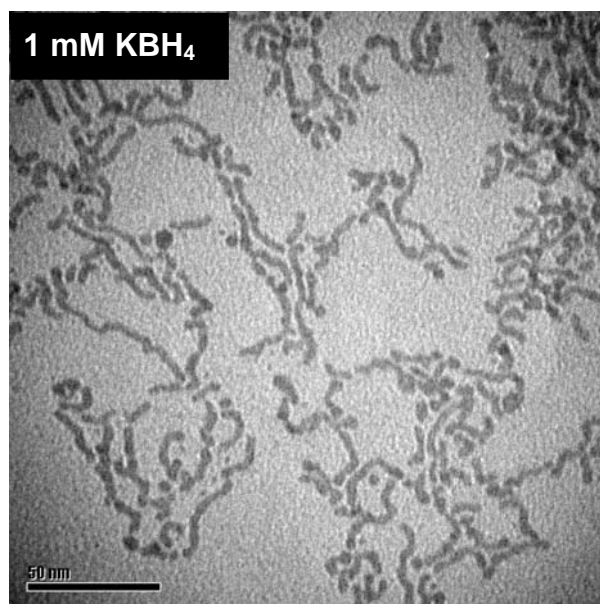
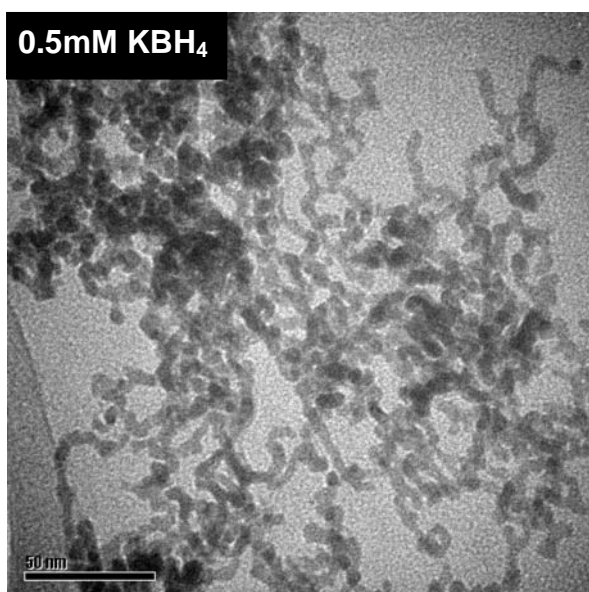


Figure S10. Transformation of Au NPs into NWs by addition of KBH_4 into the Au NP solution pre-prepared by KBH_4 Reduction. The Solution Color Changed from Red to Brick Red Immediately and then Gray. A) Au Nanostructure Synthesized by Reduction 1 mM HAuCl_4 with 1 mM KBH_4 in the Presence of 0.5 g/L TX-114; B) Au Nanostructure Synthesized by Adding 5 mM KBH_4 to A.

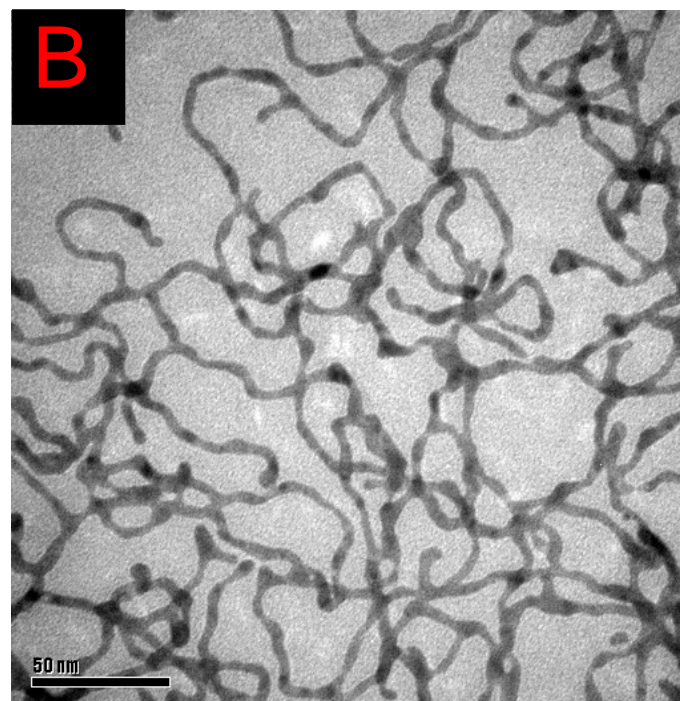
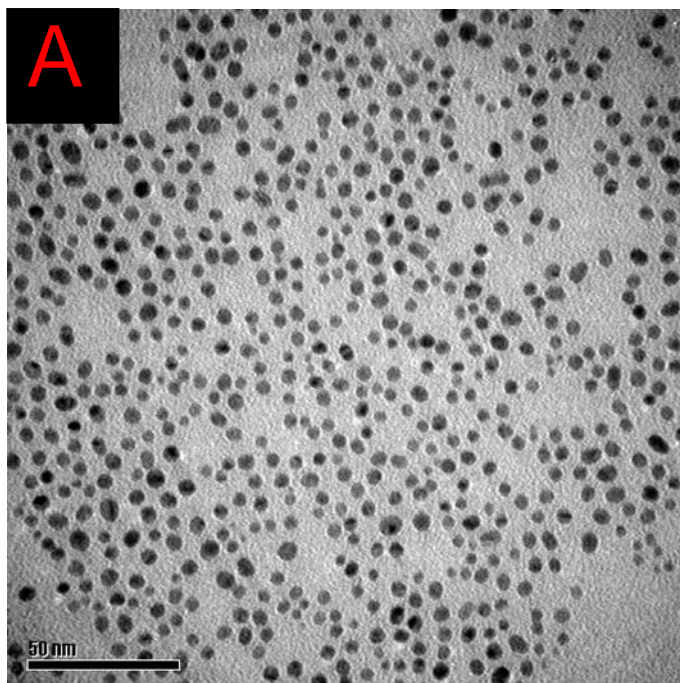


Table S4. Voltammetric characteristics of alcohols oxidation on glassy carbon electrodes modified with different NWs. The scan rate was 50 mV/s.

electrocatalyst	Reaction condition	E_f^a (V, vs Ag/AgCl)	E_b (V, vs Ag/AgCl)	J_f ($A \cdot cm^{-2} \cdot mg^{-1}$)
Au NWs	0.1 M Ethanol/0.1 M KOH	0.296	0.105	1.56
Pd NWs	1 M Ethanol/1 M KOH	-0.207	-0.393	7.96
Pd/C	1 M Ethanol /1 M KOH	-0.132	-0.322	4.2
Pt NWs	1 M Methanol/0.5 M H ₂ SO ₄	0.710	0.547	10.22
Pt/C	1 M Methanol/0.5 M H ₂ SO ₄	0.689	0.443	3.73

^a all potential and current were recorded at the 100th CV