Highly Efficient Submonolayer Pt Decorated Au Nano-catalysts for Formic Acid Oxidation

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Preparation of the Au seeds:

1 mL of 1% aqueous $HAuCl_4 \cdot 3H_2O$ was added to 100 mL of H_2O with vigorous stirring, followed by the addition of 1 mL of 1% aqueous $Na_3C_6H_5O_7$ (freshly prepared) one minute later. After an additional one minute, 1 mL of 0.075% $NaBH_4$ (freshly prepared) in 1% NaCitrate was added. The stirring was continued for 5 minutes and then the Au colloidal seed was stored at 4°C until needed.

Reduction and the growth of Pt on Au surface:

A certain amount of 0.1% aqueous H_2PtCl_6 and 0.1% aqueous $NH_2OH \cdot HCl$ was mixed with 100 mL water under vigorous stirring and heated to 60^oC for 3 hours. No color change was observed during this period. Then the gold seed suspension was added and the temperature was held constant at 60^oC for 2 hours. After 2 hours the solution was cooled to room temperature. The deposition of nanoparticles on carbon black Vulcan XC-72 was realized by mixing a certain amount of carbon with 5 mL water and sonication for 5 minutes with an ultrasonicator. Then the resulting carbon slurry was added to the nanoparticles solution prepared above and followed by continuous stirring overnight. The suspension was then filtered and washed with copious water. The final product was then dried at 70^oC in vacuum condition for 12 hours. The total metal loading (Pt+Au) is fixed at 20wt%.

Pt/C was prepared based on previous procedure reported in ref. 5b with slight modifications such as 20 wt% Pt loading instead of 10 wt% and the whole preparation was done without Ar environment.

Characterization:

X-ray diffraction (XRD) measurements were performed on a D8 Bruker AXS X-ray diffractometer using Cu Kα radiation 0.1542 nm at 40kV, 20mA, with a continuous scanning from 20° to 90°, with scan rate 0.025°/s. The samples for XRD analysis were put on Si (911) sample holder. The data were smoothed by adjacent averaging with 10 data points. The UV/vis spectra of the Au and PtAu hydrosols were measured by a Shimadzu UV2450 spectrometer equipped with quartz cells. The concentration of Au in Au hydrosol and Pt-Au hydrosols was 8 x 10^{-2} mM. Particle size and morphology were observed using JEOL 3010 transmission electron microscopy operated at 200kV. The samples were prepared by adding ethanol with the as-prepared nanoparticles, sonicated for 1 min then were dropped onto copper grids and dried in open air.

Electrochemistry characterization:

The electrochemical tests were performed by using Autolab PGSTAT302 potentiostat (Eco Chemie, Netherlands). Before each test, high-purity nitrogen was used for solution deaeration. 0.5 M H_2SO_4 electrolyte was used for blank voltammograms while 0.5 M HCOOH + 0.5 M H_2SO_4 electrolyte for formic acid oxidation reaction. Electrode potentials were measured and reported against saturated calomel electrode (SCE), which was placed close to the working electrode (glassy carbon rotating disk electrode, Pine instrument, 5 mm in diameter). The counter electrode was Pt wire. The working electrode was prepared based on a previously reported protocol.[5c] The catalyst ink was produced by dispersing 8.0 mg of 20 wt% Au/C, Pt/C or PtAu/C in 4.0 ml ethanol and ultrasonicated for 20 minutes. Ten microliter of catalyst ink was deposited via a microsyringe onto the surface of the working electrode to obtain a total metal (Pt+Au) loading of 4μg on 0.196 cm^2 glassy carbon rotating disk electrode. After drying the catalyst ink, another 10μL of 0.05% Nafion solution (diluted from 5% commercial solution with isopropanol) was dropped on top of the disk to fix the catalyst powders.

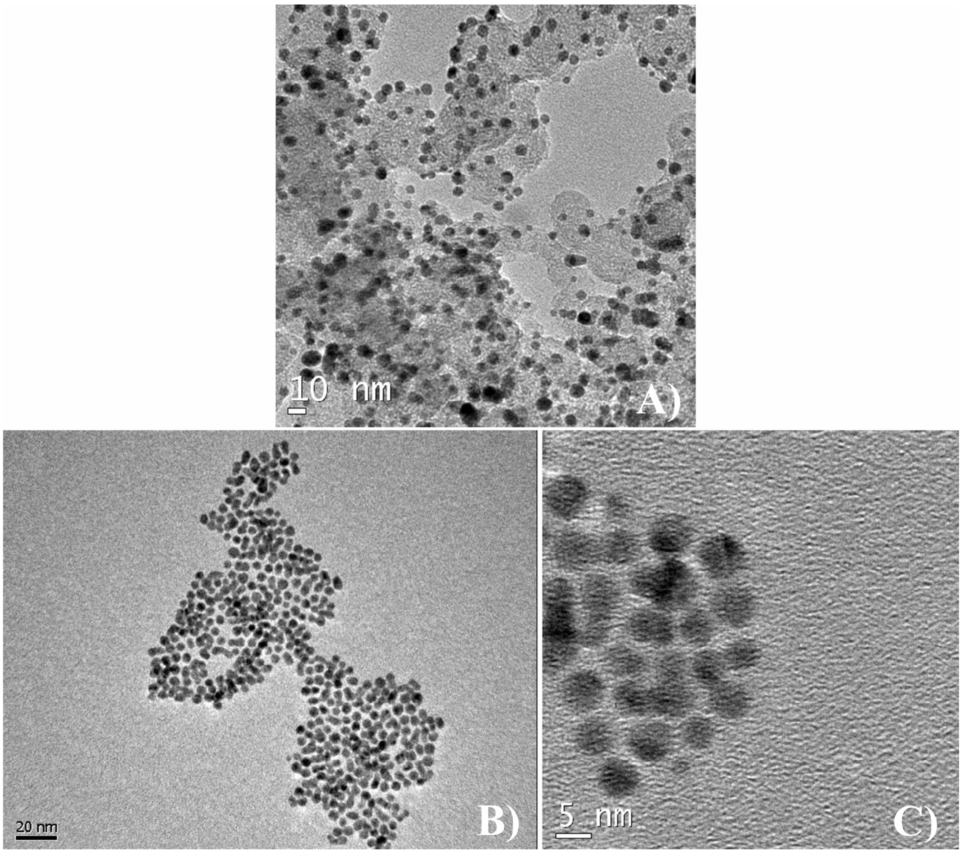

Figure S1. A) TEM image of Au seeds on carbon black.
B) TEM image of PtAu (Pt/Au=1:6). C) TEM image of PtAu (Pt/Au=1:2).

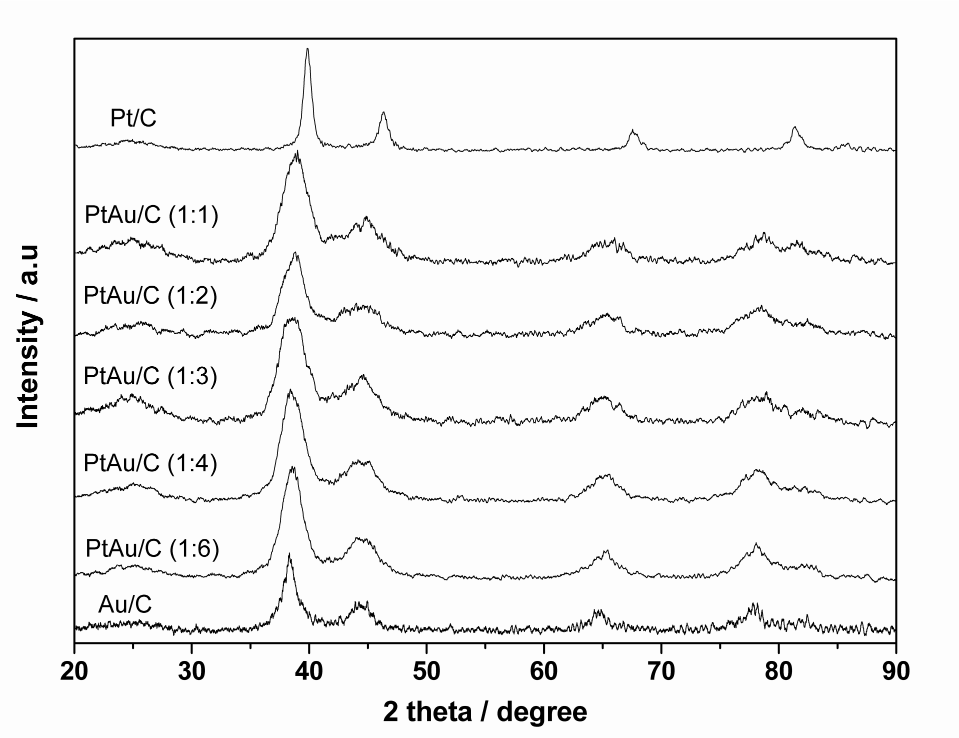

Figure S2. XRD patterns of Au/C, Pt/C and PtAu/C with different Pt/Au ratios.

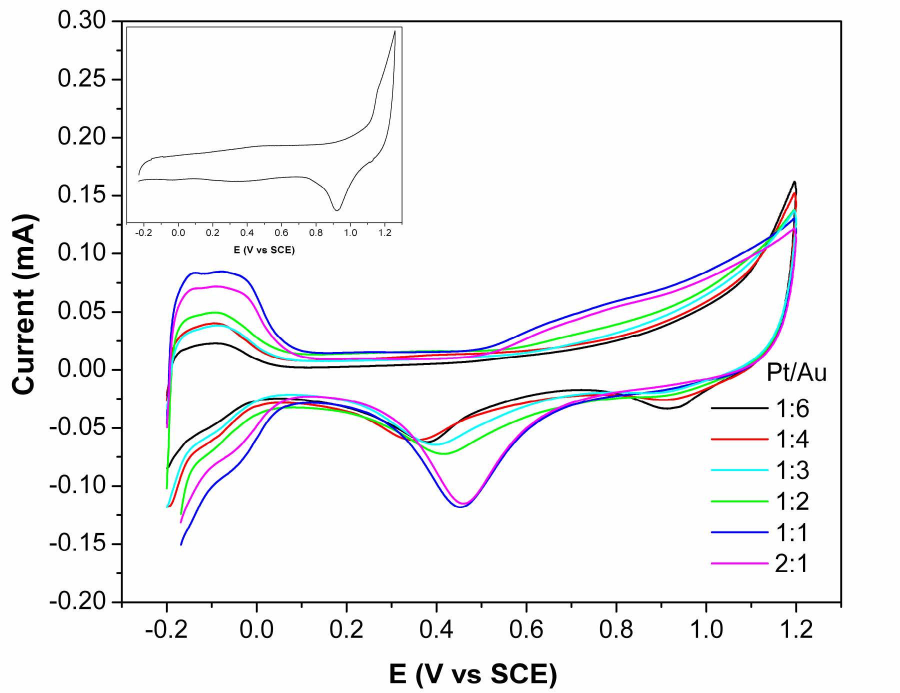

Figure S3. CV of PtAu/C with different Pt/Au ratios at scan rate of 50mVs^{-1} in N_2 purged 0.5M H_2SO_4. Total metal loading is 20 wt%. The inset shows the CV of 20wt% Au/C at 50mVs^{-1} in N_2 purged 0.5M H_2SO_4.

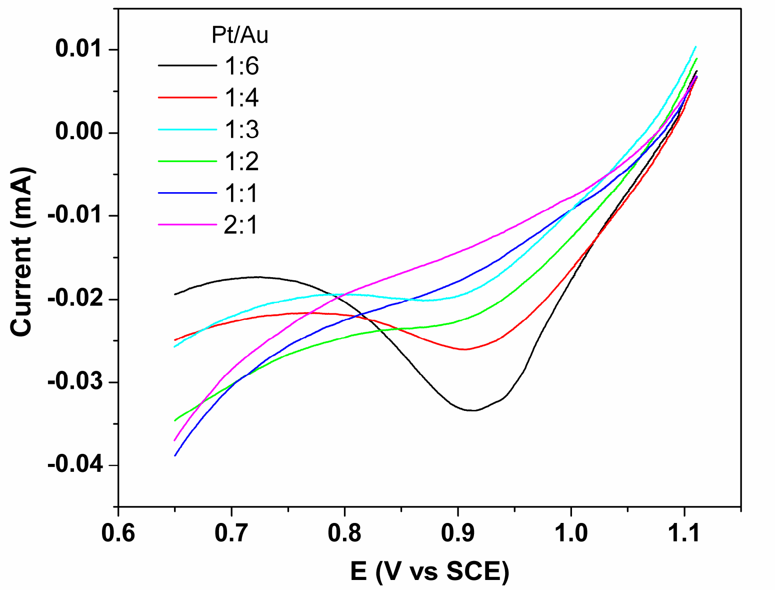

Figure S4. Cathodic scan between 1.1 V and 0.65 V of the decorated structure (Pt/Au ratio 1:6 to 1:2) and core-shell structure (Pt/Au ratio 1:1 and 2:1) at 50 mVs^{-1} in 0.5 M H_2SO_4.

Table S1. Au surface coverage by Pt.

Pt/Au	Au plasmon area*	Surface coverage
0	8.28	0%
1:6	6.70	20%
1:4	4.95	40%
1:3	2.27	73%
1:2	1.11	87%

* The Au plasmon area was calculated by integrating the area under the peak starting from 400 nm to 600 nm after background subtraction.