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One-pot synthesis of Au-based nanocrystals via a platinum group metal anions controlled growth strategy in citrate medium

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Electrochemical measurements.

Cyclic voltammetry (CV) experiments were performed in a CHI660D workstation. A platinum wire and an Ag/AgCl/3.0 M KCl electrode were used as the counter and reference electrode, respectively. A glassy carbon electrode (GCE) (3.0 mm, 0.07065 cm² in geometric area) was used as a working electrode. A typical procedure for the preparation of the GCE modified by the as-prepared Au-Pt NWs was as follows: an aqueous solution of the as-prepared catalysts (6 μ L) was drop-coated on a freshly prepared bare GCE, followed by drying at room temperature. Then, an ethanol solution of Nafion (10 μ L, 0.2 wt%) was then cast on the surface of the GCEs coated by the as-prepared catalysts, followed by drying in air for further use.

For methanol or ethanol oxidation in alkaline media, CVs were recorded between -0.60 and 0.40 V in N₂-saturated 0.30 M KOH and 1.0 M methanol or 0.50 M ethanol solution at a scan rate of 20 mV s⁻¹. Since Pt is generally known to be the key-element giving the high performance to Pt-based electrocatalysts, their mass activities were normalized by the loaded Pt, which was calculated from the coated catalysts based on the volume of catalysis ink.

Electrochemical investigations towards hydrogen evolution reaction (HER) were also performed in a standard three-electrode system in a CHI 660D workstation at room temperature. A Pt wire and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. GCE was used as the working electrode for HER. The GCEs were coated by as-prepared Au-Pt NWs (6 μ L) according to the same method used in the CV test. LSV measurements were conducted between -0.60 and 0 V (vs Ag/AgCl) in N₂-saturated 0.5 M H₂SO₄ solution at a scan rate of 5 mV s⁻¹. The current density was normalized in reference to the geometric area of GCE.”

Fig. S1 TEM image of the intermediate product of Au NWs extracted from the aqueous solutions of citrate/HAuCl₄ mixtures with incubation time of 14 min.

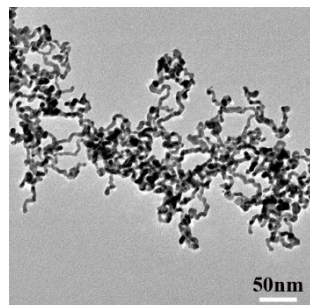


Fig. S2 HAADF-STEM-EDS mapping images of the corresponding products obtained in the aqueous solutions of citrate/HAuCl₄/ IrCl₆³⁻ mixtures at room temperature.

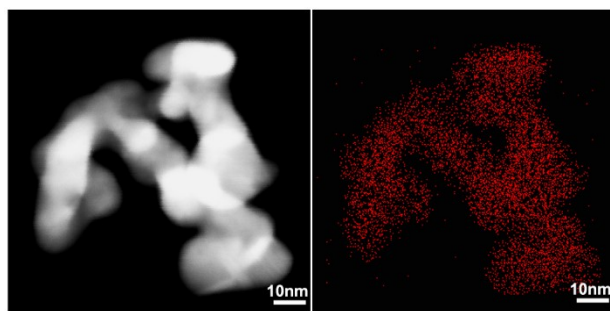


Fig. S3 TEM, HR-TEM, HAADF-STEM-EDS mapping images, and CV curve of Au-Pd NWs obtained by the reaction of PdCl_6^{4-} with Au NWs, measured in 0.30 M N_2 -saturated KOH aqueous solution in the presence of 0.50 M ethanol at room temperature.

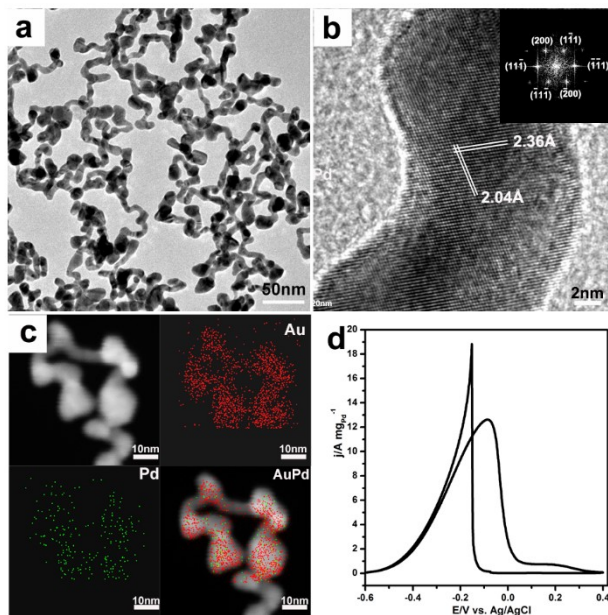


Fig. S4 TEM images of NPs obtained at different reaction times: 4 min (a), 6 min (b), 60 min (c), and 120 min (d) after addition of the citrate–HAuCl₄ premixture solution with premixing time of 14 min into the aqueous solution in the absence (A) and presence of K₂PtCl₄ (B), and K₂PtCl₆ (C). The concentrations of K₂PtCl₄, K₂PtCl₆, HAuCl₄, and citrate are 0.07, 0.07, 0.98, and 4.0 mM, respectively. The Au-to-Pt molar ratio is 14.

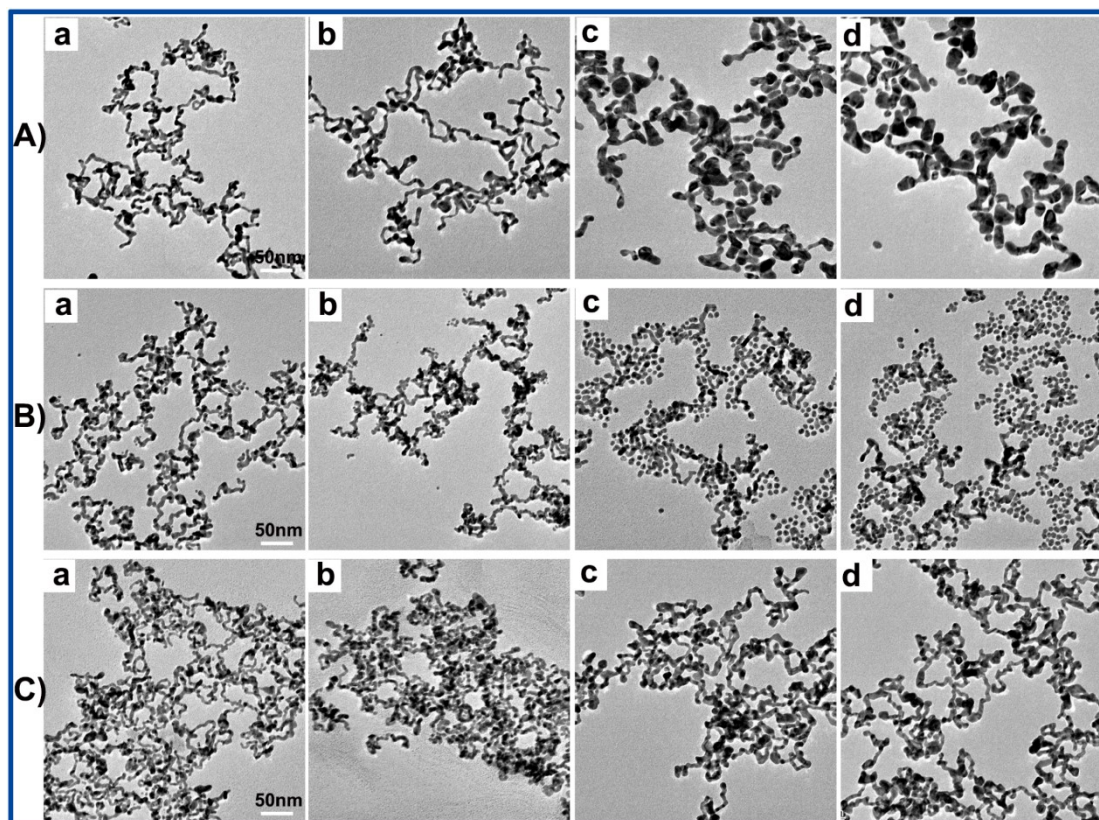


Fig. S5 TEM (A) and HAADF-STEM-EDS mapping (B) images of the Au-Pt NWs. The Au-Pt NWs were obtained as follows: First, aqueous solution of K_2PtCl_4 (17.8 μ L, 10.0 mM) was pre-incubated with the aqueous solution of $HAuCl_4$ (40 μ L, 5 mM). After about 30 min of incubation, the reaction mixture was added into the aqueous solutions of citrate/ $HAuCl_4$ mixtures containing *in situ* Au NWs templates. After stirring for 3 h at room temperature, the Au-Pt NWs were obtained.

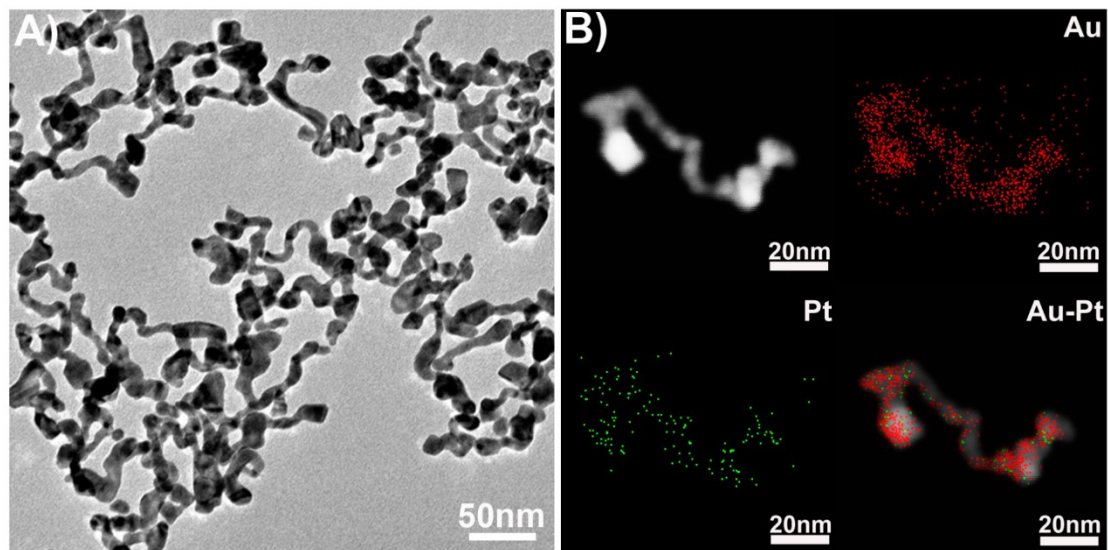


Fig. S6 CV curves of GCEs modified by Au-Pt NWs obtained at different Au-Pt molar ratios: 18 (black curve), 14 (red curve), 10 (blue curve), 6 (magenta curve), 2 (olive curve), commercial Pt/C (nave curve) and commercial Pd/C (violet curve) measured in 0.30 M KOH solution in the presence of 1 M methanol (A) or 0.50 M ethanol (B). The current densities are normalized by the Pt mass loaded on the GCE. The scan rates are 20 mV s⁻¹ (A and B).

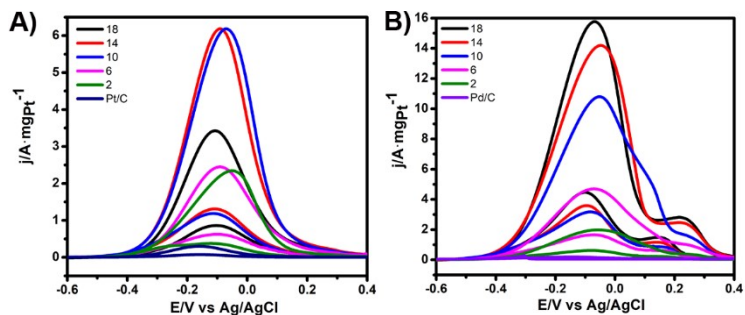


Fig. S7 (a) HER polarization curve of Au_{94.5}-Pt_{5.5} NWs and Pt/C at a scan rate of 5 mV/S in 0.5 M H₂SO₄.

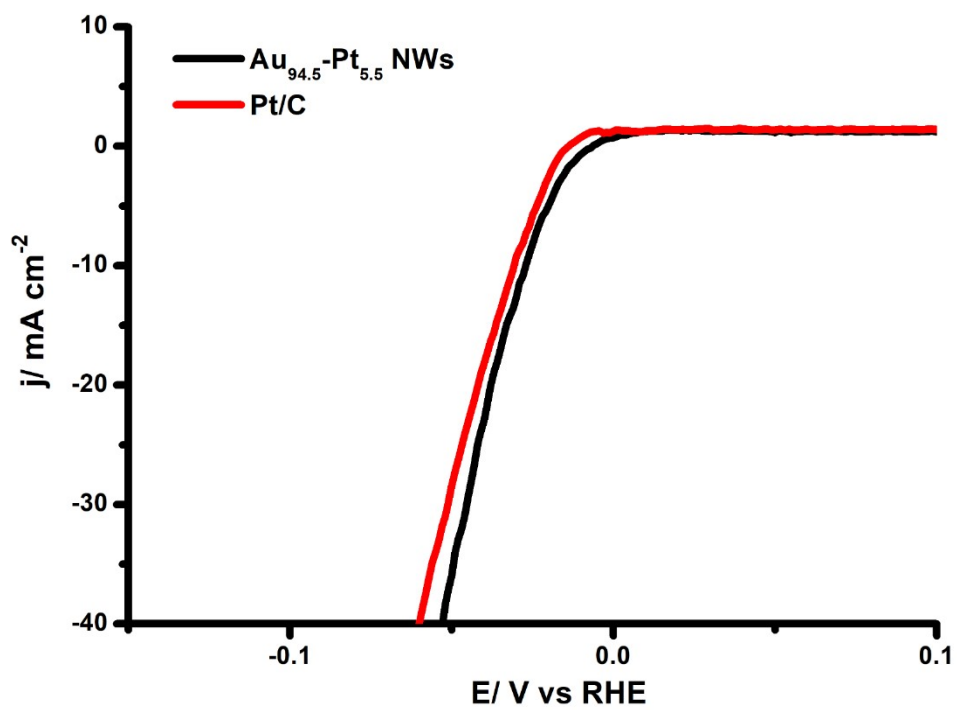


Table S1 Summary of the standard electrode potential values of Au, Ir, Pd, and Pt.

Electrode Reaction	E°/V vs NHE
$\text{PdCl}_4^{2-} + 2\text{e}^- \text{--- Pd} + 4\text{Cl}^-$	0.59
$\text{PtCl}_6^{2-} + 2\text{e}^- \text{--- PtCl}_4^{2-} + 2\text{Cl}^-$	0.726
$\text{PtCl}_6^{2-} + 4\text{e}^- \text{--- Pt} + 6\text{Cl}^-$	0.744
$\text{PtCl}_4^{2-} + 2\text{e}^- \text{--- Pt} + 4\text{Cl}^-$	0.755
$\text{IrCl}_6^{3-} + 3\text{e}^- \text{--- Ir} + 6\text{Cl}^-$	0.77
$\text{AuCl}_4^- + 3\text{e}^- \text{--- Au} + 4\text{Cl}^-$	1.002
$\text{PdCl}_6^{2-} + \text{e}^- \text{--- PdCl}_4^{2-} + 2\text{Cl}^-$	1.29

Table S2 Summary of current densities normalized by the Pt mass of GCE modified by Au-Pt NWs obtained at different Au-to-Pt molar ratios under alkaline conditions

molar ratio of Au-to-Pt	Current density normalized by Pt mass for electrocatalysis of the oxidation of methanol (A mg_{Pt}⁻¹)	Current density normalized by Pt mass for electrocatalysis of the oxidation of ethanol (A mg_{Pt}⁻¹) (A mg_{Pt}⁻¹)
18	3.427	15.77
14	6.181	14.19
10	6.184	10.80
6	2.500	4.70
2	2.343	1.98