Electronic Supplementary Information

Electrodeposition of Pt Nanostructures with Reproducible SERS Activity and Superhydrophobicity

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Evaluation of SERS Enhancement Factor (EF)

(1) SERS substrate EF (SSEF)

The SSEF can be defined as below:

$$SSEF = \frac{I_{SERS} / N_{surf}}{I_{bulk} / N_{bulk}}$$

I_{SERS}: SERS intensity of pyridine adsorbed on SERS substrates

*I*_{bulk}: Raman intensity of pyridine in a bulk solution

 N_{surf} : Number of pyridine molecules adsorbed on surfaces

N_{bulk}: Number of pyridine molecules in a solution contributing to Raman intensity

If we assume monolayer adsorption of pyridine, N_{surf} , can be calculated using the following approximation

$$N_{\rm surf} = RA/\sigma$$

R: Roughness factor of substrate

- A: Area of the laser spot
- σ : Surface area occupied by a pyridine molecule adsorbed on surfaces (~ 0.27 nm²).

 N_{bulk} cannot be obtained directly because the confocal Raman microscope possesses a sensitive depth resolution. The effectively illuminated number of pyridine molecules in the solution can be written as:

$$N_{\rm bulk} = AhcN_{\rm A}$$

c: Concentration of pyridine

N_A: Avogadro number.

h: Effective layer within which each pyridine molecule contribute to Raman intensity

The term *h* depends on the specific Raman setup, such as pinhole size and the objective lens; therefore, the *h* value for our Raman system was evaluated. From the intensity–depth profile of the integrated intensity of 520.6 cm⁻¹ band for a Si wafer in water, *h* was measured to be 660 µm.

Now the SSEF can be expressed as

$$\text{SSEF} = \frac{I_{\text{SERS}}}{I_{\text{bulk}}} \frac{hcN_A\sigma}{R}$$

For a Pt tree nanostructure prepared with 0.04 C of deposition charge

 $I_{\text{SERS}} = 1190 \text{ and } R = 69.7$

For a solution containing 0.05 M pyridine in 0.1 M NaClO₄

 $I_{\text{bulk}} = 106$

SSEF was calculated to be 812

(2) Analytical EF

The analytical EF (AEF) can be defined as below:

$$AEF = \frac{I_{SERS} / c_{SERS}}{I_{RS} / c_{RS}}$$

*I*_{SERS} : SERS intensity of ABT adsorbed on nanostructured Pt surfaces by soaking

SERS substrates in a specific concentration (c_{SERS}) of ABT solution

 $I_{\rm RS}$: Raman intensity of ABT in a bulk solution ($c_{\rm RS}$)

Following figure shows a SERS spectrum of adsorbed ABT on Pt surfaces after soaking the substrates in solutions containing different concentrations (c_{SERS}) of ABT.



AEF depends on the concentrations (c_{SERS}) as shown in the following table

$\mathcal{C}_{\mathrm{SERS}}$	I _{SERS}	$c_{\rm RS}$	I _{RS}	AEF
1 nM	68	1 M	110	6.1 x 10 ⁸
0.1 nM	21	1 M	110	1.9 x 10 ⁹



Fig. S1. Low resolution SEM images of Pt nanotree structures (0.04 C) homogeneously distributed on the electrodeposited Au substrates.



Fig. S2. SEM images of Pt electrodeposited from solutions 15 mM K_2PtCl_4 and 0.1 M H_2SO_4 at (A) -0.1 V, (B) -0.15 V, (C) -0.25 V, and (D) -0.3 V.



Fig. S3. SEM images of Pt electrodeposited from solutions containing various concentration of K_2 PtCl₄ in 0.1 M H₂SO₄ at a deposition potential of -0.2 V. Total deposition charges are 0.04 C.



Fig. S4. SEM images of Pt electrodeposited from solutions containing $15 \text{ mM K}_2\text{PtCl}_6$ in 0.1 M H₂SO₄ at various deposition potentials. Total deposition charges are 0.08 C.



Fig. S5. Current vs. time curve during electrodeposition at various deposition potential containing 15 mM K₂PtCl₄ in 0.1 M H₂SO₄. Total deposition charges are 0.04 C.



Fig. S6. Cyclic voltammograms obtained in 0.1 M HClO₄ on bare Au and Pt surfaces electrodeposited with 0.0025 C. Scan rate: 50 mV/s.



Fig. S7. (A) Cyclic voltammograms of Pt nanostructure electrode in 0.1 M HClO₄. Scan rate = 50 mV/s. (B) Dependence of the R_f of Pt deposits on the deposition charge.



Fig. S8. (A) SERS spectra obtained from five different Pt nanotree substrates independently fabricated. Each SERS spectrum was the average of five random SERS scans relative to one substrate adsorbed with 4-aminobenzenethiol. (B) Averaged SERS intensities at 1075 cm⁻¹ and 1580 cm⁻¹ measured from five different Pt tree nanostructure substrates. The laser power focused on samples was 10 mW and acquisition time was 10 s.



Fig. S9. Contact-angle profiles of water droplets $(5\mu L)$ on nanostructured Pt surfaces as a function of deposition charge.



Fig. S10. Dependence of contact-angles of water droplets (5 μ L) and SERS intensities at 1585 cm⁻¹ on the deposition charge.



Fig. S11. Dependence of f_2 values of the nanostructured Pt surfaces on the deposition charge.