

Supporting Information

Surface-Enhanced Raman Scattering-Active Substrate Prepared with New Plasmon-Activated Water

Chih-Ping Yang^{§,1}, Sheng-Uei Fang^{†,‡,1}, Kuang-Hsuan Yang[#], Hsiao-Chien Chen[§], Hui-Yen Tsai[§], Fu-Der Mai[§] and Yu-Chuan Liu^{§,*}

[§] Department of Biochemistry and Molecular Cell Biology, School of Medicine, College of Medicine, Taipei Medical University, No. 250, Wuxing St., Taipei 11031, Taiwan

[†] Division of Gastroenterology and Hepatology, Department of Internal Medicine, Taipei Medical University Hospital, No. 252, Wuxing St., Taipei 11031, Taiwan

[‡] Department of Internal Medicine, School of Medicine, College of Medicine, Taipei Medical University, No. 250, Wuxing St., Taipei 11031, Taiwan

[#] Department of Materials Science and Engineering, Vanung University, 1 Van-Nung Road, Taoyuan 32061, Taiwan

* Author to whom correspondence should be addressed. Yu-Chuan Liu, Phone: +886-2-2736-1661, ext. 3155; E-mail: liuyc@tmu.edu.tw.

¹ C.-P. Y. and S.-U. F. contributed equally to this work.

Table of Contents:

SUPPORTING EXPERIMENTAL SECTION: Chemicals and materials, ex situ and in situ preparations of PAW, preparation of the SERS-active Au substrate, adsorption of R6G onto SERS-active Au substrates and characterization of SERS-active Au substrates.

Figure S1. Reproducible experiments (Figure 2 in the text) for CVs at various ν (50-600 mV s^{-1}) of 50 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in different waters with and without resonant illumination at roughened Au substrates (samples “DIW”) prepared by using DI waters without resonant illumination (Insert: plots of anodic peak potential E_{pa} and cathodic peak potential E_{pc} vs $\ln\nu$).

Figure S2. Three reproducible experiments of CVs at various ν (50-600 mV s^{-1}) of 50 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in PAW with resonant illumination at roughened Au substrates (samples “PAW in situ”) prepared by using PAW with resonant illumination (Insert: plots of anodic peak potential E_{pa} and cathodic peak potential E_{pc} vs $\ln\nu$).

Figure S3. CVs at various ν (50-600 mV s^{-1}) of 50 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in DI water in dark atmosphere at roughened Au substrates (samples “DIW”) prepared by using DI water without resonant illumination (Insert: plots of anodic peak potential E_{pa} and cathodic peak potential E_{pc} vs $\ln\nu$).

Figure S4. Raman spectra of 2×10^{-5} M rhodamine 6G (R6G) adsorbed onto roughened Au substrates (samples “PAW”) prepared by using PAW without resonant illumination under different ORC cycles. Spectra were obtained from five selected sites on the same substrate.

Figure S5. SERS spectra of 1 mC cm^{-2} polypyrrole (PPy) film electrodeposited (in 0.1 M pyrrole and 0.1 M LiClO_4) on roughened Au substrates prepared by ORC treatments at 500 mV s^{-1} for 20 scans in 0.1 M KCl by using different waters under resonant illumination or not (The same experimental conditions shown in Figure 1c).

Figure S6. AFM 2D images of roughened Au substrates prepared by ORC treatments at 500 mV s^{-1} for 20 scans in 0.1 M KCl by using different waters under resonant illumination or not (The same experimental conditions shown in Figure 1c). The average mean roughness (Ra) was decided basing on five selected lines on the same substrate.

Figure S7. AFM 2D images of roughened Au substrates prepared by ORC treatments at 500 mV s^{-1} for 20 scans in 0.1 M KCl by using DI water with resonant illumination. The average mean roughness (Ra) was decided basing on five selected different lines on the same substrate.

SUPPORTING EXPERIMENTAL SECTION

Chemicals and Materials. KCl electrolytes, rhodamine 6G (R6G), and $\text{K}_3\text{Fe}(\text{CN})_6$ were purchased from Acros Organics. DI water (18.2 M Ω cm) was provided by a Milli-Q system. All experiments were performed in an air-conditioned room at ca. 24 °C. The water temperature (T) was ca. 23.6 °C.

Preparations of PAW ex Situ and PAW in Situ. PAW (ex situ) was prepared using a previously described method.¹ Typically, DI water (pH 7.01, T = 23.6 °C) was passed through a glass tube filled with ceramic particles onto which AuNPs had been adsorbed under resonant illumination with green light-emitting diodes (LEDs, with a wavelength maximum centered at 530 nm). Then, the created PAW (pH 7.03, T = 23.9 °C) was collected in glass sample bottles for subsequent experiments within 15 min. Differences in the pH and temperature between DI water and PAW were respectively within 0.5 pH units and 0.5 °C for different batch experiments. PAW in situ was prepared in a DI water-filled glass cell containing a roughened Au substrate with AuNPs. In the experiments, the glass cell with DI water was illuminated with green LEDs to create PAW in situ at the AuNPs. To avoid a significant increase in the water temperature, the light strip was not directly pasted onto the glass cell, but was pasted onto a transparent plastic sheet that circled the glass cell (Figure 1a). Therefore, the increased water temperature was below 1 °C. Throughout this work, unless otherwise stated, the experiment was performed under indoor fluorescent lamps.

Preparation of the SERS-Active Au Substrate. All of the electrochemical experiments were performed in a three-compartment cell at room temperature (24 °C) and were controlled by a potentiostat (model PGSTAT30, Eco Chemie). A gold sheet with a bare surface area of 0.238 cm², a 1 × 4-cm platinum sheet, and a KCl-saturated silver-silver chloride (Ag/AgCl) electrode were respectively employed as the working, counter, and reference electrodes. Before oxidation-reduction cycle (ORC) treatment, the gold electrode was mechanically polished (model Minimet 1000, Buehler) successively with 1- and 0.05- μm alumina slurries to a mirror finish. Then the electrode was cycled in a deoxygenated 0.1 M KCl aqueous solution (40 mL based on PAW or DI water) from -0.28 to +1.22 V vs. Ag/AgCl at 500 mV s⁻¹ with and without resonant illumination (green LEDs) for 20 scans. Respective durations at the cathodic and anodic vertices were 10 and 5 s. Finally, the potential was held at the cathodic vertex before the roughened Au electrode was taken from the solution and thoroughly rinsed with DI water. The prepared substrate was dried in a dark vacuum-dryer for 1 h at room temperature for subsequent use. These ORC procedures in SERS studies (excepting the scan cycles) were generally employed in our² and other laboratories.^{3,4}

Adsorption of R6G onto SERS-Active Au Substrates. For SERS measurements, 20 μL of 2×10^{-5} M R6G was dropped onto the as-prepared SERS-active Au substrates. After equilibrating for 30 min, the sample molecule-adsorbed substrates were thoroughly rinsed with DI water to remove any unbound molecules, and dried in a dark vacuum-dryer for 1 h at room temperature for subsequent tests.

Characterization of SERS-Active Au Substrates. The surface morphologies of the SERS-active Au substrates were examined by scanning electron microscopy (SEM, model JEM-6500F, JEOL) with an acceleration voltage of 30 kV. An atomic force microscope (AFM, Dimension Icon, Bruker, USA) was used to analyze the surface topography, and the size and mean roughness (Ra) of the samples. Raman spectra were recorded (Micro Raman spectrometer, Model RAMaker) using a confocal microscope employing a diode laser operating at 785 nm. A 50x, 0.36 NA Olympus objective (with a working distance of 10 mm) was used to focus the laser light on the samples. The laser spot size was ca. 2.5 μm . A thermoelectrically cooled Andor iDus charge-coupled device (CCD) with 1024 x 128 pixels operating at -40 $^{\circ}\text{C}$ was used as the detector with a resolution of 1 cm^{-1} . All spectra were calibrated with respect to silicon wafers at 520 cm^{-1} . For these measurements, a 180 $^{\circ}$ geometry was used to collect the scattered radiation. A 785 notch filter was used to filter the excitation line from the collected light. The acquisition time for each measurement was 3 s. Three sequential measurements were made for each sample. Five replicate measurements at different areas were made to verify that the spectra were truly representative of each sample. For these measurements, a spot was focused at the center of the sample; while the other four spots were focused at points ca. 1.5 mm from the center in the nominal eastern, southern, western, and northern directions. The SERS effect was evaluated on the strongest band intensity of R6G at ca. 1361 cm^{-1} on the Raman spectrum. A normalized band intensity of R6G at ca. 1361 cm^{-1} was obtained by subtracting this band from the nearby background of ca. 1424 cm^{-1} . An average band intensity was determined from five measurements on each sample. Raman mapping was achieved with a computer-controlled three axis-encoded (XYZ) motorized stage with a minimum step of 0.1 μm . The resolution of the maps was 1 x 0.5 μm , with each point exposed to 1 mW of laser power for 3 s. Each map covered an area of about 400 μm^2 and took approximately 15 min to complete. Two-dimensional (2D) SERS map data are presented with each pixel corresponding to an area under R6G of ca. 1361 cm^{-1} .

REFERENCES

- (1) Chen, H. C.; Hwang, B. J.; Mai, F. D.; Liu, Y. C.; Lin, C. M.; Kuo, H. S.; Chou, D. S.; Lee, M. J.; Yang, K. H.; Yu, C. C.; Chen, J. R.; Lo, T. Y.; Tsai, H. Y.; Yang, C. P.; Wang, C.; Hsieh, H. T.; Rick, J. *ACS Nano* **2014**, 8, 2704–2713.
- (2) Liu, Y. C.; Hsu, T. C.; Tsai, J. F. *J. Phys. Chem. C* **2007**, 111, 10570–10574.

(3) Wang, C. C. *J. Phys. Chem. C* **2008**, *112*, 5573–5578.

(4) Mosier-Boss, P. A.; Lieberman, S. H. *Langmuir* **2003**, *19*, 6826–6836.

FIGURE CAPTIONS

Figure S1. Reproducible experiments (Figure 2 in the text) for CVs at various ν (50-600 mV s^{-1}) of 50 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in different waters with and without resonant illumination at roughened Au substrates (samples “DIW”) prepared by using DI waters without resonant illumination (Insert: plots of anodic peak potential E_{pa} and cathodic peak potential E_{pc} vs $\ln\nu$). (a) In DI water without resonant illumination. (b) In PAW with resonant illumination. (c) In DI water without resonant illumination. (d) In PAW with resonant illumination.

Figure S2. Three reproducible experiments of CVs at various ν (50-600 mV s^{-1}) of 50 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in PAW with resonant illumination at roughened Au substrates (samples “PAW in situ”) prepared by using PAW with resonant illumination (Insert: plots of anodic peak potential E_{pa} and cathodic peak potential E_{pc} vs $\ln\nu$). (a) Experiment 1. (b) Experiment 2. (c) Experiment 3.

Figure S3. CVs at various ν (50-600 mV s^{-1}) of 50 mM $\text{K}_3\text{Fe}(\text{CN})_6$ in DI water in dark atmosphere at roughened Au substrates (samples “DIW”) prepared by using DI water without resonant illumination (Insert: plots of anodic peak potential E_{pa} and cathodic peak potential E_{pc} vs $\ln\nu$).

Figure S4. Raman spectra of 2×10^{-5} M rhodamine 6G (R6G) adsorbed onto roughened Au substrates (samples “PAW”) prepared by using PAW without resonant illumination under different ORC cycles. Spectra were obtained from five selected sites on the same substrate. (a) With 15 cycles. (b) With 20 cycles. (c) With 25 cycles.

Figure S5. SERS spectra of 1 mC cm^{-2} polypyrrole (PPy) film electrodeposited (in 0.1 M pyrrole and 0.1 M LiClO_4) on roughened Au substrates prepared by ORC treatments at 500 mV s^{-1} for 20 scans in 0.1 M KCl by using different waters under resonant illumination or not (The same experimental conditions shown in Figure 1c). DIW (black) represents using DI water without resonant illumination; while PAW in situ (green) represents using PAW with resonant illumination. The peak at 933 cm^{-1} is assigned to the symmetric stretching mode of ClO_4^- dopants. The broader Raman peaks of PPy appearing in the range of $1000\text{--}1150 \text{ cm}^{-1}$ and $1300\text{--}1410 \text{ cm}^{-1}$ are assigned to the C–H in-plane deformation and the ring stretching, respectively. The peak at 1600 cm^{-1} is assigned to the C=C backbone stretching of PPy (Liu, Y. C. Characteristics of Vibration Modes of Polypyrrole on Surface-Enhanced Raman Scattering Spectra. *J. Electroanal. Chem.* **2004**, *571*, 255–264.). Based on PAW in situ, the SERS enhancement of 3-fold higher intensity of PPy and the corresponding low RSD of 6% compared to DIW system (RSD of 18%) are encouraging. The calculated RSDs based on SERS intensities of PPy of the strongest bands (at ca. 1600 cm^{-1}) at five selected sites on differently roughened Au substrates.

Figure S6. AFM 2D images of roughened Au substrates prepared by ORC treatments at 500 mV s^{-1} for 20 scans in 0.1 M KCl by using different waters under resonant illumination or not (The same experimental conditions shown in Figure 1c). The average mean roughness (R_a) was decided basing on five selected lines on the same substrate. (a) Using DI water without resonant illumination. (b) Using DI water with resonant illumination. (c) Using PAW without resonant illumination. (d) Using PAW with resonant illumination.

Figure S7. AFM 2D images of roughened Au substrates prepared by ORC treatments at 500 mV s^{-1} for 20 scans in 0.1 M KCl by using DI water with resonant illumination. The average mean roughness (R_a) was decided basing on five selected different lines on the same substrate. (a) The first line. (b) The second line. (c) The third line. (d) The fourth line. (e) The fifth line.

Figure S1

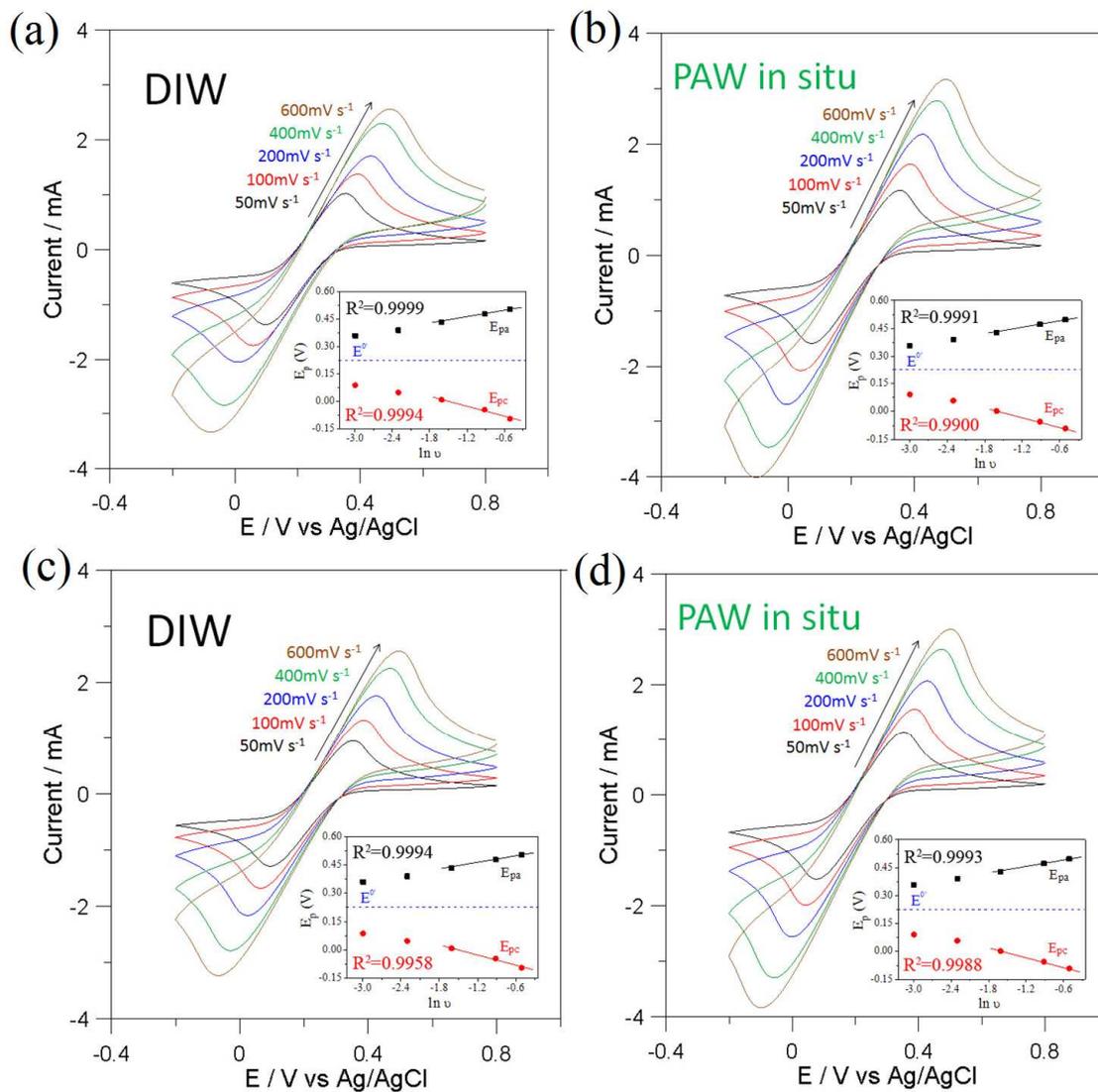


Figure S2

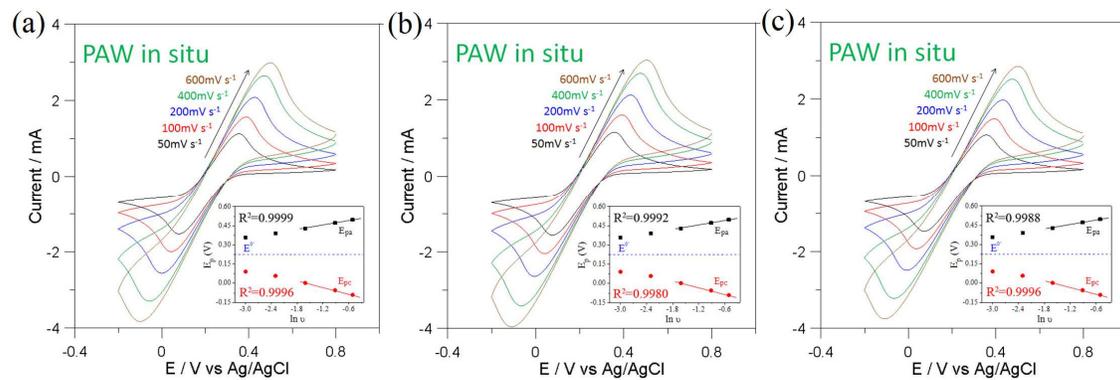


Figure S3

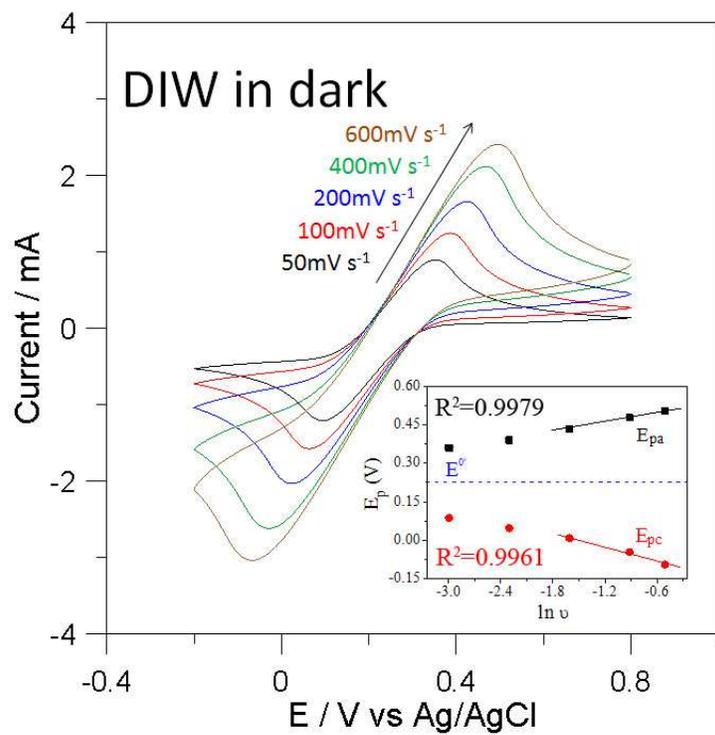


Figure S4

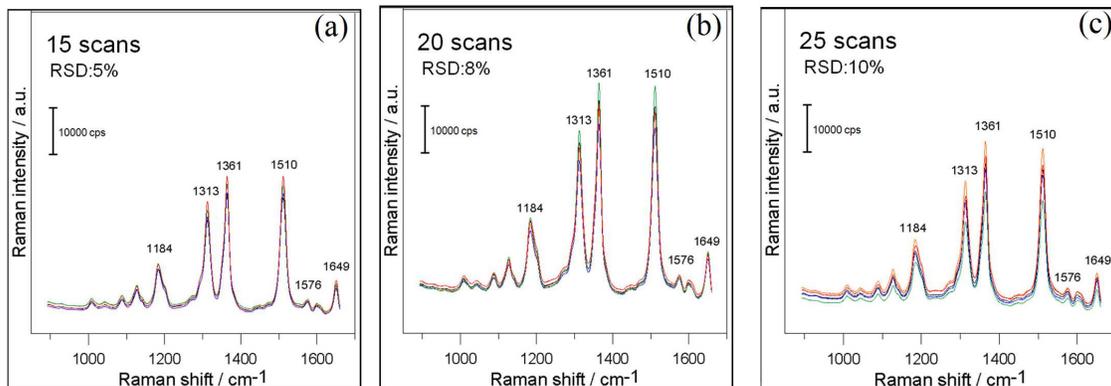


Figure S5

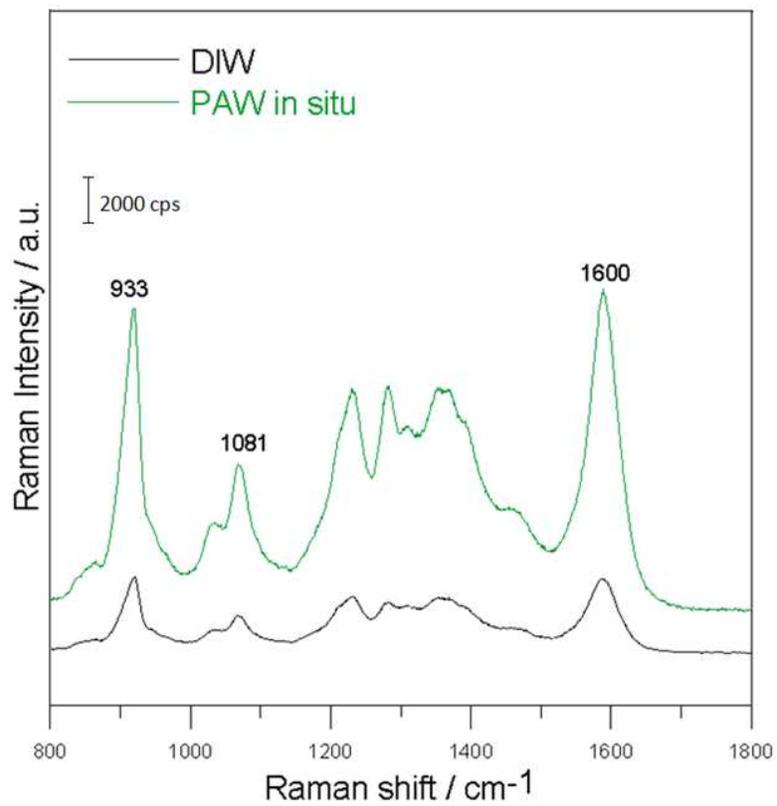


Figure S6

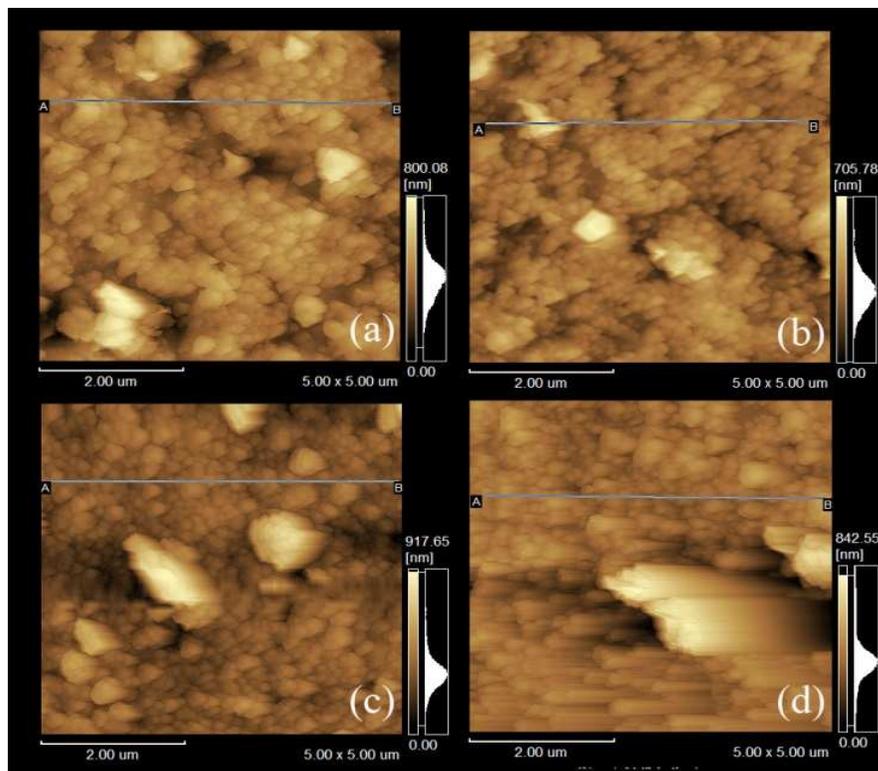
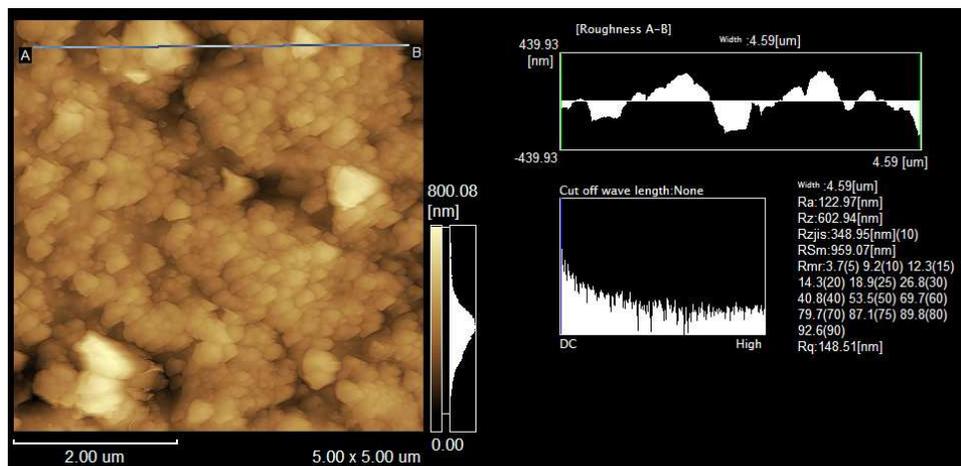
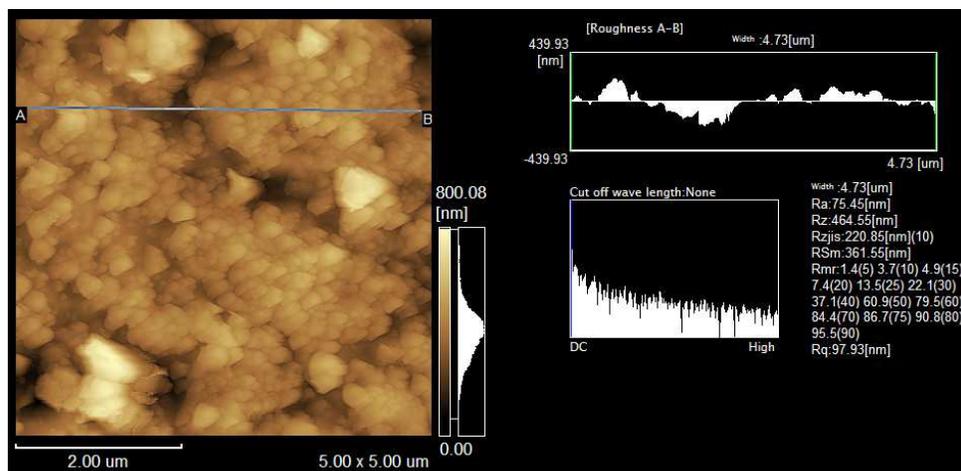


Figure S7

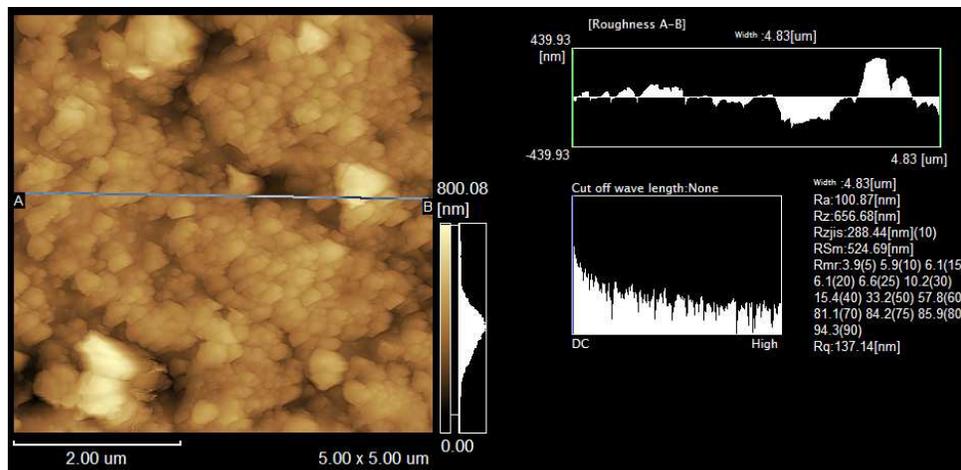
(a)



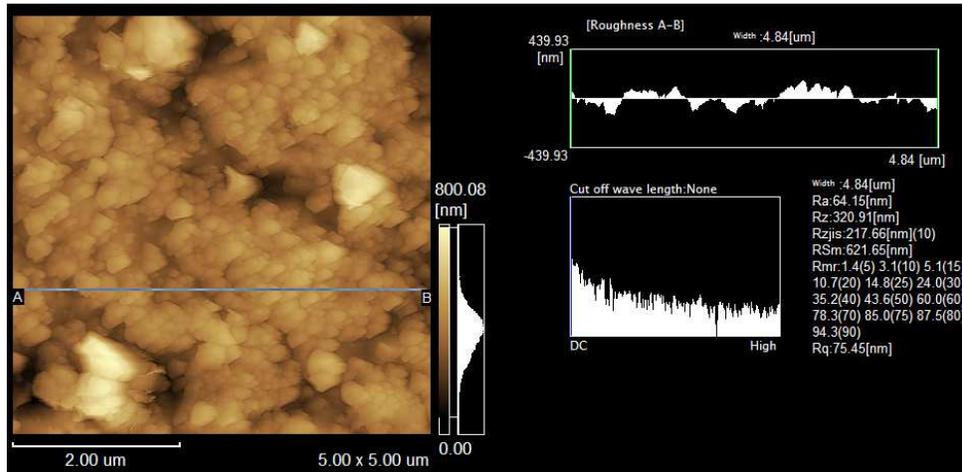
(b)



(c)



(d)



(e)

