Supporting Information

Two-Dimensional Electrochemiluminescence on Porous Silicon Platform for Explosives Detection and Discrimination

Yaoxuan Cui, Yao Jin, Xisheng Chen and Jianmin Wu*

Department of Chemistry, Zhejiang University, Hangzhou, China. 310058

Corresponding author: Jianmin Wu
*Email address: wjm-st1@zju.edu.cn

Table of Contents

1. Methods

1.1 Materials and Reagents

Silicon wafers were purchased from Lijing Silicon Materials Co. (Quzhou, China). Hydrofluoric acid (HF, 40%), methanol (MeOH), ethanol (EtOH) and acetonitrile (ACN) were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Chloroauric acid (48% Au basis) was purchased from Machlin Co. (Shanghai, China). 1, 3, 5-trinitrotoluene (TNT), 2, 4-dinitrotoluene (DNT) and 2- nitrotoluene (NT) were purchased from Aladdin Co. (Shanghai, China). Triacetone triperoxide (TATP) and Hexamethoxy amine (HMTD) were purchased from ACCUStandard Co. (U.S.). Polydimethylsiloxane (PDMS) precursor was purchased from Shenzhen Xinhao Technology Co., Ltd (Guangdong, China). All other used reagents in this experiment were of analytical grade and used without further purification.

1.2 Preparation of pSi and AuNPs-pSi

Porous Si was obtained by anodization of a boron-doped silicon wafer (resistivity 0.5-1.2 mΩ/cm) of [100] crystal orientation in an electrolyte mixture of aqueous hydrofluoric acid (48% by mass, Alatin Corp.), and ethanol (in a volume ratio of 4 : 1). Porosity of samples was controlled by the current density used in the electrochemical etch. The electrochemical cell was rinsed with deionized water after the etch step, and then dried under a nitrogen stream.

AuNPs were electrochemically deposited on the obtained pSi. The pSi chip and a platinum counter electrode acted as the cathode and anode, respectively, and the electro-deposition was performed at a constant current of 5 mA for 10-120s with a $HAuCl_4$ aqueous electrolyte for 0.01-0.1%.

1.3 Characterization of pSi and AuNPs-pSi

SEM: The morphology of pSi and AuNPs-pSi with different AuNPs deposition time was characterized by scanning electron microscopy (SEM, Hitachi Co.).

TEM: The morphology of pSi nanoparticles during voltage scanning process was characterized by transmission electron microscopy (TEM, Hitachi Co.).

FT-RIS： The porosity of pSi was determined from reflectance spectra using the spectroscopic liquid infiltration method (SLIM). The reflectance spectra were obtained using a CCD-detector-based spectrometer (USB2000+, Ocean Optics) fitted to an optical microscope via fiber optics.

The spectra were not corrected for the spectral response of the instrument or the lamp. The quantity 2nL, commonly referred to as the effective optical thickness (EOT), was determined from the Fabry–Pérot relationship: $m\lambda = 2nL$, where λ is the wavelength of maximum constructive interference for spectral fringe of order m, n is the index of refraction of the porous layer and its contents and L is the thickness of the porous layer. The EOT was determined by the Fourier transformation of the reflectivity spectrum, which resulted in a sharp peak whose position was equal to the product value of 2nL. The method for detecting the optical thickness described herein is FT-RIS.

DR-FTIR: Changing of chemical bonds at the surface of pSi during voltage scanning process diffuse reflection-infrared Fourier transform spectroscopy. PSi chip after different voltage scanning cycles were detected by diffuse reflection-infrared Fourier transform spectroscopy (NICOLET iS10, Thermo SCIENTIFIC).

XPS: The elements on the surface of pSi and modified pSi were analyzed by X-ray photoelectron spectrophotometer (XPS, VG ESCALAB MKII). The spectrometer was calibrated to the position of the 2p line of Si at a binding energy of 99.15 eV. Curve fitting of the core XPS lines was carried out using Origin software with a Gaussian-Lorentzian product function and a nonlinear Shirley background subtraction.

Contact angle measurement: Contact angles were measured on a POWERETCH®JC2000D contact angle system (Zhongchen Digital Technology Apparatus Co. Ltd, Shanghai) at ambient temperature. 1.0 μL water droplets were dropped carefully onto the surface of samples and the images were captured by the camera.

FT-RIS: FT-RIS of pSi and AuNPs-pSi with different AuNPs deposition time was monitored by USB 2000+ fiber spectrometer (QE pro, Ocean Optics).

1.4 Electrochemistry system

The three-electrode electrochemical cell for electrochemiluminescence (ECL) imaging was designed as illustrated in Scheme 1. The pSi chip as the working electrode, which was firstly put on a round Teflon support containing a groove

fitted with the size and thickness of pSi chip. Then the Teflon support was tightly fixed to the Teflon cell body via four screws and an O-ring. The Teflon cell body defined a volume of ~2 mL and a working electrode surface area of 1.1 cm^2. On the side wall of the cell body, a conduit was drilled for accommodating the silver/silver chloride (Ag/AgCl) reference electrode. And the counter electrode was a platinum wire ring placed directly above the working electrode.

1.5 Reaction of AuNPs-pSi and explosives

For explosive imaging, patterned PDMS with 4 holes (diameter = 3 mm) array was used as a array template, and aliquots (5 μL) of 0,10,30,50 μ g/mL stock solution of TNT, DNT, NT (the solvent composition is MeOH: H_2O = 1:1), TATP, H_2O_2, HMTD (the solvent composition is AcCN: H_2O = 1:1) were dropped to PDMS holes, after reaction of 30 min at 25℃, ECL images was taken.

For explosive discrimination, aliquots (5 μL) of 0,10,30,50 μg/mL stock solution of TNT, DNT, NT (the solvent composition is MeOH: H_2O = 1:1), TATP, H_2O_2, HMTD (the solvent composition is AcCN: H_2O = 1:1) were dropped to AuNPs-pSi chips, after reaction of 30 min at 25℃, ECL images was measured.

1.6 Collection of ECL images

ECL imaging was performed in 0.1M KNO_3 buffer solution. The applied cyclic potential was -0.1-1.0 V (vs Ag/AgCl/3M KCl). ECL images were captured with a Model M3154-MP lens (Computar, Japan) and theTCC-1.4HICE CCD (Mshot, China), exposure time was set to 3s and the voltage gain was set to 3V. The cross-sectional analysis of CCD images was done using ImageJ2x software, and the maximum gray value was defined as 255 units when the image was white and as 0 unit when it was black.

1.7 Collection of ECL and PL spectra

The PL spectra of pSi chip during voltage scanning process were obtained by fluorescence microscope (NE950, Nexcope), The excitation wavelength was set at 375 nm, and the fluorescent spectra was acquired by a fiber spectrometer (QE pro, Ocean Optics) coupled to the microscopy. The intergal time was set to 500ms. ECL spectra of pSi and AuNPs-pSi was acquired by the fiber spectrometer (QE pro, Ocean Optics), and the intergal time was set to 22s.

2. Supplementary Figures
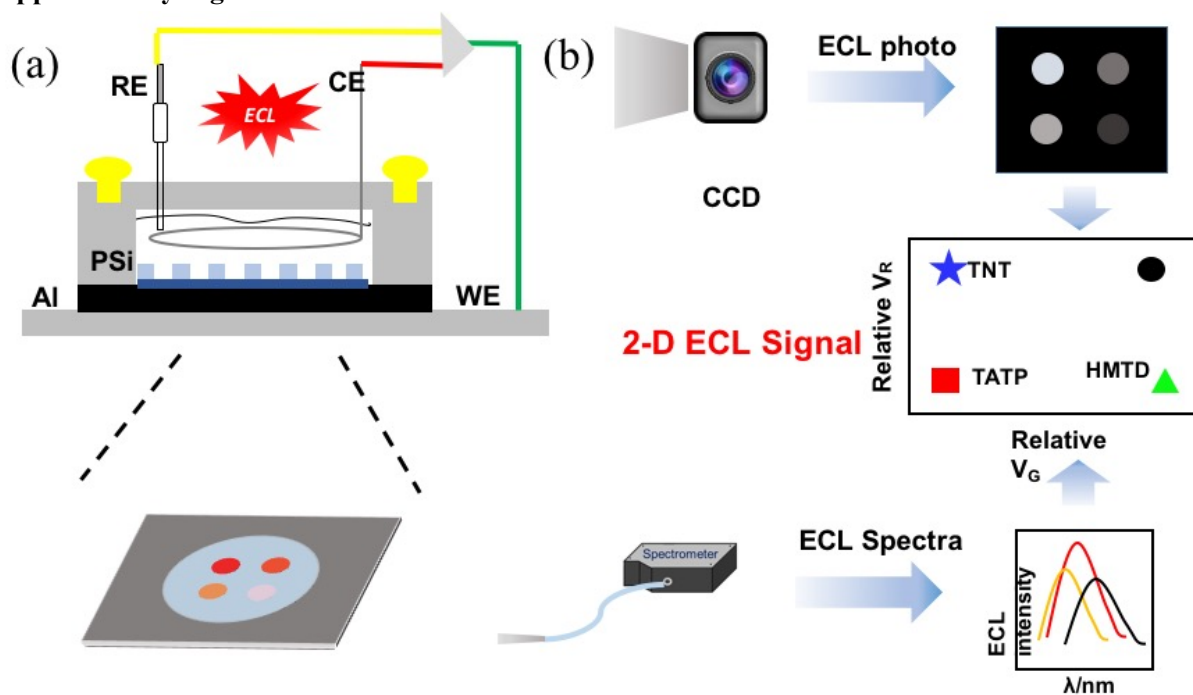
Scheme S1. ECL imaging (a) and spectra detection (b) system
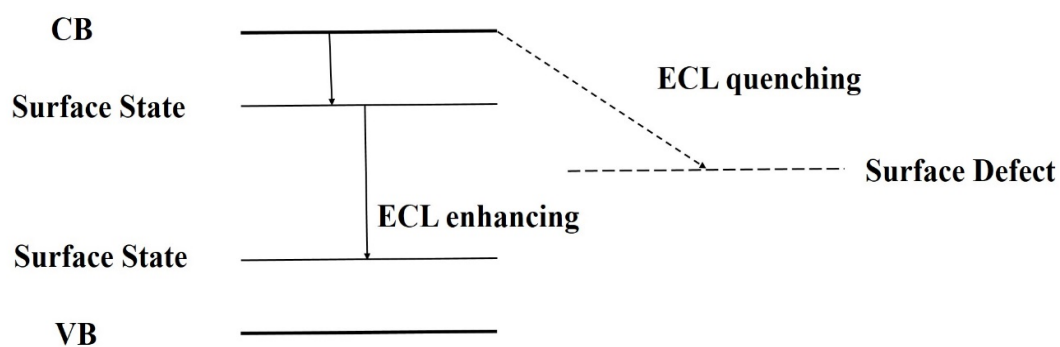
Scheme S2. Simplified kinetic scheme to model two oxidation mechanisms: electrochemistry oxidation (solid line) and peroxide oxidation (dashed line)
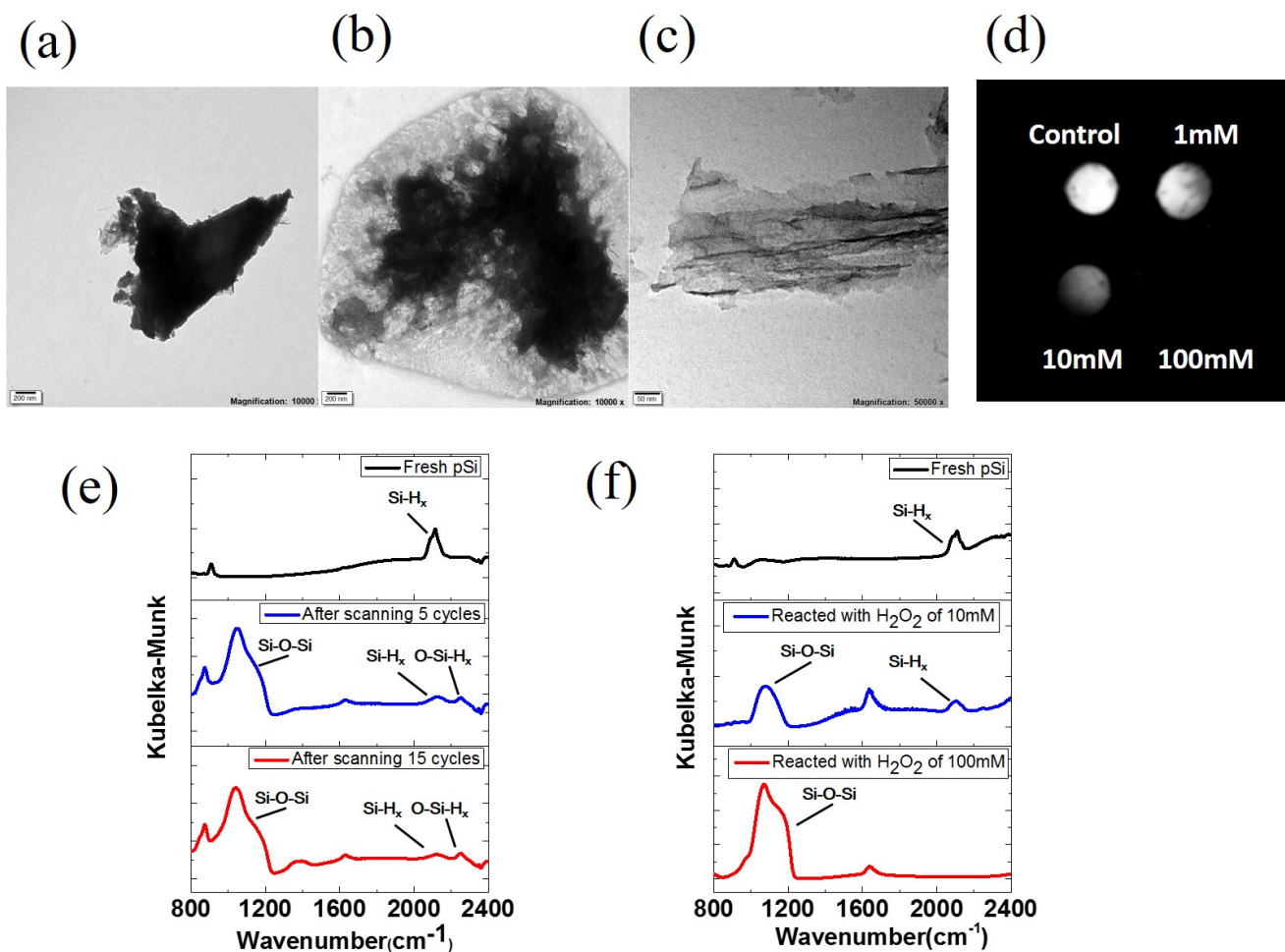
Figure S1. (a-c) TEM images of pSi particles after 0(a),5(b),15(c) voltage cycles; (d): ECL image pSi reacted with H_2O_2 of 1, 10 and 100mM after 60mins; (e) DR-FTIR curves of pSi after 0,5,15 voltage cycles; (f) DR-FTIR curves of pSi reacted with H_2O_2 of 0, 10, 100mM for 60 min
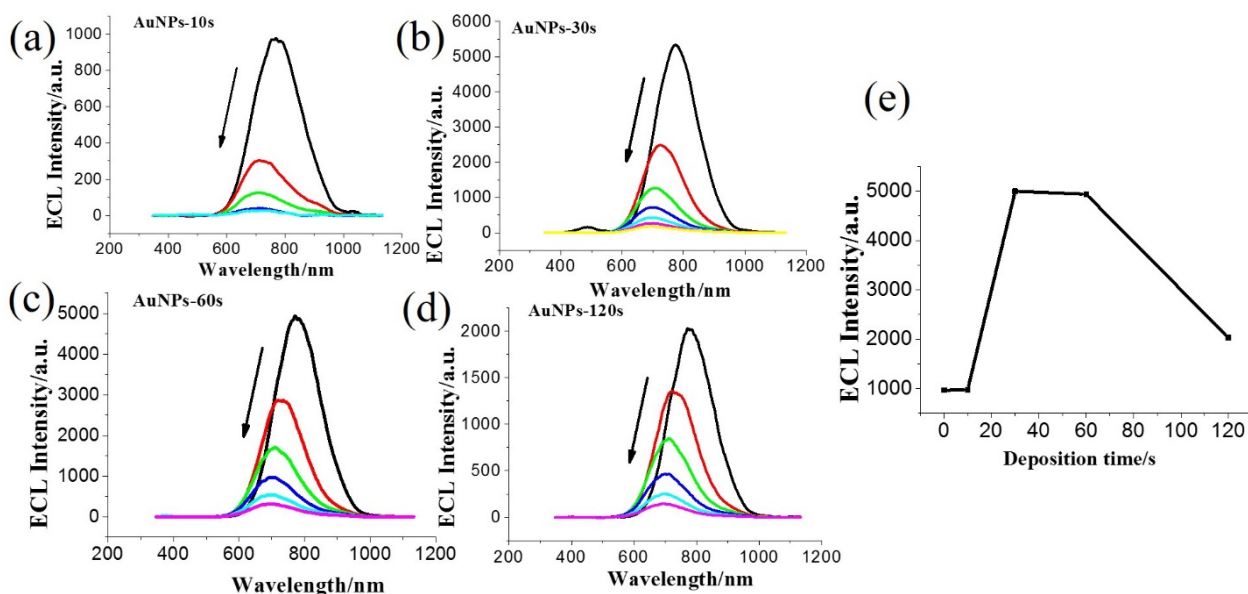
Figure S2. (a-d) ECL spectra of pSi with different AuNPs deposition time: 10s (a),30s(b), 60s(c), 120s(d); (e) change of maximum ECL intensity with AuNPs deposition time
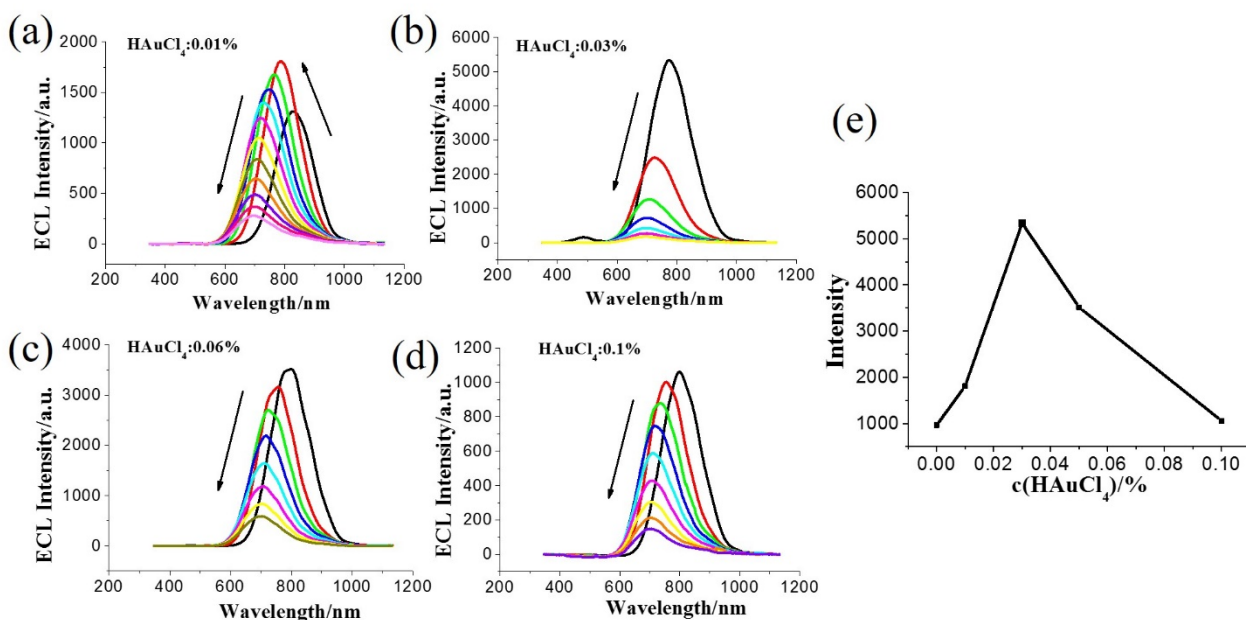

Figure S3. (a-d): ECL spectra of pSi with different $HAuCl_4$ concentration(w/v) : 0.01%(a),0.03%(b), 0.06%(c), 0.1%(d); (e) change of maximum ECL intensity with $HAuCl_4$ concentration
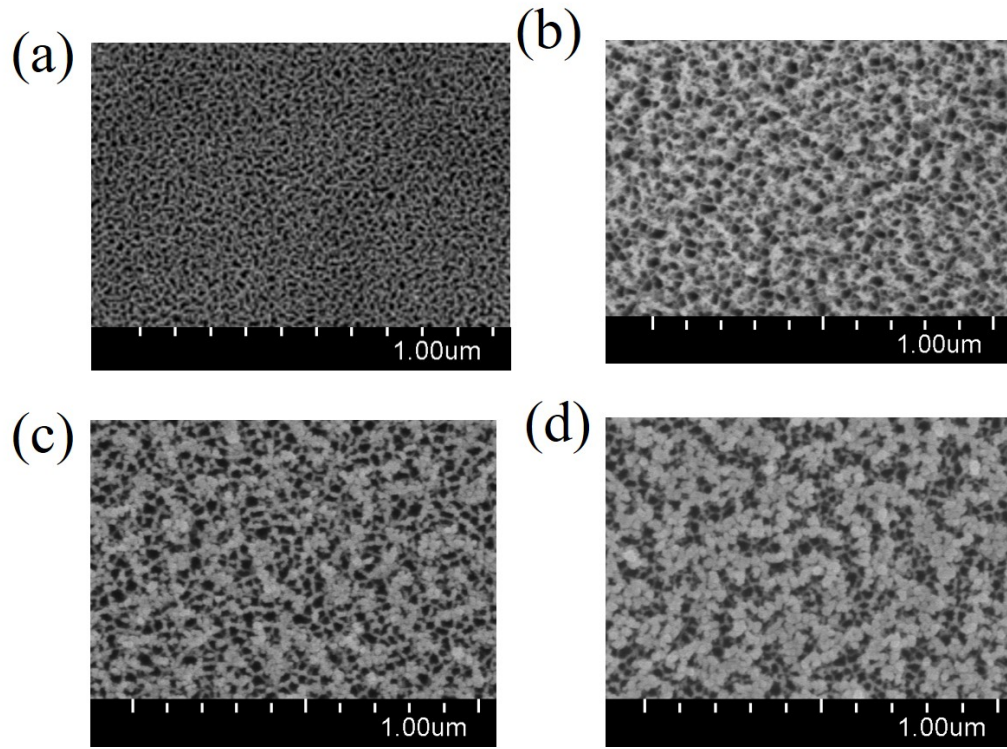
Figure S4. SEM images of pSi(a)and AuNPs-pSi with different AuNPs deposition time:0(a),30s(b),60s(c),120s(d)
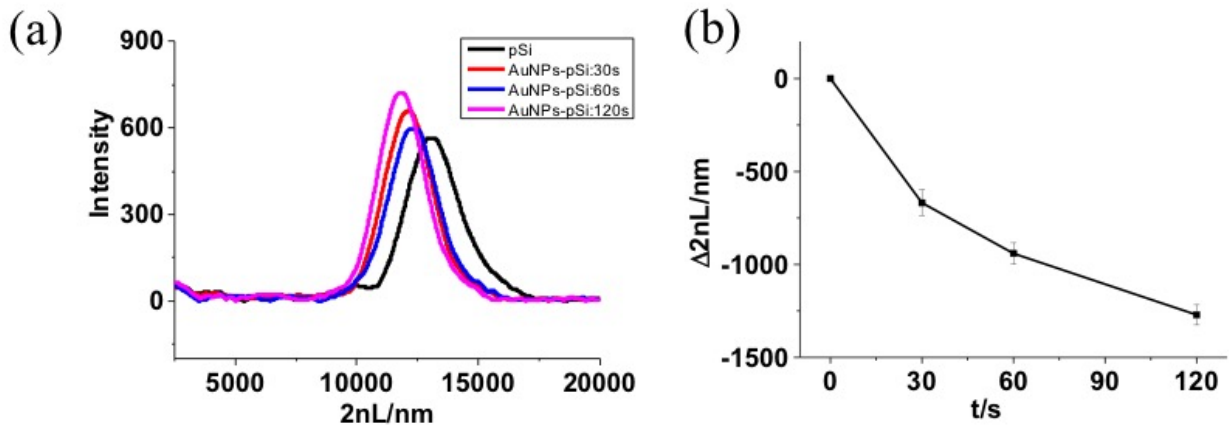

Figure S5. (a) FT-RIS spectra of pSi and AuNPs-pSi with AuNPs deposition time of 30s, 60s, 120s; (b) changes of 2nL values (EOT $_{AuNPs-pSi}$ - EOT $_{pSi}$) at AuNPs deposition time of 30s, 60s, 120s, a significant decrease in the optical thickness was found in the FFT spectrum of pSi-AuNPs as the duration of deposition of AuNPs increased. The blue shift phenomenon can be explained by the Bruggman equation [1]. After the deposition of AuNPs, the porous layer can be regarded as a homogeneous dielectric material composed of Si、SiO$_2$ and Au. Given that both n$_{Au}$ and n$_{SiO2}$ are less than n$_{Si}$, the n_{eff} of the whole porous layer decreases, leading to the blue shift in the 2nL value.
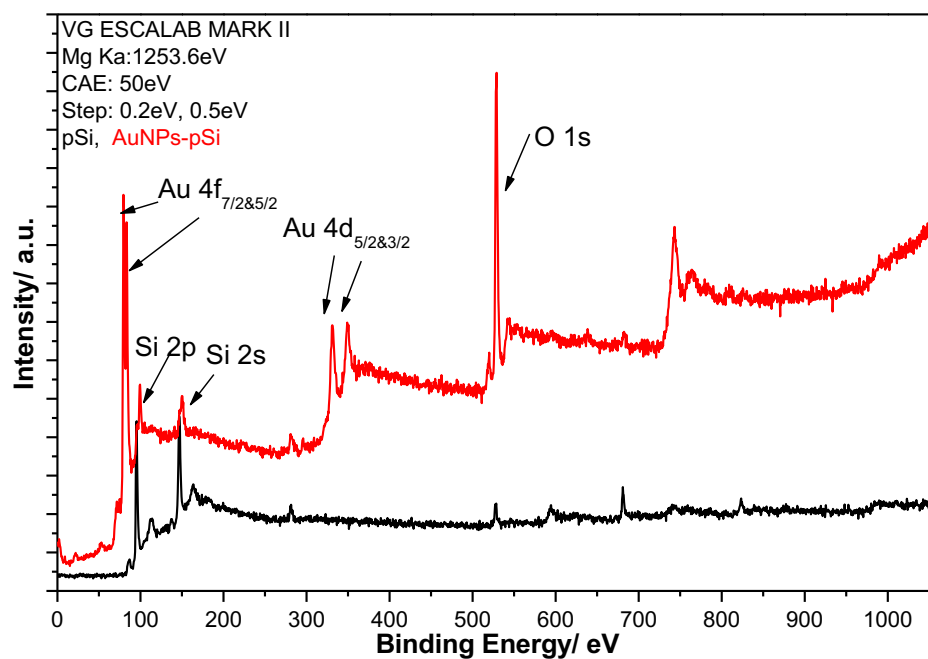
Figure S6. X-ray photoelectron spectroscopy of pSi and AuNPs-pSi with AuNPs deposition time of 30s
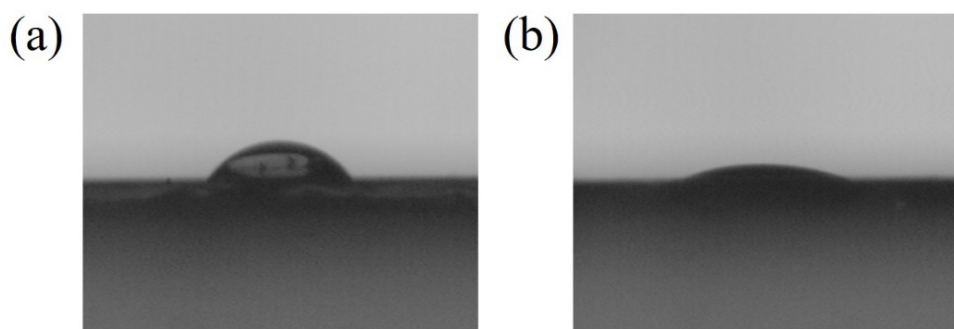

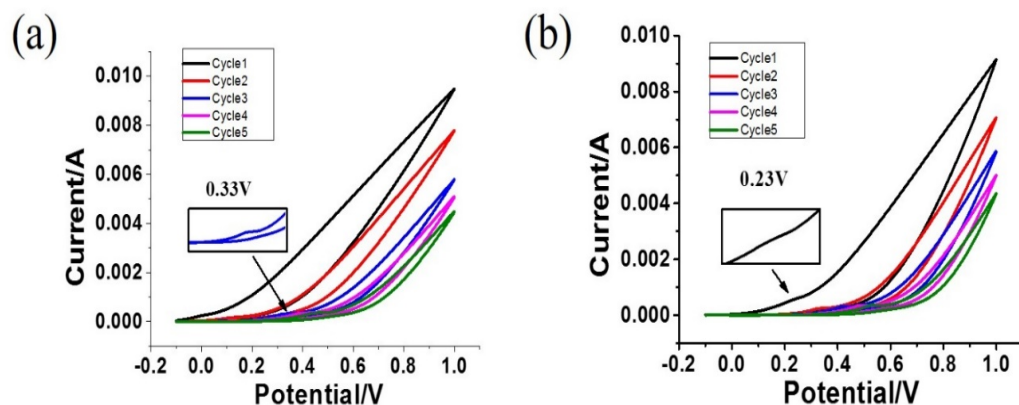**Figure S7**. Images of water contact angle test for pSi(a) and AuNPs-pSi(b)

Figure S8. C-V curves of pSi (a) and AuNPs-pSi (b). The C-V measurements were performed in 0.1M KNO_3 as the electrolyte of the pSi/liquid cell, and the voltage of pSi was cycled from -0.1 to +1.0 V (vs. Ag/AgCl) at a scan rate of 0.1 V/min.
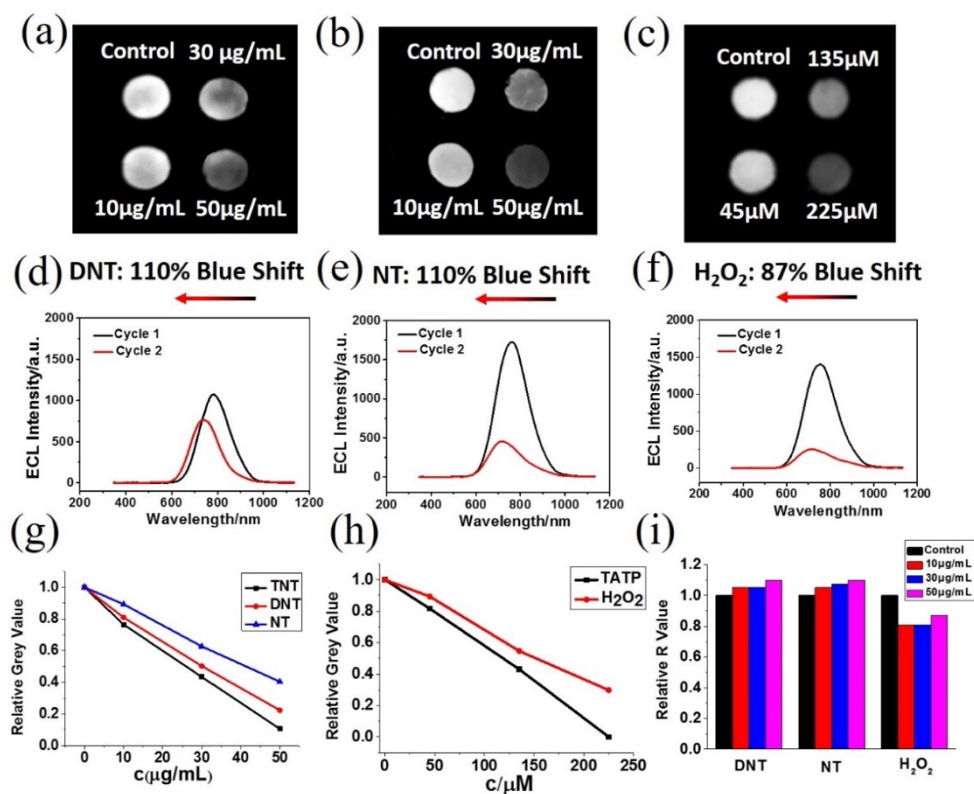

Figure S9. (a-c) ECL image of AuNPs-pSi after reacted with DNT(a), NT(b), H_2O_2(c) for 5 min; (d) Relative grey value of three ECL images; (d-f) ECL peak position changes between 1 and 2 voltage scanning cycle of DNT(d), NT(e), H_2O_2(f) of 50ug/mL; (g) Relative grey value of AuNPs-pSi after reacted with TNT, DNT and NT; (h) Relative grey value of AuNPs-pSi after reacted with TATP and H_2O_2 (i) Relative R value of AuNPs-pSi after reacted with DNT, NT, H_2O_2 for 5 min

References:

[1] Astrova, E.V.; Tolmachev V.A.; Effective refractive index and composition of oxidized porous silicon films. *Mater. Sci. Eng.* **2000**, B69–70, 142–148.