Supporting Information

A Photoelectrochemical Sensor Based on a Reliable Basic Photoactive Matrix Possessing Good Analytical Performance for miRNA-21 Detection

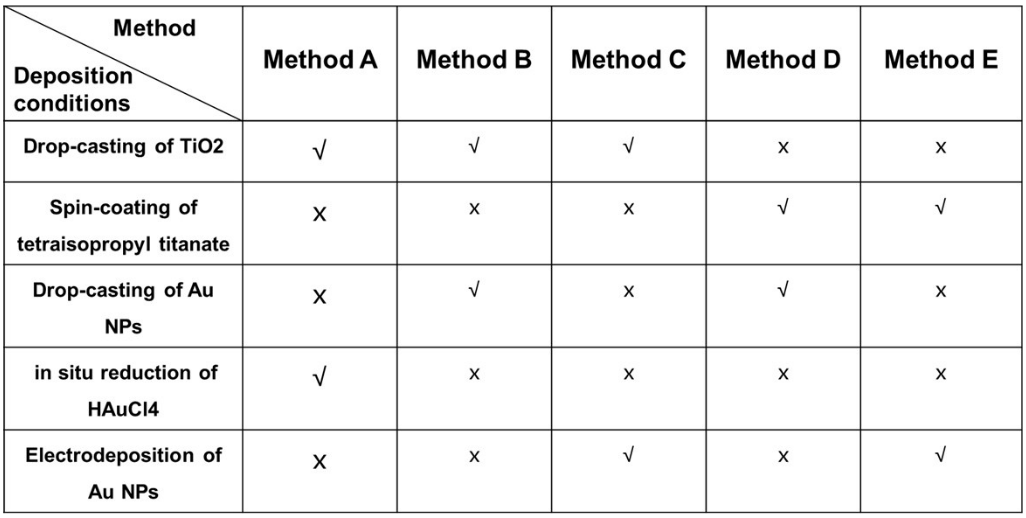
Nina Fu[a], Lulu Wang[a], Xin Zou[a], Chang Li[a], Shengyu Zhang[a], Baomin Zhao[a,*], Yu Gao[a], Lianhui Wang [a,*]

[a] Key Laboratory for Organic Electronics and Information Displays & Jiangsu Key Laboratory for Biosensors, Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023. Correspondence: iambmzhao@njupt.edu.cn; iamlhwang@njupt.edu.cn; tel.:+86-25-8586-6332

Synthesis of CdTe−COOH QDs. The water-soluble CdTe-COOH was synthesized via the previously reported procedure with optimization.[1,2] In a three-necked flask, 0.6 mmol of $CdCl_2$ and 1 mmol of MPA are mixed in a 120 mL solution. Under stirring of a stirrer, 1.0 M NaOH is added to make the pH value reached 11.8. After degassing pure nitrogen in the bottle for 30 minutes, 120 mg of $NaBH_4$ and 0.06 mmol of $NaTeO_3$ were added so that the molar ratio of Cd^{2+} : Te^{2-} : MPA was 1 : 0.1 : 1.7. Subsequently, under an argon atmosphere, the mixed solution was heated to reflux at 100 °C for 6 hr. After the reaction was cooled to room temperature, CdTe-COOH quantum dots was collected by remove the solvents and ultracentrifugation.

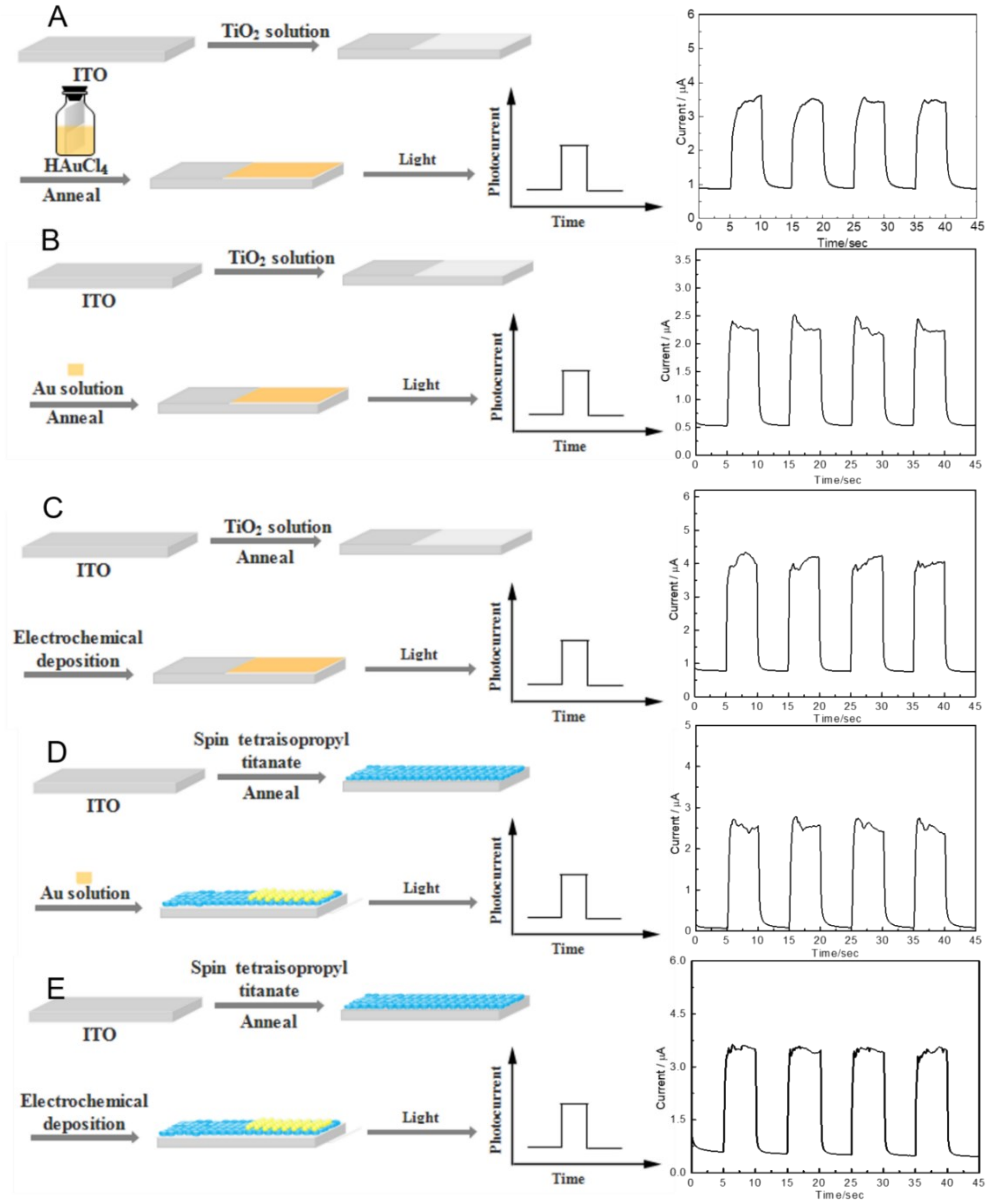
Preparation of the ITO/TiO_2/AuNPs Electrode.

Table S1. Comparison of five sequential deposition methods for Au NPs decorated TiO_2 on ITO slices.



Method Deposition conditions	Method A	Method B	Method C	Method D	Method E
Drop-casting of TiO2	√	√	√	x	x
Spin-coating of tetraisopropyl titanate	x	x	x	√	√
Drop-casting of Au NPs	x	√	x	√	x
in situ reduction of HAuCl4	√	x	x	x	x
Electrodeposition of Au NPs	x	x	√	x	√

ITO/TiO_2/AuNPs photoanodes were prepared through five different methods.



Scheme S1. The five different fabrication methods toward the ITO/TiO_2/AuNPs photoanodes (Method A, B, C, D and E) and their typical *i-t* curves under 530 nm light irradiation.

Method A: Dispose 3 mg/ml TiO_2 powder suspension and sonicate for 5 minutes so that TiO_2 powder is uniformly dispersed in deionized water. Subsequently, 10 μL of the TiO_2 suspension solution is dropped on ITO slices with a fixed modification area of ~0.3 cm^2 using a fixed groove. After air drying, immersing in 0.01 mM $HAuCl_4$ solution for 4 hours, $[AuCl(OH)_3]^-$ is formed on the surface of TiO_2. The unreacted $HAuCl_4$ solution is gently rinsed with deionized water, followed by thermal annealing at 450°C for 2 hr before cooling to room temperature in N_2. The ITO/TiO_2/AuNPs photoanodes are finally fabricated, which shall be placed in a ventilated and dry place for use.

Method B: The deposition of TiO_2 layer on ITO slices is the same operated as described in Method A. Then, a certain amount of gold nanoparticles solution is loaded onto TiO_2 film dropwise. After Au NPs are adsorbed on the surface of TiO_2, the as-prepared electrode is annealed at 450 ^oC for 2 hr. Then, the photoanodes are cooled to room temperature and placed in a ventilated and dry place for use.

Method C: The deposition of TiO_2 layer on ITO slices is the same operated as described in Method A. Gold nanoparticles are in-situ electrodeposited onto TiO_2 film using the following deposition conditions: electrodeposition potential is 0.3 V, deposition time is 3600 seconds and the electrolyte solution is 0.2 mM $HAuCl_4$ solution. After the decoration of gold nanoparticles on TiO_2 film, the electrodes are stored in a ventilated and dry place for use.

Method D: After the cleaned ITO slices are subjected to plasma UV-ozone treatment to increase the work function of the ITO surface. Thus, the formed surface structure is easily spin-coated with organic solutions. An appropriate amount of tetraisopropyl titanate precursor is spin-coated on the ITO slice. The spin speed is 2000 rpm, the acceleration is 1000 rpm/s, and the spin-on time lasts for 40 seconds. Subsequently, the ITO/TiO_2 electrodes are thermally annealed at 450 ^oC for 2 hr. After they are cooled to room temperature, a certain amount of Au nanoparticle solution was dropped onto the as-prepared electrode to form a layer of Au NPs.

Method E: The deposition of TiO_2 layer on ITO slices is the same operated as described in Method D. Subsequently, Au nanoparticles are electrodeposited as described in Method C. After Au NPs are decorated, the ITO/TiO_2/Au NPs anode are dried in air at room temperature. Finally, the electrode was further dried in a muffle furnace and annealed at 350 ^oC for 1 hour before cooling to room temperature to form a stable and compact ITO/TiO_2/Au NPs photoanode.

REFERENCE

(1) Zou, L.; Gu, Z. Y.; Zhang, N.; Zhang, Y. L.; Fang, Z.; Zhu, W. H.; Zhong, X. H., Ultrafast synthesis of highly luminescent green- to near infrared-emitting CdTe nanocrystals in aqueous phase. *J. Mater. Chem.* **2008**, *18*, 2807−2815.

(2) Wang, R. F.; Wang, Y. L.; Feng, Q. L.; Zhou, L. Y.; Gong, F. Z.; Lan, Y. W., Synthesis and Characterization of Cysteamine-CdTe Quantum Dots via One-step Aqueous Method. *Mater. Lett.* **2012**, 66, 261−263.

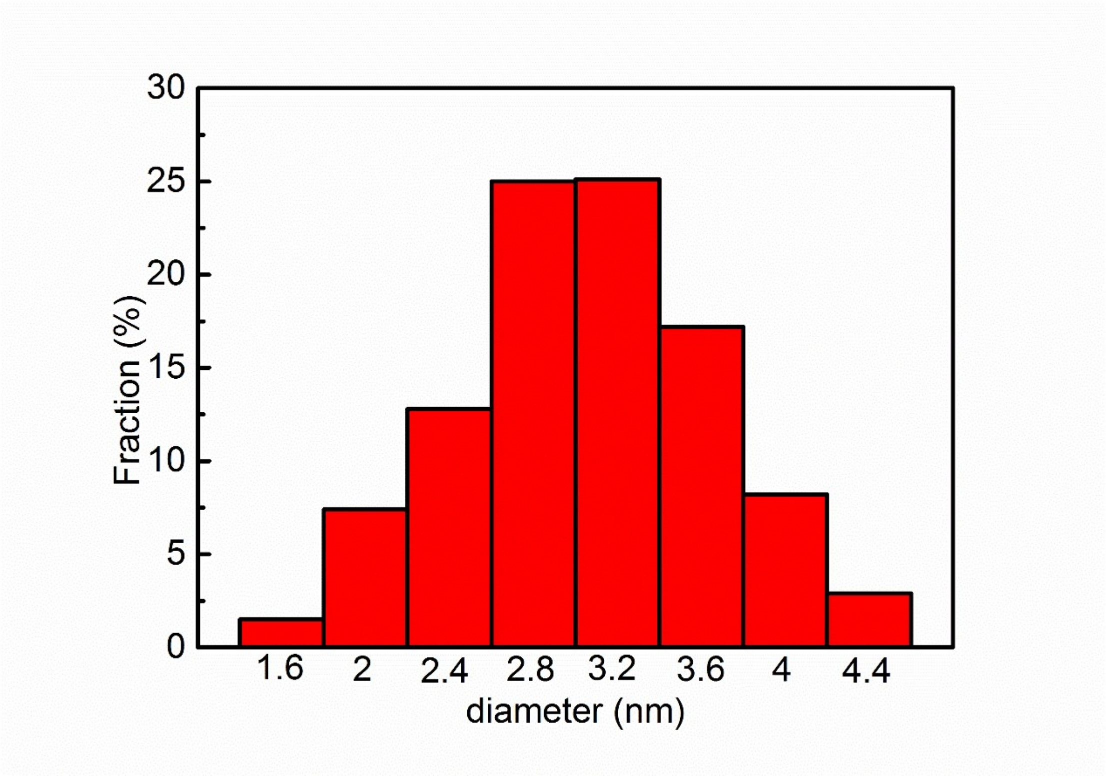


Fig S1. DLS profiles of CdTe-COOH QDs.

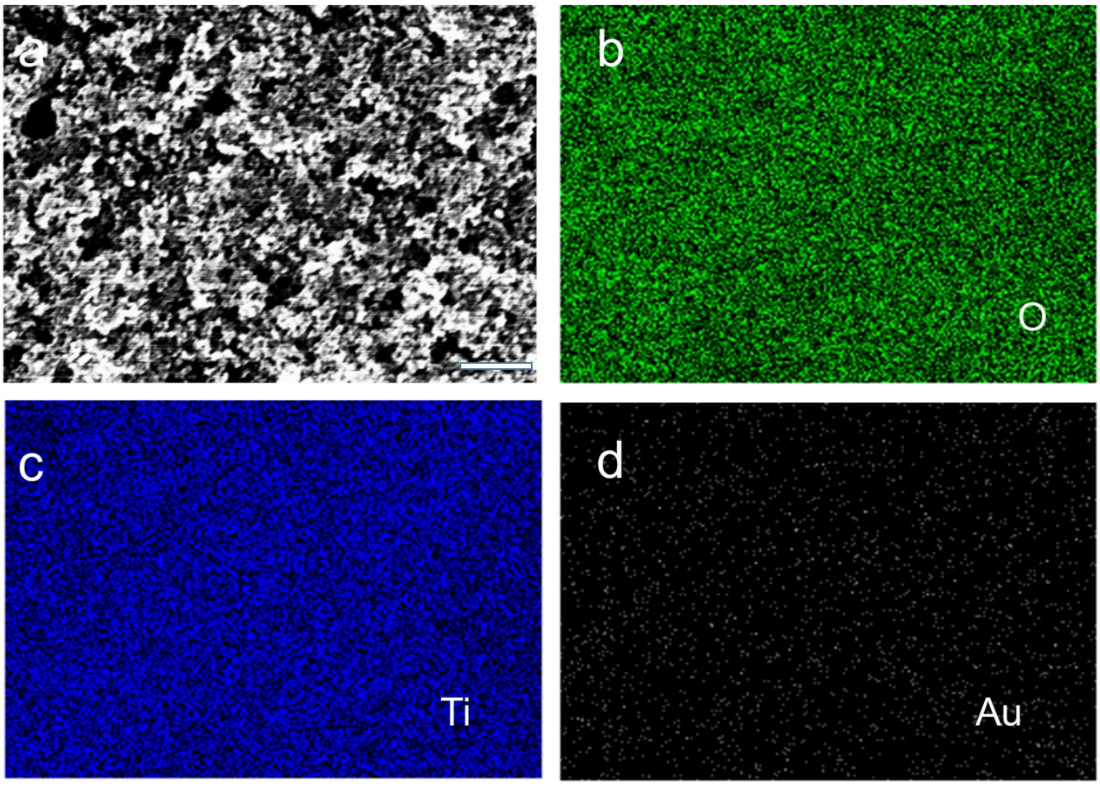


Figure S2. a) SEM image of ITO/TiO_2/AuNPs deposited by Method A (Scale bar, 2 μm), b) Elemental mapping image for oxygen, c) Elemental mapping image for Titanium, d) Elemental mapping image for gold.

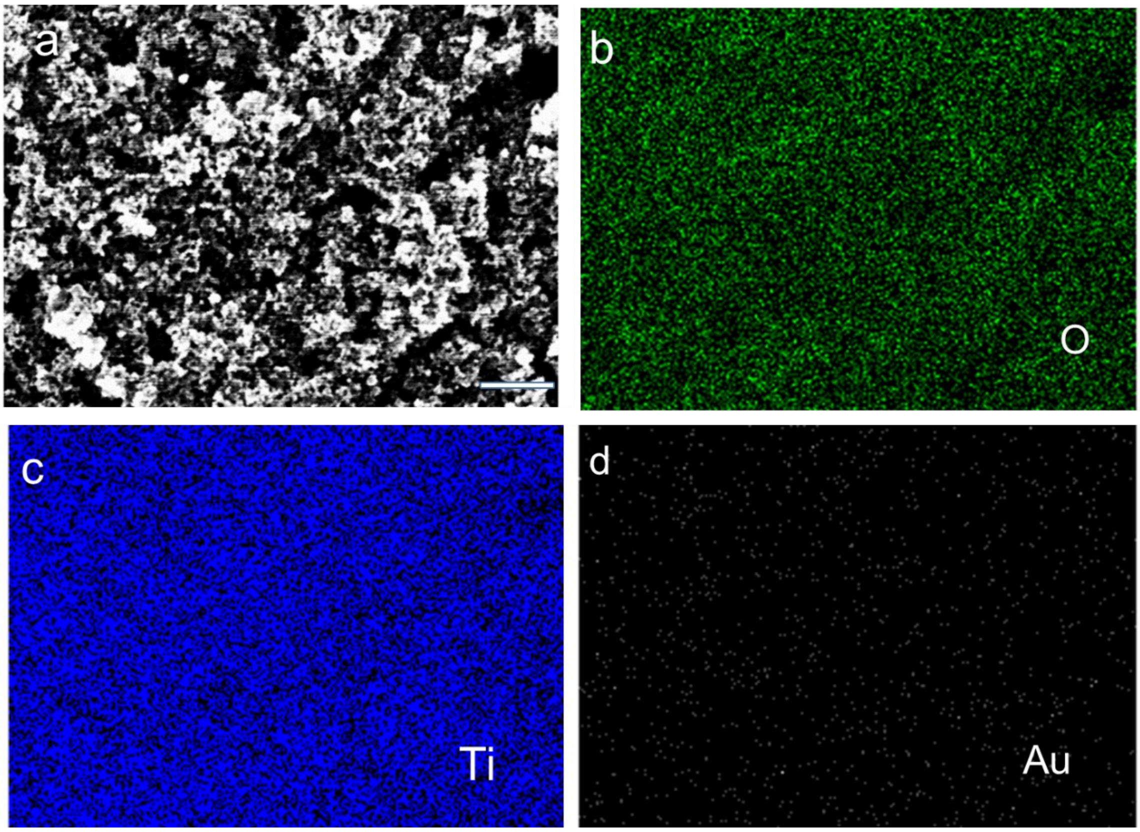


Figure S3. a) SEM image of ITO/TiO_2/AuNPs deposited by Method B (Scale bar, 2 μm), b) Elemental mapping image for oxygen, c) Elemental mapping image for Titanium, d) Elemental mapping image for gold.

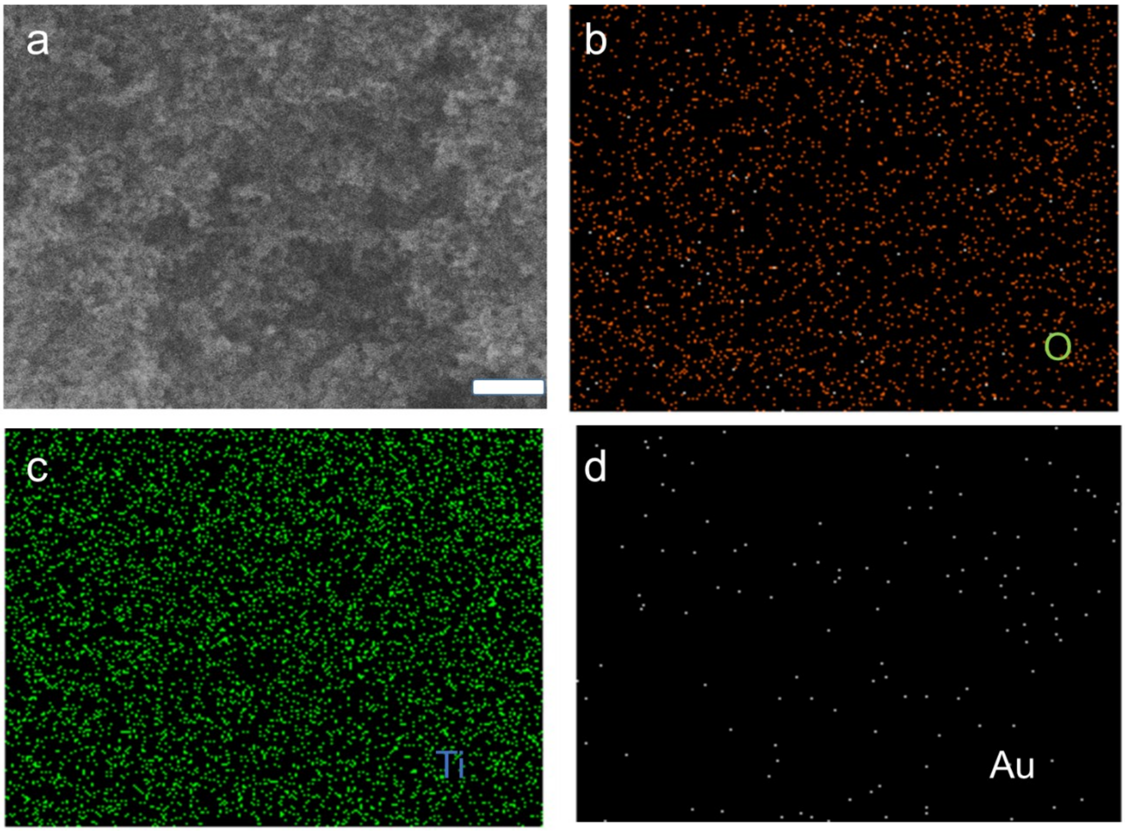


Figure S4. a) SEM image of ITO/TiO_2/AuNPs deposited by Method C (Scale bar, 2 μm), b) Elemental mapping image for oxygen, c) Elemental mapping image for Titanium, d) Elemental mapping image for gold.

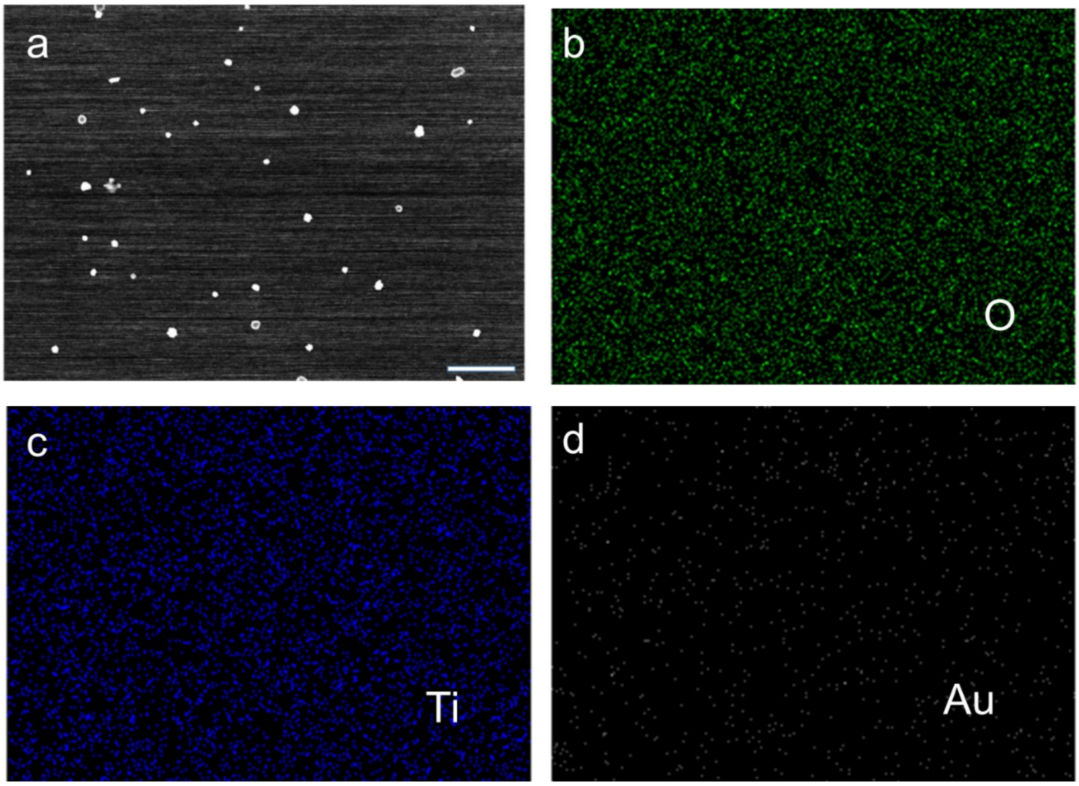


Figure S5. a) SEM image of ITO/TiO_2/AuNPs deposited by Method D (Scale bar, 2 μm), b) Elemental mapping image for oxygen, c) Elemental mapping image for Titanium, d) Elemental mapping image for gold.

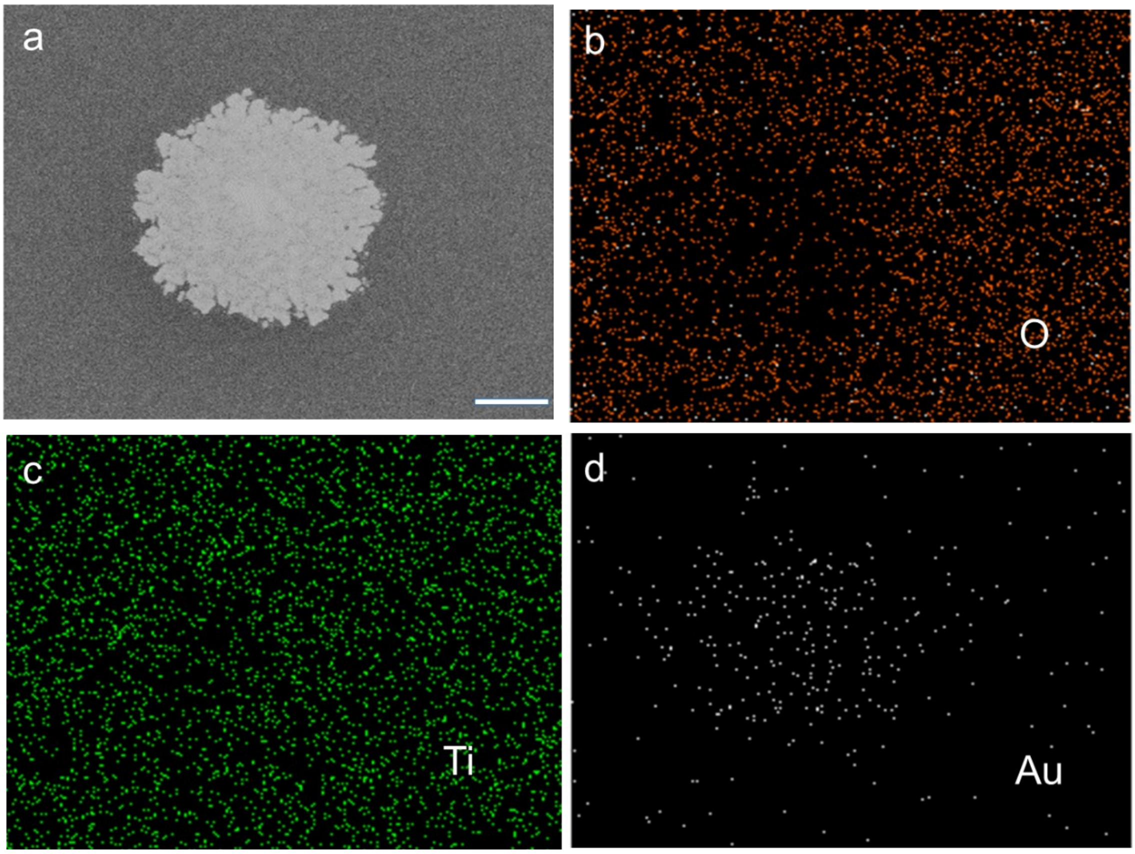


Figure S6. a) SEM image of ITO/TiO_2/AuNPs deposited by Method E (Scale bar, 2 μm), b) Elemental mapping image for oxygen, c) Elemental mapping image for titanium, d) Elemental mapping image for gold.

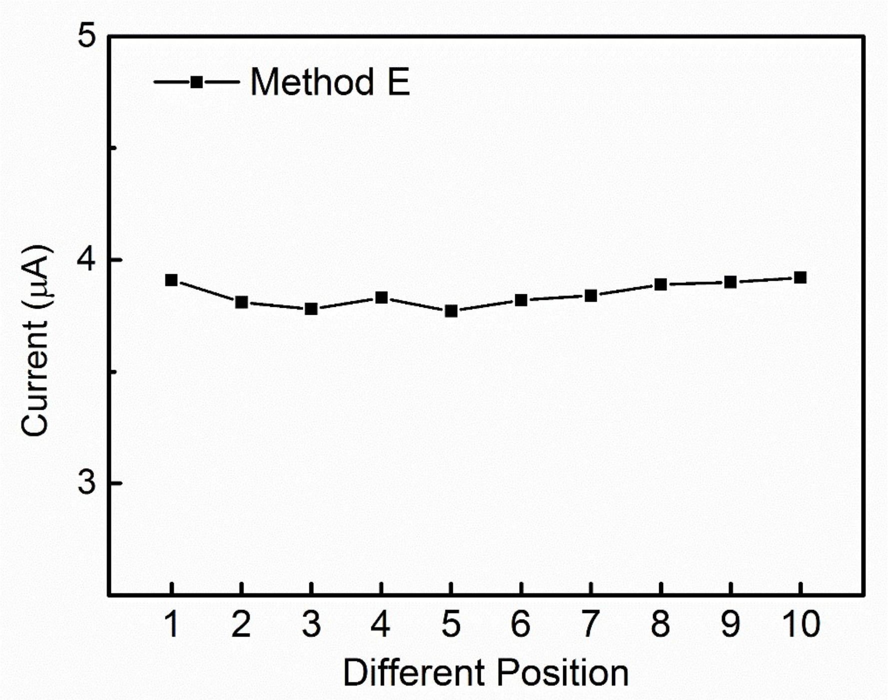


Figure S7. The photocurrents of ten different spots on a larger ITO/TiO_2/AuNPs electrods were measured (under 530 nm laser excitation).

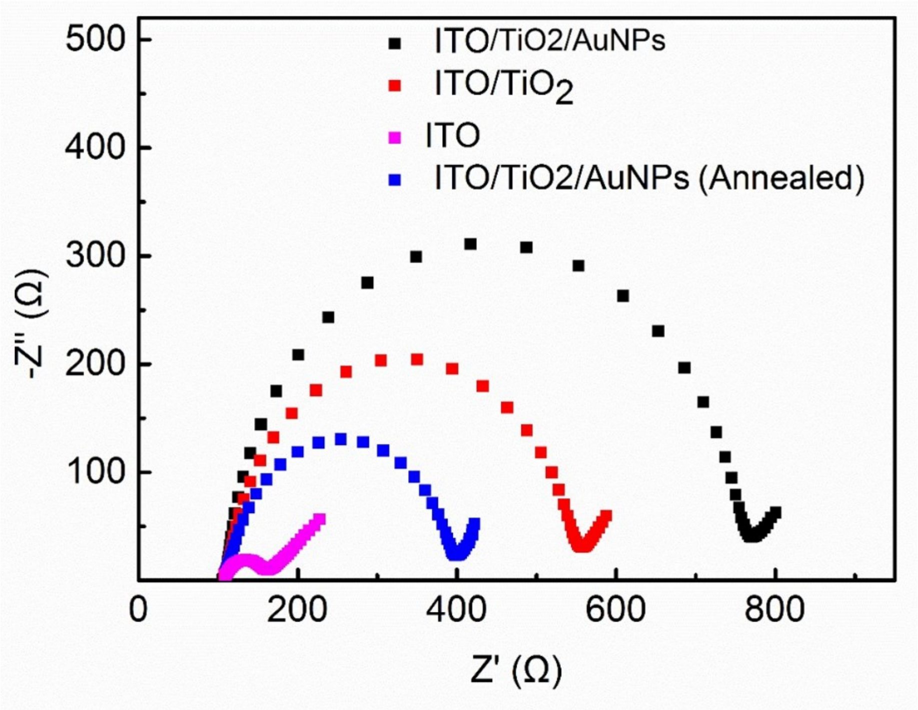


Figure S8. EIS curves for bare ITO (pink), ITO/TiO$_2$ (red), ITO/TiO$_2$/AuNPs (black), and ITO/TiO$_2$/AuNPs with thermal treatment (blue).