

# Supplementary Information

For

## A Universal Method for Preparing Functional ITO Electrodes with Ultrahigh Stability

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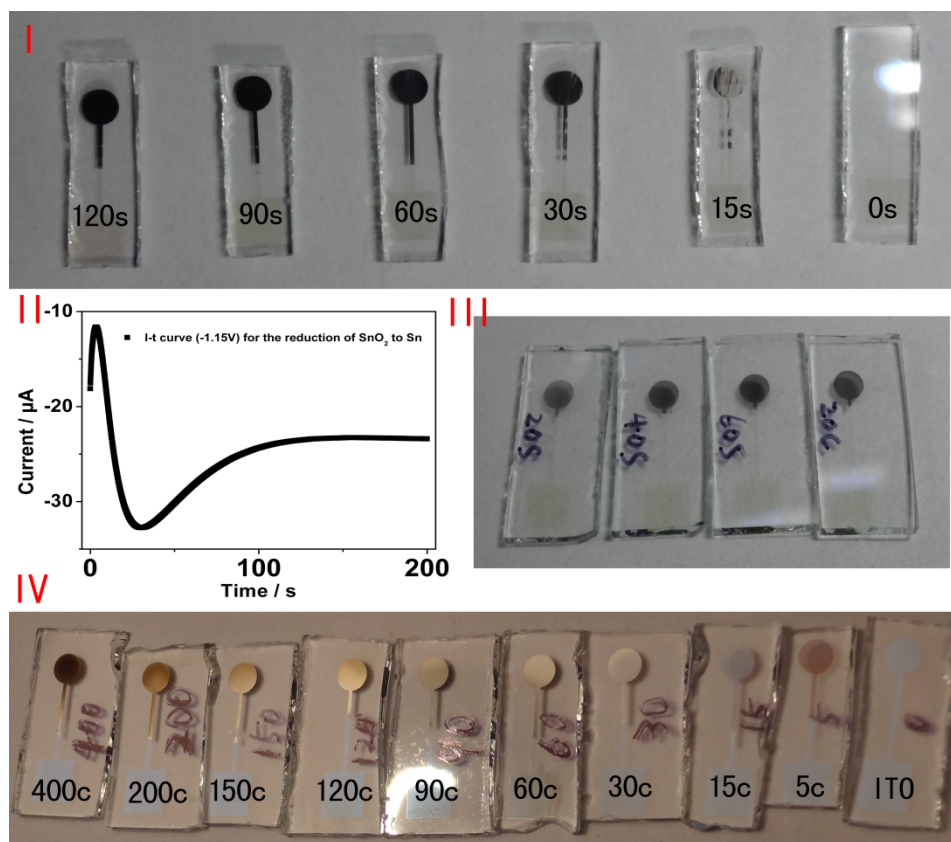
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### **Universal modification process of the M/ITO electrode.**

All the ITO substrates used were first washed with detergent, sonicated in acetone, ethanol and water for 5 min successively and then dried with the nitrogen gas. Then, three easy steps were performed to electrodeposite different materials onto the patterned ITO electrode surface with ultrahigh stability. The surface of the patterned ITO electrode (Substrate 1) was reduced into a thin film of In-Sn (Substrate 2) by applying a constant potential of -1.15 V (**Fig. S1III**). At first, we tried to construct Pt film on this substrate simply by the replacement reaction. However, the In-Sn layer disappeared gradually and left the ITO electrode (substrate 3) when the substrate 2 was immersed into the chloroplatinic acid solution (1, 10 or 100 mM). We have also tried to electrodeposite Pt layer onto the In-Sn/ITO electrode but failed as well. Very occasionally, substrate 3 was used as the deposition substrate, and it was found that the deposited Pt film on this substrate possessed surprising mechanical stability. Then, the aqua regia

was employed to destroy the In-Sn layer on the substrate 2. Experimental results demonstrated that the obtained substrate was equivalent to the substrate 3. As such, the deposition strategy was established: (1) reduction; (2) stripping by aqua regia; (3) electrodeposition.



**Fig. S1.** (I) Reduction time optimization. (II) The i-t curve for the reduction of the ITO substrate. (III) Comparison of the potentiostatic method and the double-pulse method for Pt electrodeposition. (IV) Optimization of the deposition cycle for Pt.

### Optimization of the strategy.

In this section, Pt was employed as an example for the optimization of the deposition conditions. First of all, the reduction time of the original ITO substrate was tested. As shown in **Fig. S1I**, The stability of the electrodeposited Pt layer was increased with the reduction time. The Pt film on the ITO can be erased easily, when the reduction time was less than 30 s. However, when the potential was applied for more than ( $\geq$ ) 60 s, the resulting layer became very stable. Also, we found that even the reduction time

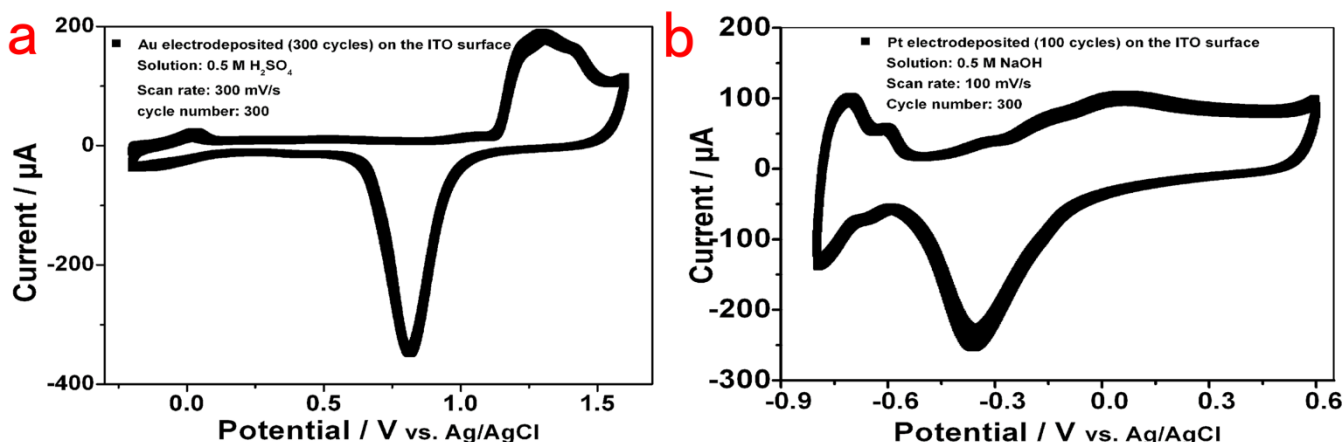
reached 200 s; the obtained substrate was also suitable for the following electrodeposition process. As to the stripping time, it was found that 2 s was enough for the aqua regia to remove the In-Sn layer completely. Then the double-pulse electrodeposition method (positive potential: 1.20 V-1 s; negative potential: -0.4-1s V; 20 cycles) and the potentiostatic method (-0.4V, 20 s, 40 s and 60 s) were performed for comparisons. As sketched in **Fig. S1III**, the double-pulse method exhibited higher deposition efficiency than that of the potentiostatic method. Thus, the double-pulse method was selected in all the following experiments for the Pt deposition. Besides, the cycle number was also optimized. When the cycle number was between 30 and 150, the deposited film exhibited beautiful metallic sheen. In addition, if the cycle number was less than 30, the resulting was transparent to some extent, whereas the surface of the obtained electrode turned black if the cycle number was more than 200. However, it was found that the thickness ( $\sim 172 \pm 10$  nm, measured by Changchun Institute of Optics, Fine Mechanics and Physics) or deposition cycle ( $\sim 400$  cycles) has no great influence on the mechanical stability of the Pt/ITO (M/ITO) electrodes obtained by the RSED strategy (**Fig. S1IV**). All the optimized electrodeposition solutions and conditions were listed in Table S1.

<b>Material</b>	<b>Deposition solution</b>	<b>Method</b>	<b>Parameters</b>
Au	10 mM HAuCl <sub>4</sub>	Double-pulse	0.5 V - 0.5 s; -0.2 V - 1 s
Pt	10 mM H <sub>2</sub> PtCl <sub>6</sub>	Double-pulse	1.2 V - 0.5 s; -0.4 V - 1 s
Pd	10 mM H <sub>2</sub> PdCl <sub>4</sub>	Double-pulse	0.5 V - 0.5 s; -0.15 V - 1 s
Ag	0.25 M AgNO <sub>3</sub> +0.75M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> +0.43M NaHSO <sub>3</sub>	Double-pulse	0 V - 0.1 s; -0.25 V - 1 s
Cu	0.1 M CuSO <sub>4</sub> +0.1M H <sub>2</sub> SO <sub>4</sub>	Double-pulse	0.3 V - 0.1 s; -0.4 V - 1 s
PB	0.1 M KCl+0.1 M HCl+2.5 mM FeCl <sub>3</sub> +2.5 mM K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	potentiostatic method	0.4 V
MnO <sub>2</sub>	100 mM C <sub>4</sub> H <sub>5</sub> MnO <sub>4</sub>	potentiostatic method	0.6 V

**Table S1.** Deposition parameters and conditions for Au, Pt, Pd, Ag, Cu, PB, MnO<sub>2</sub>. Noted that the deposition time can be tuned according to practical demands.

### Chemical and long-term Stability of the M/ITO Electrode.

Besides the mechanical stability, the chemical stability of M/ITO electrodes were also tested in 0.5 M sulfuric acid and 0.5 M sodium hydroxide solutions with cyclic voltammetry (CV), respectively. As shown in Fig. S2a, no obvious change of the Au/ITO electrode was observed after 300 cycles in 0.5 M sulfuric acid solution, and the current were fairly stable (30-300 cycles). Similar result was also found in 0.5 M sodium hydroxide solutions with a Pt/ITO working electrode (Fig. S2b). Another important feature was that the resulting electrodes showed a good long-term stability (except for the Ag/ITO electrode, which would be oxidized by the oxygen and turns black), which endowed them to be stored in the air for at least half a year without any change of the mechanical and chemical performance.

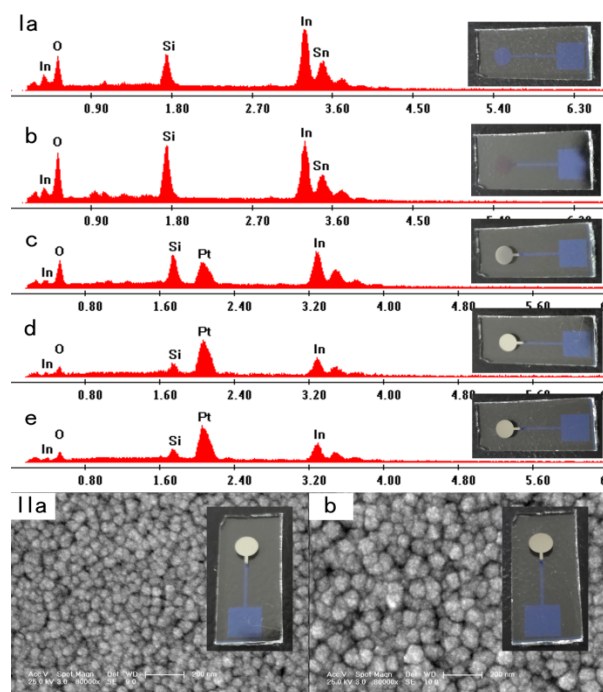


**Fig. S2.** The chemical stability of the M/ITO electrode obtained from the RSED strategy. (a) Au/ITO electrode in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (b) Pt/ITO electrode in 0.5 M NaOH.

### Mechanism Demonstration.

In this section, the scanning electron microscopy (SEM) and the energy dispersive X-Ray spectroscopy (EDX) were employed to characterize the whole process of the reduction-stripping-electrodeposition strategy (RSED). Comparing the original ITO electrode with the ITO substrate after

the Step 2, the contents of Si and O were increased, which indicated that the left ITO layer was thinner than the unprocessed ITO (**Fig. S3Ia and b**). After 30 cycles' deposition, a peak of Pt appeared in the EDX spectrogram (**Fig. S3Ic**), and the content of Pt increased obviously with the deposition cycle (**Fig. S3Id and Fig. S3Ie**). From the SEM images in **Fig. 3** and **Fig. S3II**, we found that the size of the Pt nanoparticle was increased with the cycle number, and the grown nanoparticles were assembled by smaller nano blocks.



**Fig. S3. (I)** EDX spectrograms of the deposition processes: **a)** original ITO; **b)** ITO substrate after the electro-reduction and stripping process; **c)** Pt/ITO-30 cycles; **d)** Pt/ITO-90 cycles; **e)** Pt/ITO-150 cycles. **(II)** SEM images (scale bar: 200 nm) for the resulting Pt/ITO electrode: **a)** 90 cycles; **b)** 150 cycles.

#### Experimental conditions for the Hg(II) sensing with Au/ITO electrode.

To increase the sensitivity, Hg(II) was preconcentrated at -0.2 V for 120 s in 0.1 M HCl under stirring. Then, differential pulse anodic stripping voltammetry (DPASV, step increment: 4 mV, amplitude: 50 mV, pulse period: 0.2 s, potential range: -0.2 to 0.8 V vs. Ag/AgCl) was applied for the determination

of Hg(II) under the optimized conditions. Prior to the next cycle, the potential of 0.9 V was applied for 90 s to clean the Au/ITO surface.

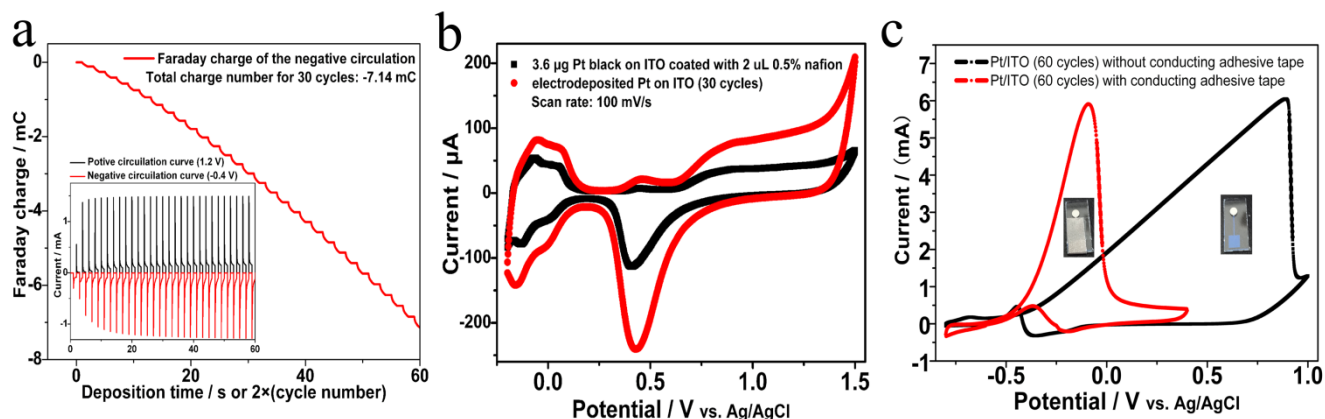
### **Pt/ITO electrode used in the methanol electro-oxidation**

As characterized earlier, the electrodeposited film is constructed by nano blocks, which indicates that the surface area of such film is extremely large. Along with the high stability of it, the obtained electrode is very promising for the electrochemical catalytic reactions. In this experiment, the Pt/ITO electrode was used as the electro-catalytic interface for the methanol electro-oxidation (1M NaOH + 0.5M CH<sub>3</sub>OH). First of all, the theoretical amount of the electrodeposited Pt was tested and calculated. As shown in **Fig. S4a**, the area of the negative deposition curve for 30 cycles was 7.14, which represented the total Faraday charge (for Pt electrodeposition) was 7.14 mC. According to Faraday's law, the amount of deposited Pt reached 3.61  $\mu$ g in 30 cycles. As a comparison, the same amount of the commercial Pt black catalyst dipped on the ITO electrode (3.6  $\mu$ g, coated with 2  $\mu$ L of 0.5% nafion) was characterized simultaneously. In 1 M H<sub>2</sub>SO<sub>4</sub> solution, the electrochemical active area of the electrodeposited Pt/ITO electrode was larger than that of the Pt black modified ITO electrode (**Fig. S4b**). Interestingly, the Pt/ITO electrode prepared by the RSED exhibited a much higher catalytic activity than the Pt-black/ITO electrode. From **Fig. 4b**, it was found that the catalytic performance of the electrodeposited Pt/ITO electrode was nearly equivalent to the Pt-black (3.6  $\mu$ g)/ITO electrode when the deposition cycle was only 10. While the cycle number reached 30, the catalytic activity of the obtained electrode was much higher than that of the Pt-black modified ITO electrode. Note that the positive shift of the peak potential with the cycle number was caused by the resistance of the ITO electrode, which can be eliminated by using a wider electrode lead or a conducting adhesive tape. Therefore, the catalytic performance can be improved simply by increasing the deposition cycle. In addition, it was believable that the catalytic performance can be further promoted by using other electrochemical methods or parameters for the material deposition on the preprocessed ITO substrate. From all the above results, the reasons why the Pt/ITO electrode possessed such good catalyst performance was concluded as: **a)** the

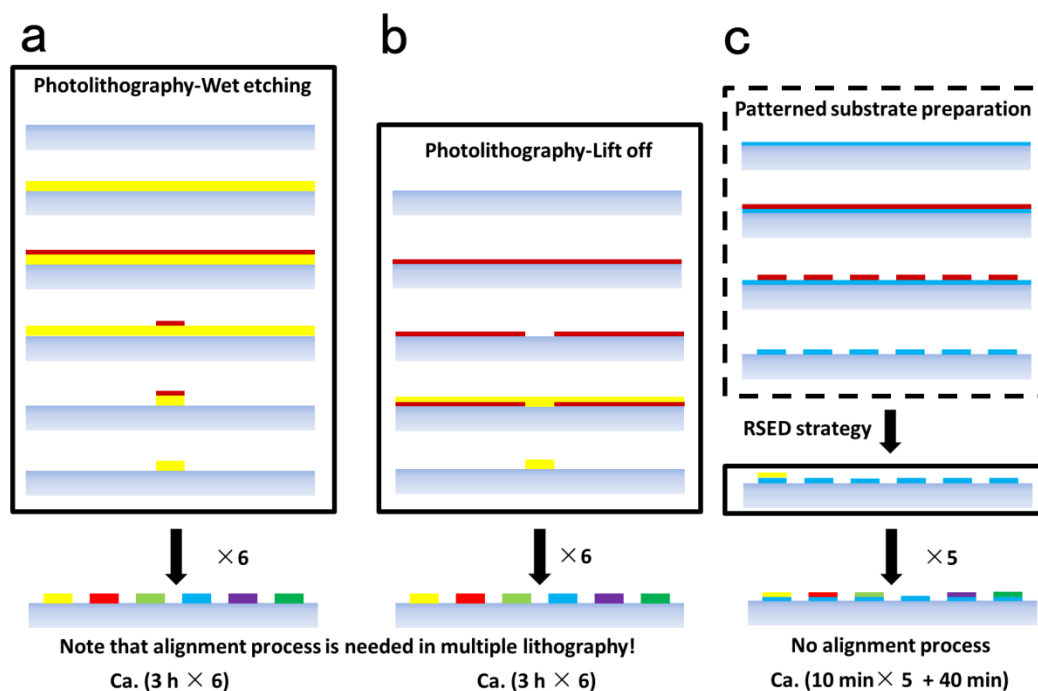
nano structure of the electrode provides it ultrahigh surface area; **b**) high and controllable capacity of Pt; **c**) zero distance (or even minus distance) between the electrodeposited film, ITO substrate and the reactive molecules accelerates the electron transfer among them; **d**) the super stability (both chemical and mechanical) of the resulting electrode ensures the perfect catalytic stability and activity (without additives). Besides the methanol electro-oxidation, from **Fig. 4b**, the reductive peak at about 0.4 V also implied the bright prospect of this electrode as the catalyst for oxygen reduction reaction. All these results demonstrate that the RSED strategy holds great promise in designing multifunctional electrochemical system with small size and high integration, including sensors, fuel cells, photoelectrochemical devices and so on.

During the electrocatalytic oxidation of methanol by Pt/ITO electrode, two strange phenomena were observed (**Fig. 4b**). First of all, the potential of the peak current was positively shifted with the deposition cycle. Secondly, the peak value of the current density was also increased with the cycle number obviously, but the slope of the positive scanning circulation increased only a little. At first, we thought that these strange phenomena may imply the poor catalytic activity of the Pt/ITO electrode obtained by the RSED. However, when the commercial Pt black catalyst was tested on a same ITO electrode, similar phenomena were observed, which didn't appear within a glassy-carbon electrode. Thus, there must be something wrong with the previous inference. Then we turned to test the resistance of the patterned ITO electrode. It was found that the used ITO electrode with a microscale lead (500  $\mu\text{m}$  wide and 7 mm long) exhibited a resistance of ca. 170  $\Omega$ . More interestingly, the rate of the peak potential to the peak current was about 137  $\Omega$  (**Fig. S4**). We supposed that these two resistances were directly related. The resistance of the patterned electrode and the solution resistance were connected in parallel, thus the total resistance was less than 170  $\Omega$ . Then the gradually increased slope was induced by the decreased electrode resistance with the increased deposition cycle. Finally, the catalytic performance of a Pt/ITO electrode (60 cycles) was tested with and without a conducting adhesive tape to demonstrate this inference (Note: a transparent tape was used to protect the conducting tape from

being immersed into solution). Interestingly, the peak potential was decreased from 0.8 V to -0.1 V without any decrease of the peak current. This result means that the deduction proposed above is absolutely right. Most importantly, the result also proved that the excellent catalytic performance of the Pt/ITO electrode prepared by the RSED.



**Fig. S4.** (a) Electrodeposition curve and its integrated area curve of the negative circulation. (b) The comparison of the electrochemical active area between Pt/ITO electrode (30 cycles) and the Pt-black (3.6 µg) modified ITO electrode. (c) The catalytic performance of the Pt/ITO electrode with or without a conducting adhesive



**Fig. S5.** The comparison between traditional method and our RSED strategy. (a) and (b) Photolithography based strategy. (b) RSED strategy.