

## Supporting Information

### Reductant-Assisted Synthesis, Characterization and Photovoltaic Characteristics of Ligand-Protected Gold Nanoparticles

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## Materials and Experimental Sections

### 1. Synthesis of TiO<sub>2</sub> Colloidal solution

Synthesis of TiO<sub>2</sub> colloidal solution has been described as follows:

Ethanol absolute and de-ionized (DI) water (each 100ml) were mixed thoroughly followed by the addition of 10 ml of Tetra-butyletitanate into the mixed solution. This is marked as solution-A. Precipitates were formed at once in the solution-A, and collected through filtration followed by washing with DI water twice. A separate solution-B was prepared by pouring 1 ml HNO<sub>3</sub> and 10 ml HAc into DI water (140ml), and heated to 80°C under constant stirring using magnetic stirrer. The white precipitates (from the solution-A) obtained through filtration and washing were added to the solution-B maintained at 80°C. The mixed solution was kept on vigorous stirring for more

than 3 hours followed by thermal treatment in Teflon-lined autoclave at 200 for 12 hours. The white slurry obtained after thermal treatment, was concentrated to 1/3 of its volume. PEG-20000 by 10 wt % of slurry was added to the dense white slurry. This white slurry is the TiO<sub>2</sub> paste which became TiO<sub>2</sub> colloidal solution after addition of a few drops of Triton-X.

## **2. Synthesis of ligand-protected Au NPs**

### **2.1 Synthesis of glutathione-protected Au NPs without any reductant (Au-GSH-A NPs)**

Briefly, 4 ml of aq. solutions of AuCl<sub>3</sub>.HCl.4H<sub>2</sub>O (20g/L) and 4.6 ml of L-glutathione (20g/L) were added to 90 ml DI water followed by stirring for 2 hour until the colorless solution was obtained. Reducing agent has not been added in the solution. Nitrogen was used to de-aerate the solution. The resultant colorless solution was kept again on stirring in water bath at 25°C for 24 hours. Au-GSH NPs formed in aqueous solutions were purified by adding acetonitrile to Au-GSH aq.solution (3:1). The centrifugation process was performed at 10000 rpm for 20 minutes to obtain metal NPs. The Au-GSH NPs, later on, were dispersed in DI water to a desired concentration. The concentration of Au-GSH NPs in DI water was adjusted between 0.60~0.70 by wt%. The pH value should be between 2~6. The adjustment in pH was made through the addition of NaOH and acetic acid. In this pH range, the –COO<sup>-</sup> group of glutathione molecule is electrostatically attached with the positively charged TiO<sub>2</sub>. In all types of NPs, the pH value has been controlled between the ranges mentioned above.

### **2.2 Synthesis of glutathione-protected Au NPs employing glucose as reductant (Au-GSH-B NPs)**

Briefly, 0.25 mM mmol of gold salt ( $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ ) was dissolved in 50 ml DI water. Later on 0.25 mM L-Glutathione was added to the mixed solution and aged for 30 min under stirring. 0.40 g glucose in 10 ml DI water was separately prepared and added to the mixed solution under constant stirring and aged for 15 hours. Dropwise addition of this mixed solution to methanol (50 ml) for stirred for 40 min. Nitrogen was used to de-aerate the solution. The resultant solution was centrifuged at 10000 rpm for 15 minutes and the obtained precipitates were thoroughly washed twice with  $\text{CH}_3\text{OH}$ . The metal NPs were dried in vacuum and dispersed in DI water to the desired concentration. The concentration of Au-GSH NPs in DI water was adjusted between 0.60~0.70 by wt%.

### **2.3 Synthesis of glutathione-protected Au NPs employing $\text{NaBH}_4$ as reductant (Au-GSH-C NPs)**

In short, for the synthesis of Au-GSH-C CLs, 0.25 mmol of gold salt ( $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ ) was added to DI water (50ml). Later on 0.25 mM L-Glutathione was added to the mixed solution and aged for 30 min under stirring. An ice-cold  $\text{NaBH}_4$  (0.2M, 10 ml) was added to the mixed solution. Vigorous stirring continued for minimum 12 hours followed by dropwise addition into 50ml Methanol. The precipitates thud obtained were collected using centrifugation at 10000 rpm for 20 min. The precipitates then thoroughly washed with methanol and dried in vacuum followed by the dispersion into DI water. The concentration of Au-GSH NPs in DI water was adjusted between 0.60~0.70 by wt%.

## **2.4 Synthesis of glutathione-protected Au NPs employing tri-sodium citrate as reductant (Au-GSH-D NPs)**

Briefly, for the synthesis of Au-GSH-C CLs, 0.25 mmol of gold salt ( $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ ) was added to DI water (50ml). Later on 0.25 mM L-Glutathione was added to the mixed solution and aged for 30 min under stirring. 0.40 g tri-sodium citrate dihydrate in 10 ml DI water was separately prepared and added to the mixed solution under constant stirring and aged for 15 hours. Dropwise addition of this mixed solution to methanol (50 ml) for stirred for 40 min. Nitrogen was used to de-aerate the solution. The resultant solution was centrifuged at 10000 rpm for 15 minutes and the obtained precipitates were thoroughly washed twice with  $\text{CH}_3\text{OH}$ . The metal NPs were dried in vacuum and dispersed in DI water to the desired concentration. The concentration of Au-GSH NPs in DI water was adjusted between 0.60~0.70 by wt%.

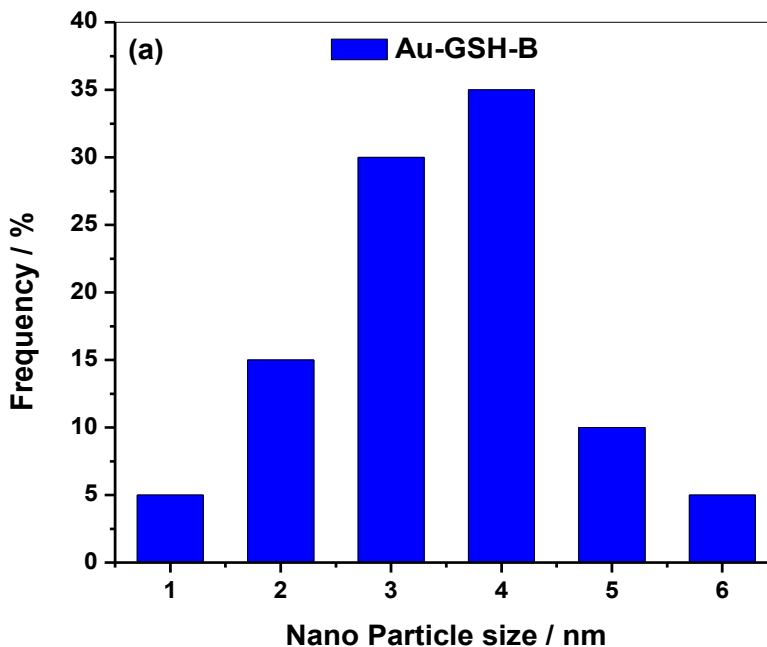
### **Fabrication of Pt counter electrode**

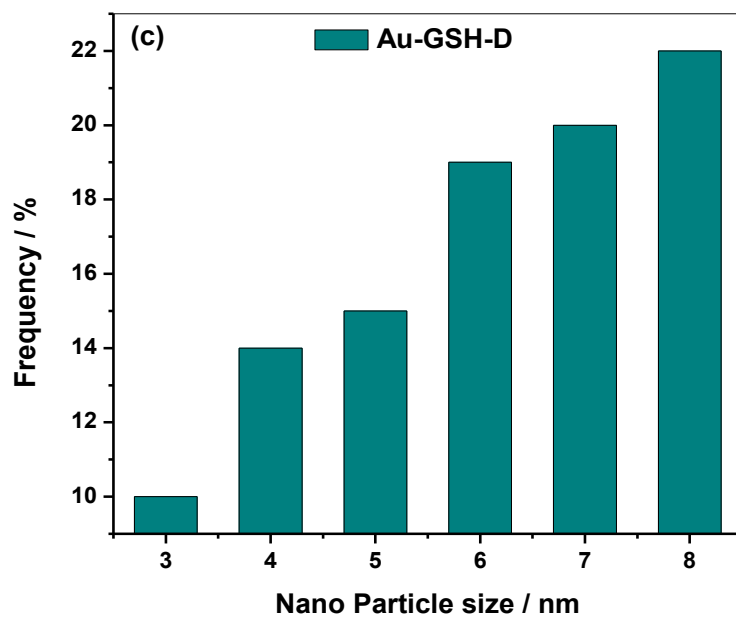
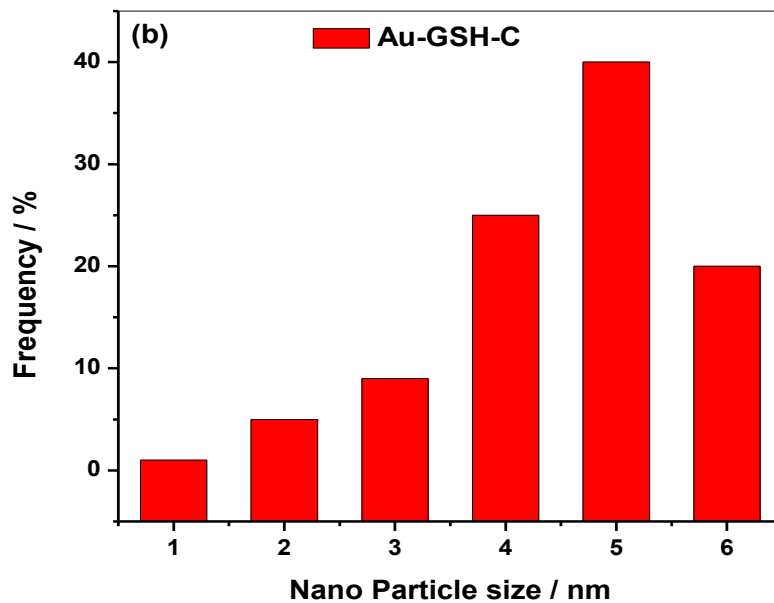
Platinum counter electrodes (CEs) were fabricated by drop-casting a solution of  $\text{H}_2\text{PtCl}_6$  (2 mg of Pt in 1 ml ethanol) on the pre-cleaned fluorine-doped tin oxide (FTO), followed by sintering at 400°C for 15 min.

### **3. Fabrication of NPs sensitized solar cells (NPSCs)**

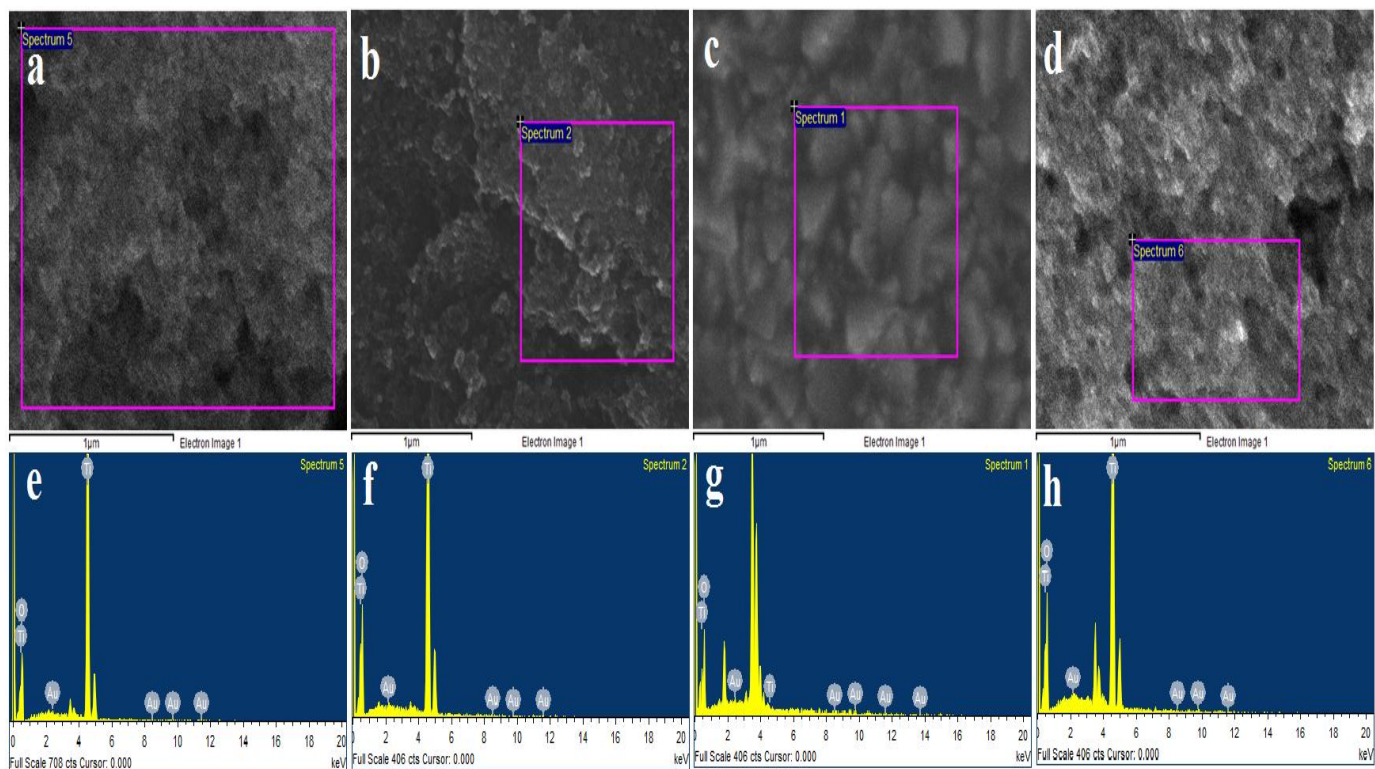
FTO substrates were cleaned with acetone, ethanol and DI water under ultrasonic agitation for 15 min each. Spin-coating technique was employed to deposit  $\text{TiO}_2$  colloidal solution on FTO substrate. Spin coating technique was performed at 3000 rpm for 45 seconds. Spin-coating process was performed twice to achieve  $\text{TiO}_2$  thickness on FTO up to 5 microns. Controlled heat treatment was performed at the following parameters: 2 hours at 25°C, 10 min at 80° C, 15 min at 325°C, 10 min at 375°C and then finally 30 min at 470°C. Heating rate in each case was 5°C/min. Finally,  $\text{TiCl}_4$  treatment was performed in an aq. solution of 40mM  $\text{TiCl}_4$  at 70°C for

30 min followed by sintering at above mentioned heat treatment cycle. Deposition of Au-GSH NPs on TiO<sub>2</sub> photoanodes was accomplished by immersing photoanodes in NPs solutions for 40 hours. Subsequently, photoanodes were washed thoroughly with ethanol and water. NPSCs were assembled using Pt coated FTO as a counter electrode and mTiO<sub>2</sub> as working electrode. Both electrodes were sandwiched using Surlyn as a spacer (40μm). Electrolyte containing 0.22 M Co (bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub>, 0.033M Co (bpy)<sub>3</sub>(PF<sub>6</sub>)<sub>3</sub>, 0.1 M LiClO<sub>4</sub>, and 0.5 M 4-tert-butylepyridine in acetonitrile, was injected into the cell through the pre-drilled hole on the Pt coated FTO counter electrode under vacuum. Finally the hole was sealed using extra Surlyn to avoid the leakage of electrolyte. Active area of the solar cell was marked as 0.145 cm<sup>2</sup>.

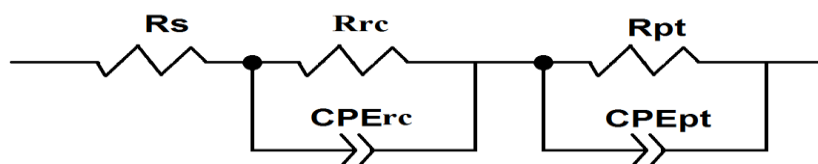




**Figure S1.** Histograms showing the distribution of NPs size of (a) Au-GSH-B NPs, (b) Au-GSH-C NPs, and (c) Au-GSH-D NPs



**Figure S2.** SEM images (a~d) of mTiO<sub>2</sub> photoanodes modified with Au-GSH-A, Au-GSH-B, Au-GSH-C, and Au-GSH-D, respectively. Figures (e~h) are the corresponding EDX spectra



**Figure S3.** The equivalent circuit for NPSCs