

Supporting Information

for

Quasi Core-Shell Nitrogen-Doped Graphene/Cobalt Sulfide Conductive Catalyst for Highly Efficient Dye-Sensitized Solar Cells**

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(I) Experimental details

Preparation of Graphene Oxide (GO):

GO was synthesized from graphite powder by a modified Hummers method. Graphite (3 g) and NaNO_3 (1.5 g) were stirred together in concentrated H_2SO_4 (69 mL, 98%) in an ice bath for 24 h. After this, under the condition of stirring and temperature not more than 20°C , KMnO_4 (9 g) was added slowly. Then, the mixture was transferred into 35°C water bath and vigorously stirred for 30 min. Subsequently, 138 mL of water was gradually added to the mixture and stirred for 30 min in the case of the temperature increased to $95\pm 5^\circ\text{C}$. Further, 213 mL of H_2O was to dilute the mixture and moderate amount of H_2O_2 (30%) was added to neutralize the unreacted KMnO_4 . Finally, the resulting brown colored mixture was washed with diluted HCl (5%), ethanol, and warm water, and then dispersed in H_2O for next step used.

Preparation of the quasi core-shell structure NDG/CoS catalyst:

Core-shell structure NDG/CoS was synthesized from liquid phase of the reactants using the in-situ solvothermal self-assembly method. Cobalt nitrate hexahydrate and thiourea were used as the precursors. Initially, 10 ml (1 M) solution of Cobalt nitrate hexahydrate prepared in double distilled water was taken in a glass beaker with 100 ml in capacity. Appropriate quantities of triethanolamine (TEA), and ammonia (25% AR) were added to form a complex and then 10 mL (1 M) thiourea was added with a continuous stirring ($\text{pH}\approx 11$) drop by drop. Afterwards 10 mL GO (6.0 mg/mL) was dispersed into the above solution under magnetic stirring for more than 0.5 h, and then the reactor was heated up to 200°C and kept at this temperature for 12 h. After cooling down to the room temperature naturally, the resulted black solid powders (NDG/CoS) were collected by centrifugation, washing with ethanol and water for three times, respectively. Afterwards, the as-prepared NDG/CoS solution was under ultrasonic treatment for 3 h, and sprayed-coating onto the Fluorine doped Tin Oxide (FTO) glass. Then the films were dried in the oven at 300°C for 3 h.

Preparation of G/CoS hybrid counter electrodes:

G/CoS was synthesized in the same condition as NDG/CoS except without ammonia. 10 ml (1 M) solution of Cobalt nitrate hexahydrate prepared in double distilled water was taken in a glass beaker with 100 ml in capacity. Appropriate quantities of triethanolamine (TEA) was added to form a complex and then 10 mL (1 M) thiourea was added drop by drop. Then 10 mL GO was dispersed into the above solution under magnetic stirring for more than 0.5 h and then the reactor was heated up to 200°C and kept at this temperature for 12 h. After cooling down to the room temperature naturally, the resulted black solid powders (G/CoS) were collected by centrifugation, washing with ethanol and water for three times, respectively. Moreover, the as-prepared G/CoS solution was under ultrasonic treatment for 3 h, and sprayed-coating onto the Fluorine doped Tin Oxide (FTO) glass. Then the films were dried in the oven at 300°C for 3 h.

Preparation of NDG counter electrodes:

10mL GO (6.0 mg/mL) was dispersed into the above solution under magnetic stirring for more than 0.5 h. Appropriate quantities of ammonia (25% AR) and 10 mL (1 M) thiourea were added form a complex. Further, the mixture was transferred into a Teflon-lined autoclave, sealed, and heated from room temperature to 200 ° C for 12 h. After cooling down to room temperature naturally, the resulting black solid powers (NDG) were collected by centrifugation, washing with ethanol and water for three times, respectively. Moreover, 3 mg as-prepared NDG sample was dispersed in 10 mL isopropanol using ultrasonication, and the NDG electrode was fabricated by spin coating onto the Fluorine doped Tin Oxide (FTO) glass. Then the films were dried in the oven at 300 ° C for 3 h.

Fabrication of Dye-sensitized solar cells:

The TiO₂ paste according to the previous reports was prepared. ^[S1] ^[S2] A TiO₂ film loaded on the FTO glass with dense transparent TiO₂ nanoparticle film (~13 μm in thickness, 18 nm in diameter) and a scattering layer (~5 μm in thickness, 400 nm in diameter) were prepared by a screen-printing method onto Fluorine doped Tin Oxide (FTO) glass, respectively. The substrate was sintered at 500 ° C for 1 h and cooled to 100 ° C to generate the anatase nanocrystals. After sintering, the TiO₂ electrode was immersed in TiCl₄ (40 mM) aqueous solution at 70 ° C for 30 min. The film was then annealed at 450 ° C for 30 min. In the following step, the mesoporous TiO₂ was sensitized in N749 solution for 24 hours, the photoanode was sealed with a counter electrode by Surlyn films (40 μm in thickness) by Hot-press machine. Further, an electrolyte which consisted of an acetonitrile solution of 0.6 M (1,2-dimethyl- 3-propyl) imidazolium iodide, 0.05 M I₂ , 0.5 M TBP, and 0.1 M LiI was used to backfill through the hole in the counter electrodes of all the cells and then sealed them with a Surlyn film covered with a thin glass slide under heat.

(II) Characterizations and measurements:

Morphologies of as-obtained products were observed on a field emission scanning electron microscopic (FESEM, FEI Sirion 200). Transmission electron microscopy (TEM, JEOL JEM-2010F) images were obtained under an acceleration voltage of 200 kV. UV-vis absorption spectra were recorded using a Hitachi U-4100 (Japan) spectrophotometer. The crystal structures of the counter electrode samples were characterized by powder X-ray diffraction (XRD) through a Goniometer Ultima IV (185nm) diffractometer with Cu K α radiation, excited at 40 kV and 40 mA. Elemental composition of composites was analyzed by X-ray photoelectron spectroscopy (XPS), Kartos Axis Ultra with monochromatized Al K α radiation (1486.6 eV).

Electrochemical impedance spectroscopy (EIS) measurements were obtained with an impedance analyzer (Zahner IM6, Germany) at zero bias potential. The impedance studies were carried out by simulating open-circuit conditions in the atmosphere, and an AC potential amplitude of 5 mV over a frequency range of 0.01–10⁵ Hz in the dark conditions. The resultant impedance spectra was analyzed by means of the Z-view software. The Tafel polarization curves were measured using the Zahner electrochemical workstation system at a scan rate of 10 mV s⁻¹. Additionally, all the EIS and Tafel measurements were based on a symmetric configuration consisting of two identical electrodes filled with the redox electrolyte which was to be used in the DSSCs. Cyclic voltammetry (CV) were executed in a three electrode system with different CEs as the working electrode, a platinum wire as the counter electrode, and Ag/Ag⁺ electrode as the reference electrode, which was calibrated with a ferrocene solution after the CV measurements, at a scanning rate of 50 mVs⁻¹. The electrode was dipped in an anhydrous acetonitrile solution containing 0.1 mM LiClO₄, 10 mM LiI, and 1 mM I₂.

For the photovoltaic measurements, devices were equipped with a UV cut-off filter and masked with a thin metal mask to give an active area of 0.25 cm². J-V curves of the DSSCs were measured with a digital source meter (Keithley2400) under simulated solar illumination at 100 mW cm⁻², AM1.5 G standard (Wacom, Japan). The excitation beam coming from a 300 W xenon lamp (ILC Technology) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.) and chopped at approximately 4 Hz. During J-V measurements, a black metal mask was used with an aperture area of 0.25 cm².^[S3]

(III). Supplementary Results

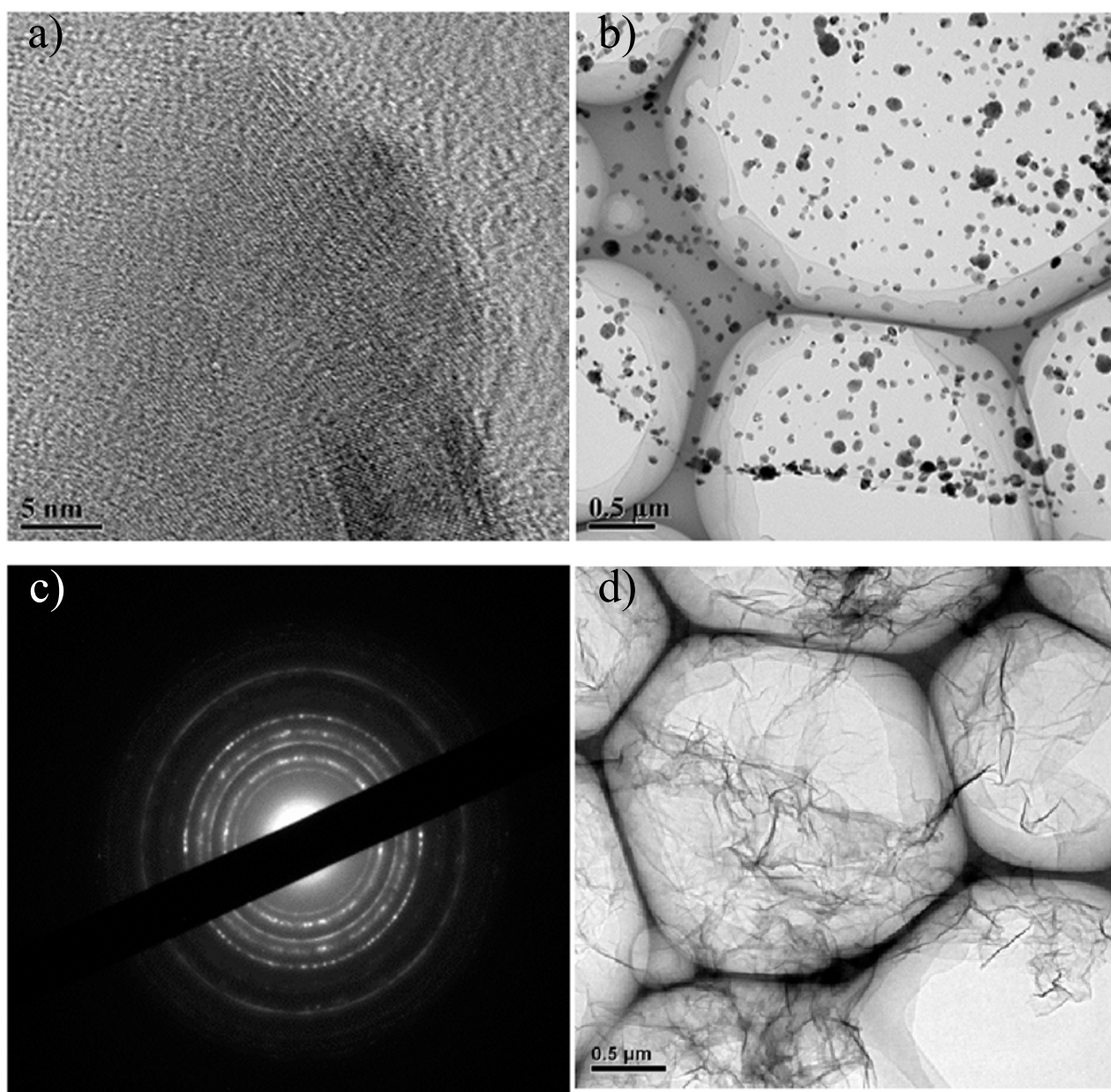


Figure S1. HR-TEM images of (a, b) G/CoS, (c) SAED pattern of the G/CoS, (d) TEM image of NDG

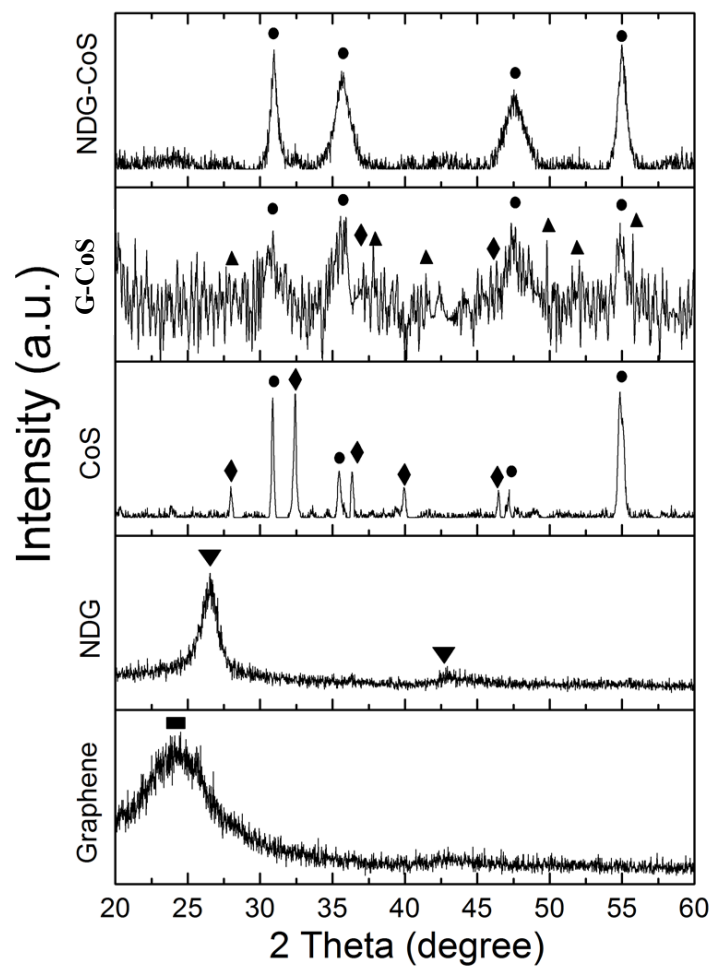


Figure S2. XRD patterns of the NDG/CoS, CoS/G, CoS, NDG, Graphene; ● represents CoS phase, ◆ represents CoS₂ phase, ▲ represents the CoS_{1.097} phase, ▼ represents the NDG, ■ represents the reduced graphene oxide.

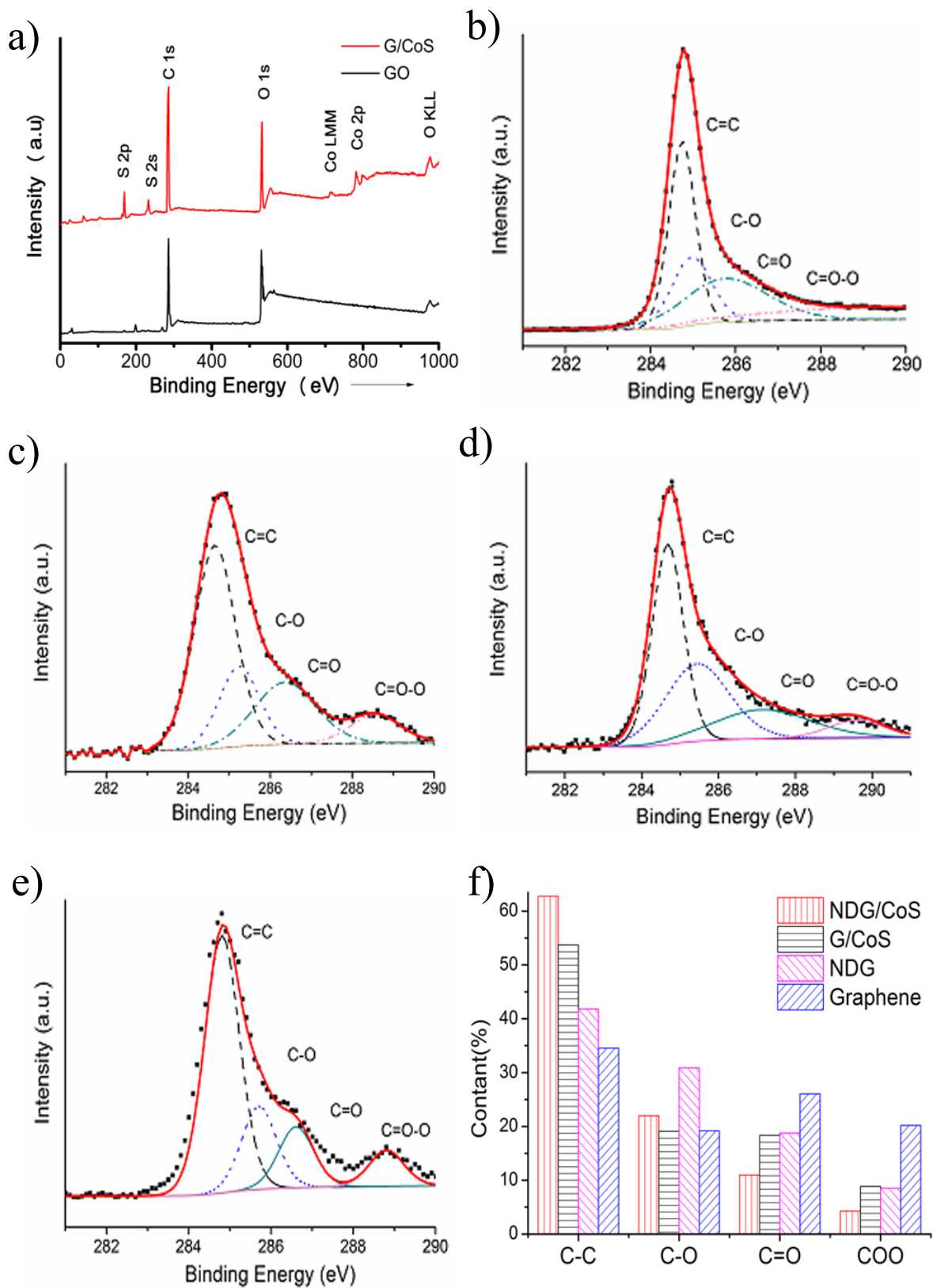


Figure S3. (a) XPS survey spectra of G/CoS and graphene oxide (GO), XPS C1s survey spectra of (b) NDG/CoS, (c) G/CoS, (d) NDG, and (e) GO. (f) Percentage of C1s four types in above materials.

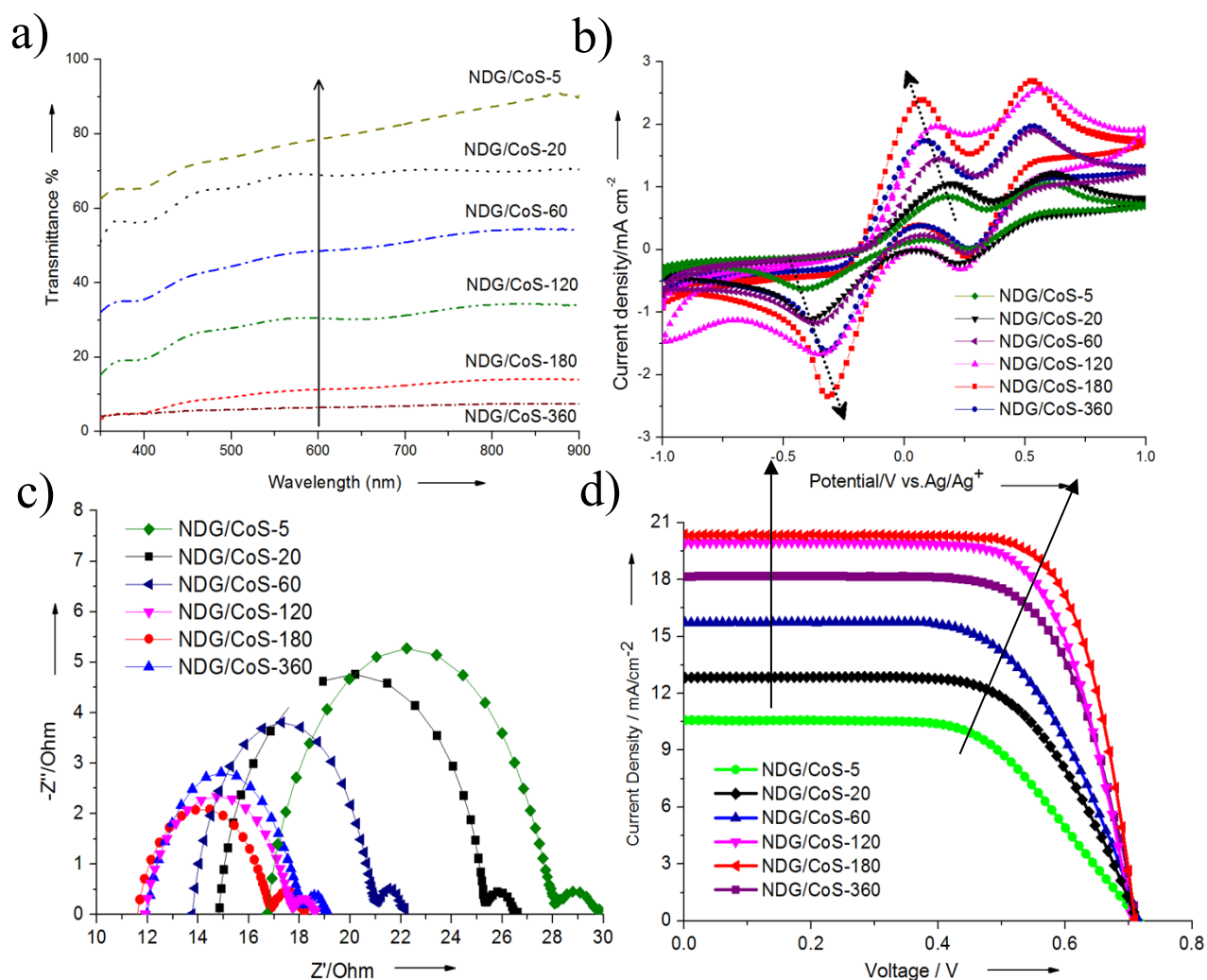


Figure S4. (a) The transmittance spectrum in the visible light of the samples with different numbers of coating by 5, 20, 60, 120, 180 and 360 s to estimate the relative thickness of the electrode. (b) Cyclic voltammograms of these NDG/CoS counter electrodes. (c) EIS of these NDG/CoS counter electrodes with a symmetric sandwich-like structure. (d) I-V characteristics of DSSCs with these NDG/CoS counter electrodes. The DSSCs were measured under AM 1.5 illumination with a metal mask. The active area of all DSSCs is 0.25 cm².

Figure.S4a shows the transmittance spectrum in the visible light of the samples with different numbers of coating by 5, 20, 60, 120, 180 and 360 s to estimate the relative thickness of the electrode. The transmittance at a wavelength of 600 nm of 79 %, 69 %, 48%, 30%, 11%, and 6% showed the increased thickness with increased coating time. Specifically, it should be noted that as increasing the thickness, the surface density of NDG/CoS on the substrate is improved. Figure.S4b shows the I-V characteristics of

DSSCs with these NDG/CoS counter electrodes. By increasing the thickness of the counter electrodes, J_{SC} and FF was improved, but V_{OC} were almost unchanged. No substantial effect on V_{OC} was attributed to the fact that V_{OC} was determined by the energy level offset of the photoanode and redox potential of the electrolytes. The improved JSC was mainly attributed to the increased catalytic performance which can be confirmed by E_{pp} of CV and R_{ct} of EIS and the increased refection of the counter electrode. Moreover, the improved J_{SC} was mainly attributed to increased R_s of EIS and the improved catalytic performance.

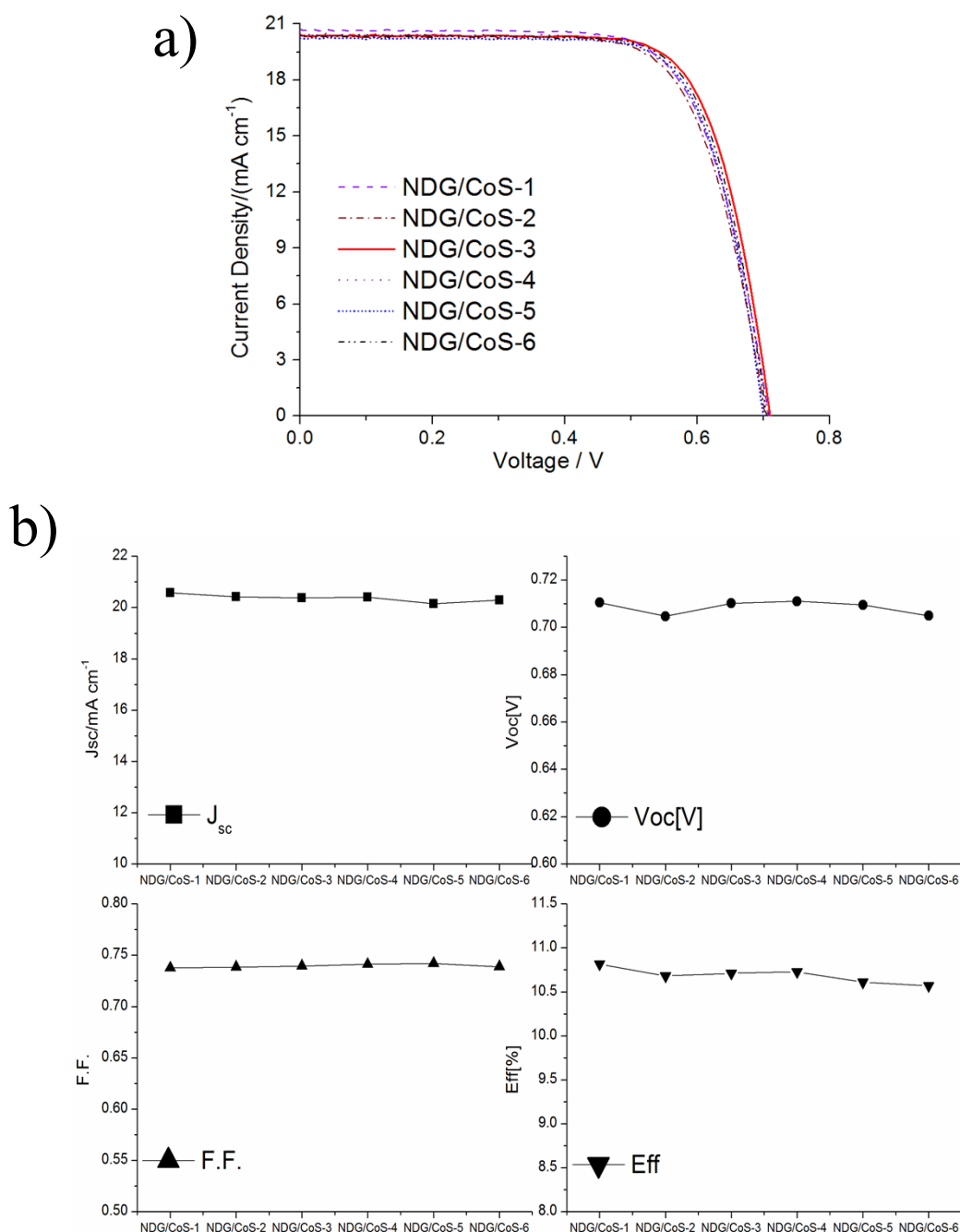


Figure S5. (a) J - V characteristics of DSSCs with NDG/CoS based counter electrodes which prepared at the same condition and the DSSCs were measured under AM 1.5 illumination with a metal mask. The active area of all DSSCs is 0.25 cm². (b) The detailed resulting data of photovoltaic performance of the DSSCs using NDG/CoS CEs.

The repeatability test of the DSSCs done in the same condition and found a good result is that the efficiency of DSSC range from 10.57 % to 10.84 %, so we chose the 10.71% data. In addition, the average efficiency of DSSCs based the NDG/CoS hybrid was 10.70 %.

References

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