Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

p-Doped Three-Dimensional Graphene Nano-Networks Superior to Platinum as a Counter Electrode for Dye-Sensitized Solar Cells

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Experimental Section

Preparation of CS/PVA-$FeCl_3$•$6H_2O$ disk

$FeCl_3 \cdot 6H_2O$ and Poly vinyl alcohol (PVA, Mw = 31,000-50,000) were acquired from Sigma Aldrich and used without any further purification. After PVA (10 wt%) was dissolved in DI-water at 90 °C and then mixed with percentages of 350 phr (phr: part per hundred parts of resin) by weight of $FeCl_3 \cdot 6H_2O$. PVA/$FeCl_3$ disk was prepared by self-assembly of CS, as reported elsewhere. Any impurities in the solution were filtered through a 0.2 μm cellulose acetate syringe filter and the filtrated solution was infiltrated at CS/PVA-$FeCl_3$•$6H_2O$ disk. The prepared disk was dried in a vacuum oven for one day at room temperature. In order to enhance the conductivity, 3D-GNs were p-doped by dipping in HNO_3 solution for 30 min followed by washing in D.I. water.

Fabrication of the 3D-GNs

The 3D-GN/Fe powder was fabricated by self-assembly in a quartz tube (Scientech Co.) under 1,000 °C in a H_2 (100 sccm)/Ar atmosphere at 4 torr for 30 min. After 30 min of CVD growth of graphene, the quartz tube was rapidly cooled to room temperature. To remove the SiO_2 particles and iron, the 3D-GN@SiO_2/Fe powder was immersed in HF (10 %) for 3 hrs and HCl (10 %) for 12 hrs.

Fabrication of the 3D-GN paste

50 mg of each 3D-GN was dispersed in 30 ml of absolute EtOH and then added to 2.75 g of terpineol. After adding ethyl cellulose (0.5 g : 5 g of 10 % solution in ethanol), the EtOH was evaporated in an oven at 120 ^{o}C for 5 hrs. 4 ml of IPA was added to the dried paste to obtain proper viscosity.

Fabrication of DSSCs

TiO_2 paste (DyesolDSL 18NR-T) was coated on 40 mM $TiCl_4$ treated FTO glass by doctor blading followed by drying at 120 ^{o}C for 10 min. The film was then sintered at 500 ^{o}C for 15 min. This doctor blading procedure with the paste (coating, drying, and annealing) was repeated to achieve a working electrode with appropriate thickness. The TiO_2 film was treated with a 40 mM $TiCl_4$ solution at 70 ^{o}C for 30 min, rinsed with water and ethanol, then sintered at 500 ^{o}C for 30 min. The TiO_2 electrode with an area of 0.21cm^2 (3 mm x 7 mm) was immersed in a 0.5 mM N719 dye (Solaronix) solution in absolute ethanol and kept at room temperature for 24 hrs. To prepare the 3D-GN counter electrode, the 3D-GN paste was coated on the FTO substrate and placed in an oven set to 400 ^{o}C for 5 min and this was repeated 4 times. In the case of the Pt counter electrode, 40 mM of H_2PtCl_6/IPA solution was spincoated on FTO glass several times and then sintered at 500 ^{o}C for 30 min. The dye-adsorbed TiO_2 photoanode and counter electrodes (Pt, 3D-GN) were assembled into a sandwich-type cell with 60 μm hot-melt Surlyn (Solaronix). The electrolyte which consists of 0.03 M I_2 (Sigma Aldrich), 0.1 M guanidinium thiocyanate (Sigma Aldrich), 0.6 M 1-butyl-3-methylimidazolium iodide (Sigma Aldrich), and 0.5 M 4-tert-butyl pyridine (Sigma Aldrich) in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15) was injected through a hole from the back side of the counter electrode.

Fabrication of Symmetrical Cells

A symmetrical sandwich dummy cell was fabricated from two identical 3D-GNs/FTO or Pt/FTO sheets, which were separated by 60-μm thick Surlyn tape as a sealant and spacer leaving a 0.4 x 0.8 cm^2 active area. The electrolyte which consists of 0.03 M I_2, 0.1 M guanidinium thiocyanate, 0.6 M 1-butyl-3-methylimidazolium iodide, and 0.5 M 4-tert-butyl pyridine in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15) was injected through a hole from the back side of FTO glass.

Characterization of 3D-GNs

The morphology of the samples was characterized by SEM (Hitachi, 10 kV), TEM (JEM-2100, 200 kV). Surface area determination was performed by Brunauer-Emmett-Teller (BET) methods using Belsorp-Max (BEL JAPAN Inc.). The conductivities of 3D-GNs were extracted from the sheet resistances which were characterized by 4 point-probe (Dasol Eng, FPP-RS8, pin-spacing 1 mm, pin-radius 100 um). To measure sheet resistances of 3D-GNs, the pellet with a diameter of 13 mm and thickness of 7 μm was prepared by mechanical milling and subsequent pressurizing (1,000 kg/cm^2) of the 3D-GNs. The palletized powders are composed of 80 wt% of 3D-GNs, 10 wt% of acetylene black, and 10 wt% of PVDF.

Electrochemical measurements

J-V characterization was carried out under a 1 Sun condition with an Oriel SOL3A solar simulator by obtaining the open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF), and overall efficiency (η). Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were conducted with Solartron 1280 and VMP3 (Biologic), respectively. For CV, Ag/$AgNO_3$ and a Pt mesh were used as a reference electrode and counter electrode, respectively. The electrolyte for CV was prepared with 0.5 mM I_2, 5 mM LiI, and 100 mM $LiClO_4$ in acetonitrile, and the scan rate was 50 mV/s.

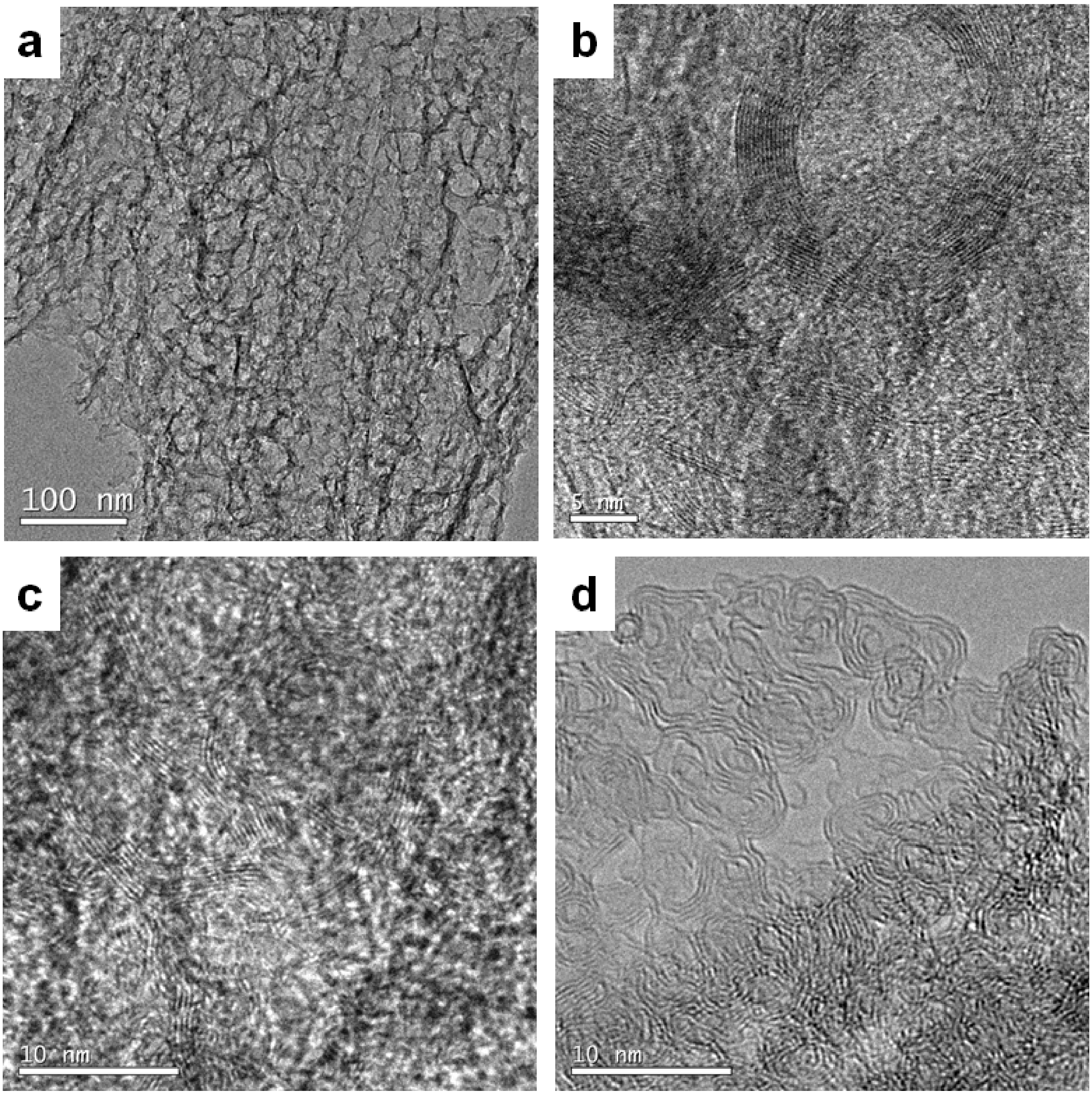


Figure S1. TEM images of the 3D-GNs in different areas

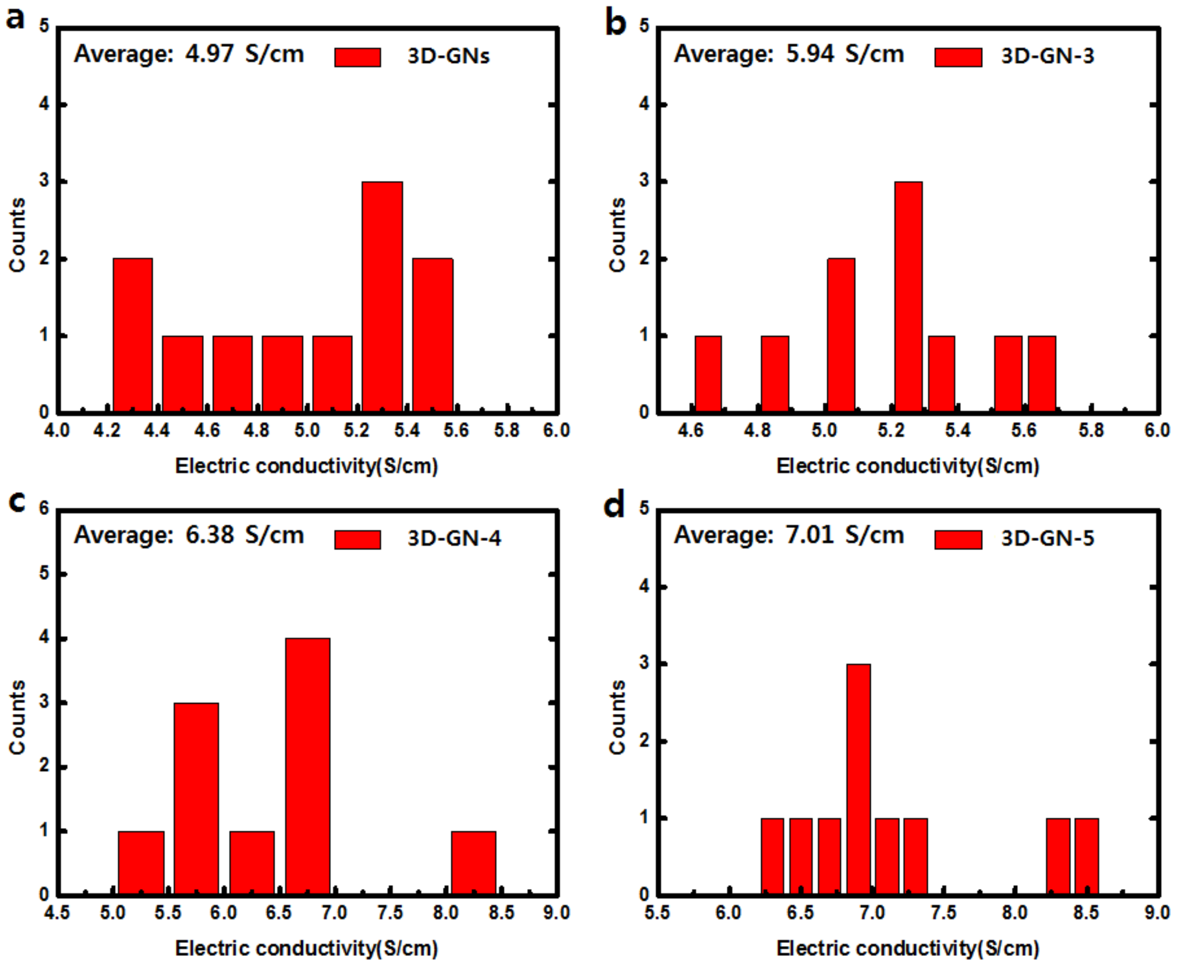


Figure S2. The electric conductivity of 3D-GN powders: pristine 3D-GNs (a), 3D-GN-3 (b), 3D-GN-4 (c), and 3D-GN-5 (d).

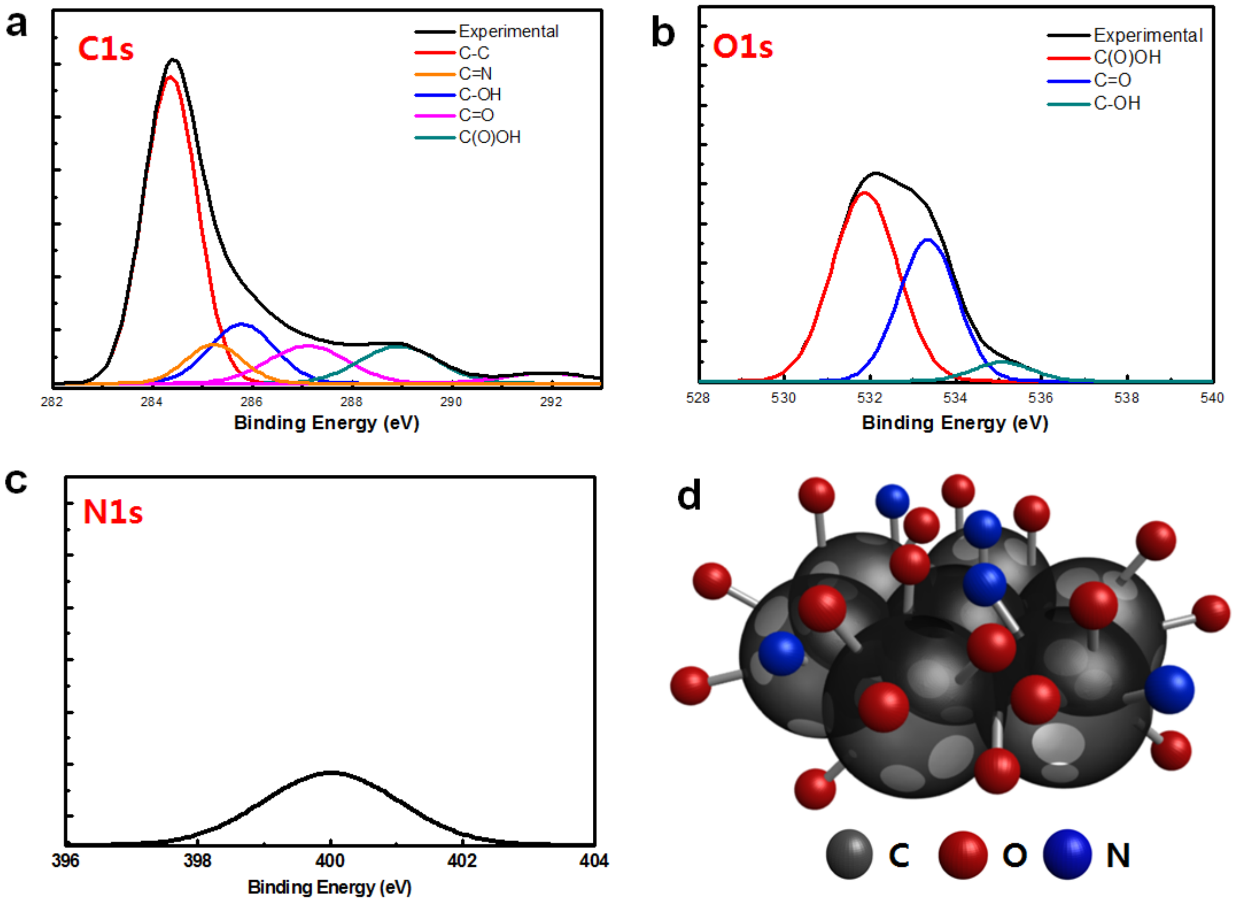
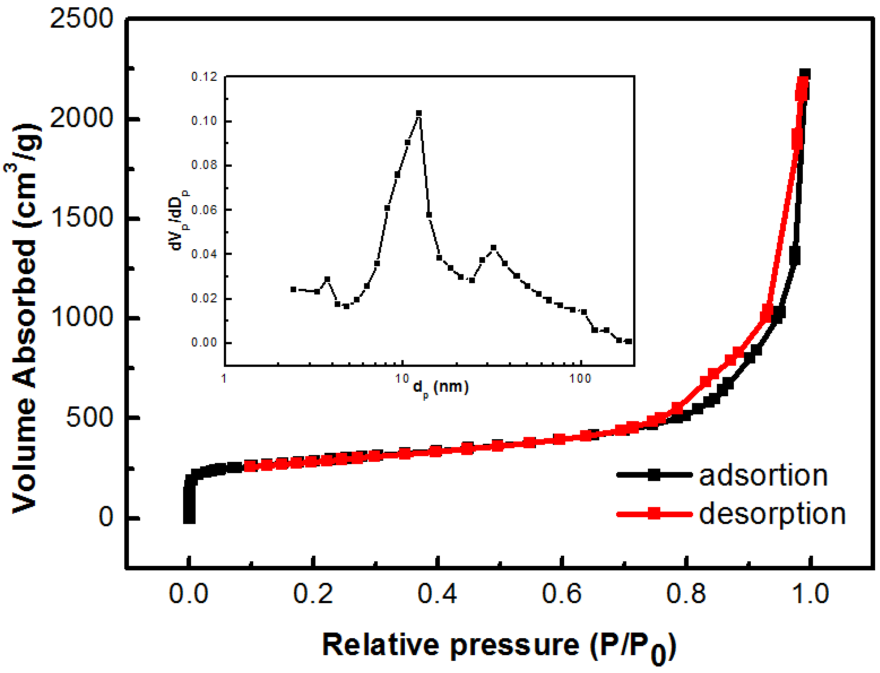
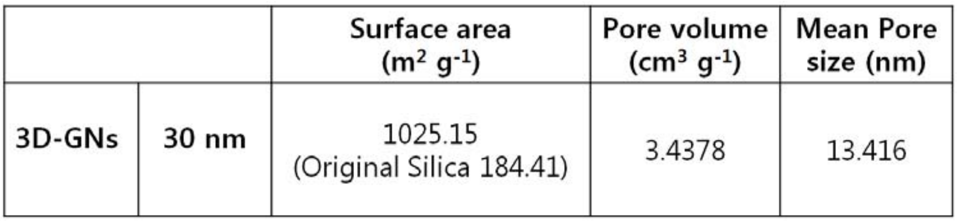


Figure S3. XPS spectra of (a) C1s, (b) O1s, (c) N1s and schematic molecular structure of 3D-GN-5.





		Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Mean Pore size (nm)
3D-GNs	30 nm	1025.15 (Original Silica 184.41)	3.4378	13.416

Figure S4. BET analysis of 3D-GNs with a pore diameter of 30 nm. The inset is pore-size distribution curve. The specific values are summarized in the table.

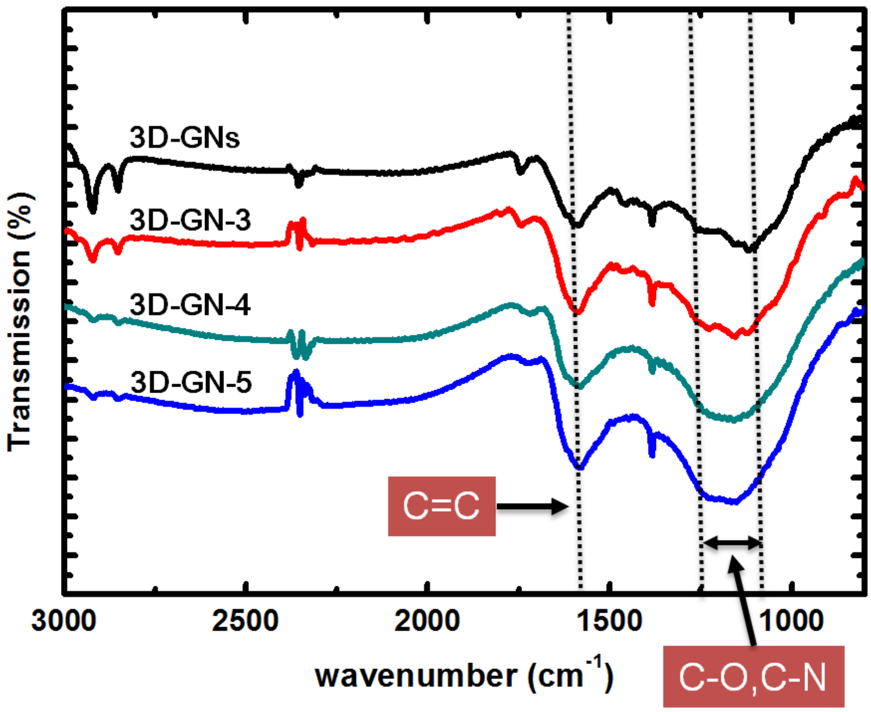


Figure S5. FTIR spectra of 3D-GNs, 3D-GN-3, 3D-GN-4, and 3D-GN-5.

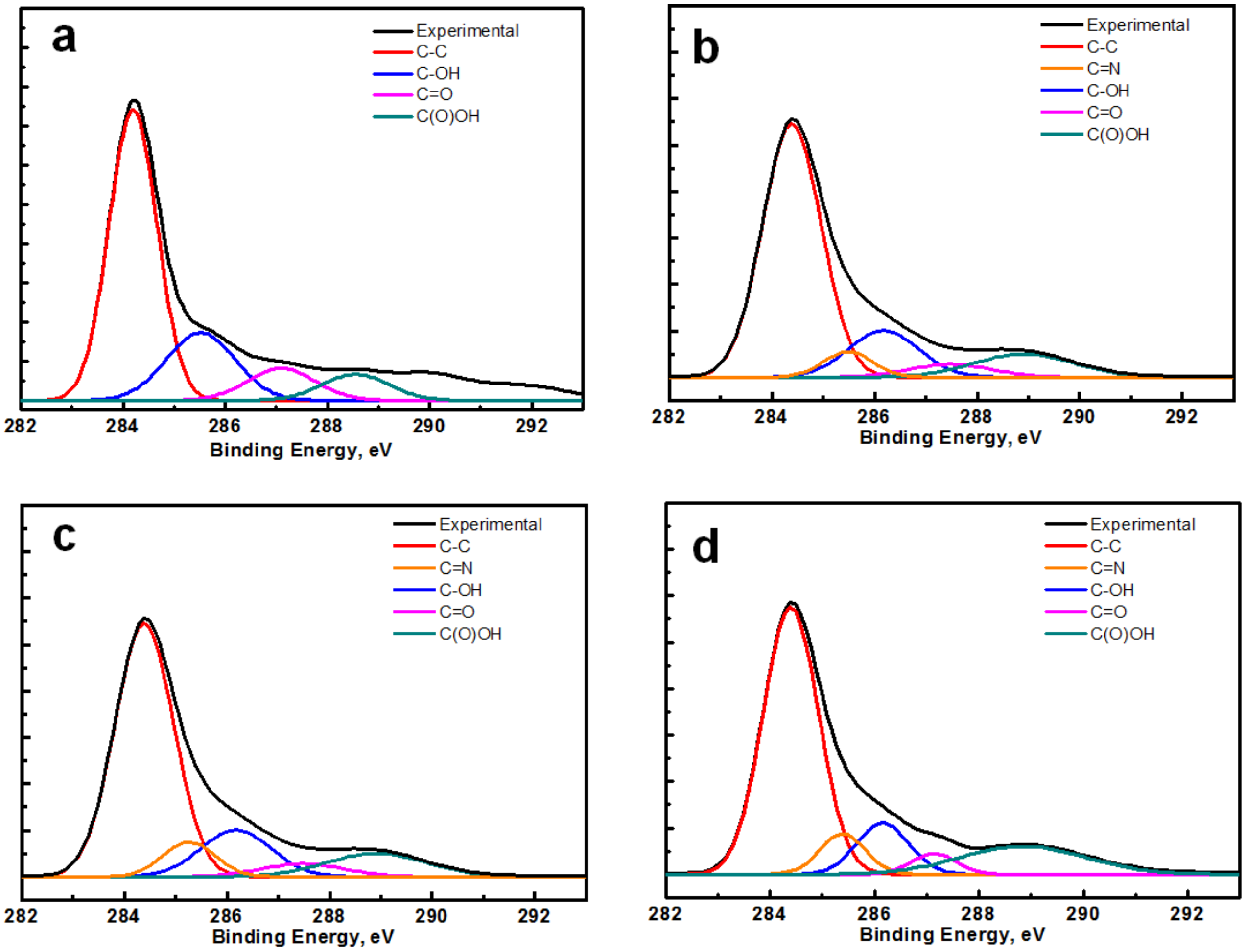


Figure S6. XPS of C1s of pristine 3D-GNs (a), 3D-GN-3 (b), 3D-GN-4 (c), and 3D-GN-5 (d).

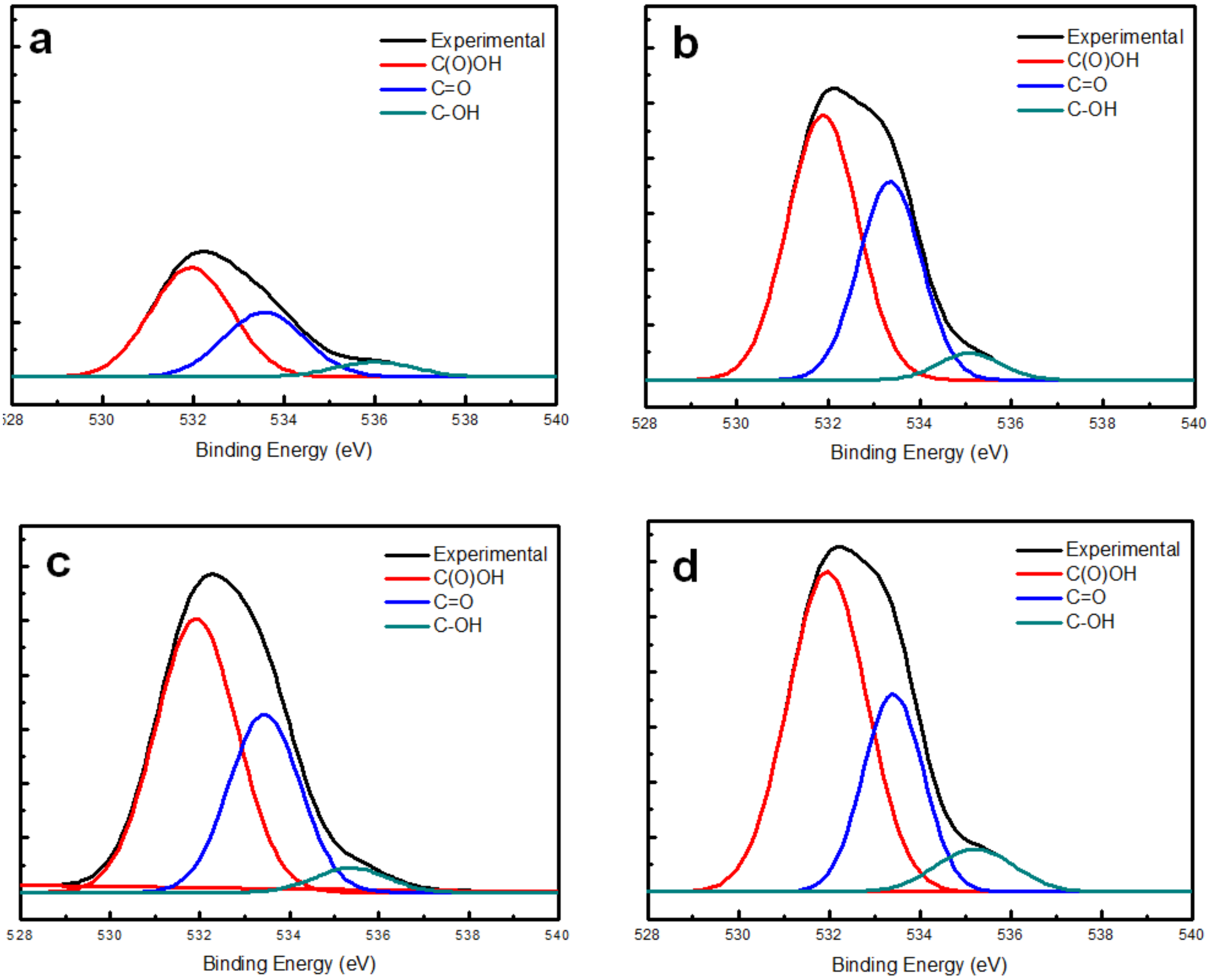
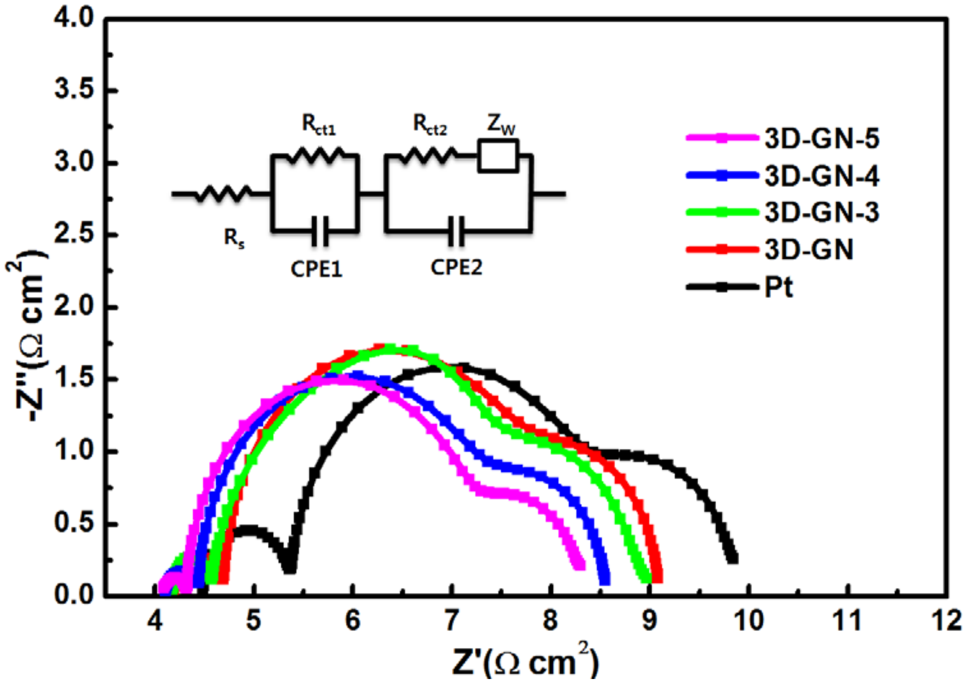


Figure S7. XPS of O 1s of pristine 3D-GNs (a), 3D-GN-3 (b), 3D-GN-4 (c), and 3D-GN-5 (d).



	R_s	R_{ct1}	R_{ct2}	Z_w
3D-GN-5	4.084	2.36E-01	2.302	1.674
3D-GN-4	4.104	3.36E-01	2.322	1.784
3D-GN-3	4.168	3.92E-01	2.246	2.152
3D-GN	4.192	4.92E-01	2.13	2.264
Pt	4.486	8.46E-01	2.06	2.45

Figure S8. Electrochemical impedance spectroscopy (EIS) curves of the full cells. The inset is an equivalent circuit used for fitting the data.

Recent articles[1,2] reported the presence of another semicircle (charge transport impedance, R_{trans} and C_{trap}) which appears at very high frequency regions due to the pores in the structures. However, we could not observe it in our experimental conditions, performed with the symmetric or full cell devices.

1. J. Mater. Chem. A, 1, 3202, 2013.

2. ACS nano, 4, 3503, 2010.

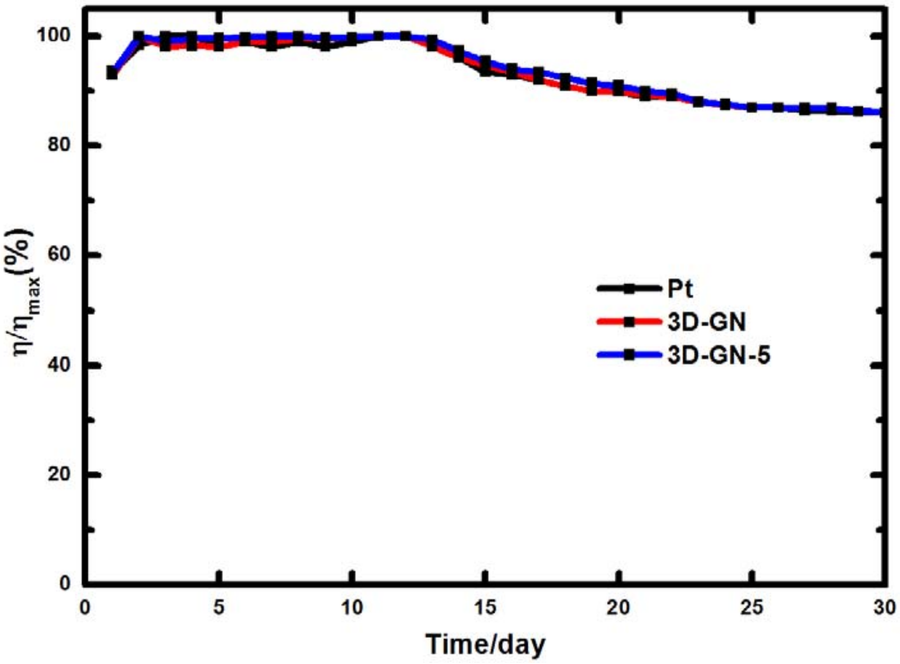


Figure S9. Long term stability of DSSC cells with a CE of Pt, pristine 3D-GNs, and p-doped 3D-GNs (3D-GN-5).

The efficiency of the p-doped sample increased, reaching its maximum in one day (as usual), remained at over 99% and retained this level for 12 days, after which the level gradually decreased to 87% of the maximum for another 17 days. The decrease can be attributed to several commonly raised issues associated with the cell fabrication, one being the evaporation of the electrolyte. Importantly, the degree of efficiency reduction of the p-doped sample over time is very close to that of Pt. The great stability of p-doped 3D-GNs is likely attributed to the lower degree of doping of our 3D-GNs (due to great conductivity, appropriate oxygen content, and large surface area of pristine 3D-GNs) and the firm covalent bonds between -NO_3 and the lattice of graphene.