

# Hierarchical vertically-oriented graphene as a catalytic counter electrode in dye-sensitized solar cells

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## Experimental

Mesoporous TiO<sub>2</sub> films were prepared by doctor-blade casting of a Titania paste (Ti-Nanoxide D, Solaronix) onto FTO-coated glass substrates with 12 Ω/□ sheet resistance (Solaronix). A 9.8-nm TiO<sub>2</sub> blocking/protection layer was coated on all FTO glasses using atomic layer deposition (ALD) before applying mesoporous TiO<sub>2</sub>. The procedure of ALD was described elsewhere.<sup>1</sup> After drying in air, the TiO<sub>2</sub>-FTO glasses were sintered at 500 °C for 30 min in air. The resulting TiO<sub>2</sub> photoanode was then immersed in an anhydrous ethanol solution containing 2 × 10<sup>-4</sup> M of purified N719 dye sealed in a dark vessel for 24 h. The dye-sensitized photoanodes were rinsed with ethanol and air-dried immediately before solar cell assembly. The Pt/FTO CEs were prepared by drop casting a 0.005 M H<sub>2</sub>PtCl<sub>6</sub> aqueous solution on FTO glasses. After drying in air at room temperature, the CEs were elevated to 500 °C in air and maintained for 30 min.

The VG sheets were grown on stainless steel plates for CEs using a direct current plasma-enhanced chemical vapor deposition (dc-PECVD) that was described elsewhere.<sup>2,3</sup> Briefly, prior to the growth, the substrate was brought to 700 °C and held at that temperature for 10 min in an Ar flow of 1,000 standard cubic centimeters per minute (sccm). Then the Ar flow was switched to a mixed Ar/Ar + H<sub>2</sub>O vapor/CH<sub>4</sub> flow and a high voltage (-3.5 kV) was turned on to ignite the plasma. The water vapor was introduced into the PECVD reactor by an Ar flow through a water bubbler. The flow rate of CH<sub>4</sub> was 100 sccm, while the total flow rate of Ar/Ar + H<sub>2</sub>O vapor was kept at 1,000 sccm. The two discharge electrodes were separated by a distance of 0.5 cm. VG growth duration was 30 min for all samples. The VG CEs grown with (100+900), (300+700), (600+400), and (1,000+0) sccm of (Ar with H<sub>2</sub>O + pure dry Argon) vapor are denoted as VG-1, VG-2, VG-3, and VG-4, respectively.

To assemble a DSSC, hot-melt sealing foil (25 microns, Meltonix 1170-25, Solaronix) was sandwiched between the photoanode and the CE. Light pressure was applied on the anode/spacer/cathode assembly on a hot plate at 150 °C to seal the cell. I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolyte (Iodolyte AN-50, Solaronix) was introduced into the cells by capillary force. No further sealing process was adopted.

To assemble a dummy cell of VG, two symmetric VG samples facing each other were packaged with the same procedure except for the TiO<sub>2</sub> anode.

A field-emission scanning electron microscope (SEM) (Hitachi S 4800) equipped with a Bruker Quantax energy-dispersive X-ray spectrometry (EDS) system was used to observe the morphology of the VG cathodes; the SEM renders a resolution of 1.4 nm at 1 kV acceleration voltage. High-resolution transmission electron microscopy (HRTEM) characterization of the VG nanosheets was carried out using a Hitachi H 9000 NAR TEM, which has a point resolution of 0.18 nm at 300 kV in the phase contrast HRTEM imaging mode.

The photocurrent-voltage characteristics were obtained under simulated solar illumination (solar simulator, Newport, 94021A) at one sun (AM 1.5G, 100 mW/cm<sup>2</sup>) using a Keithley 2420 source meter equipped with a calibrated Si-reference cell (Oriel, P/N 91150V). The incident-photon-to-electron conversion efficiency (IPCE) of solar cells was analyzed using a system consisting of a 300-W xenon lamp simulated light source (Newport 66902), a monochromator (Newport cornerstone 74125), and a radiometer (Newport Merlin 70104). The photon flux of light incident on the samples was calibrated using a silicon photodiode (Newport 70356). Measurements were typically made at 10 nm wavelength intervals between 350 and 1,100 nm.

The electrochemical impedance spectroscopy (EIS) measurements of DSSCs were conducted using an electrochemical workstation (CH Instruments 600D) under AM 1.5G simulated solar illumination at 100 mW/cm<sup>2</sup>. EIS spectra were recorded over a frequency range of 100 kHz – 10 mHz. The applied bias voltage and ac amplitude were set at open circuit voltage ( $V_{OC}$ ) of the cells and 5 mV, respectively. However, obviously EIS measurements of VG dummy cells were carried out in the dark. Cyclic voltammetry (CV) was carried out in the range of -0.5 ~1.0 V at a scan rate of 20 mV/s. The CV testing was conducted on a three-electrode system, in which a Pt wire and an Ag/AgCl (3.0 M KCl) electrode were used as a counter electrode and a reference electrode, respectively. VG and Pt/FTO were used as a working electrode immersed in a 1.0 mM LiI and 0.1 mM I<sub>2</sub> acetonitrile solution containing 0.1 M LiClO<sub>4</sub>.

DFT calculations were performed using highly precise full potential linearized augmented plane wave (FLAPW) method <sup>4</sup> as implemented in *flair* <sup>5</sup>. The cutoff energies of the plane wave basis and the potential representations were 18 and 144Ry, respectively. Muffin-tin radii of 1.2  $a_B$  were used for both C and O, while they were 2.2  $a_B$  and 0.6  $a_B$  for I and H. The generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof (PBE91) parameterization <sup>6</sup> was used for the exchange-correlation potential treatment. For summation in Brillouin zone, equivalent  $12 \times 12$   $k$  grid of graphene  $1 \times 1$  cell was chosen in Monkhorst-Pack scheme for energy convergence. To avoid spurious interaction between adjacent layers, the vacuum region was taken as at least 12 Å. Experimental lattice constant 2.46 Å was used for pure graphene cell. Geometries of all configurations were fully relaxed with force criteria 0.02 eV/Å.

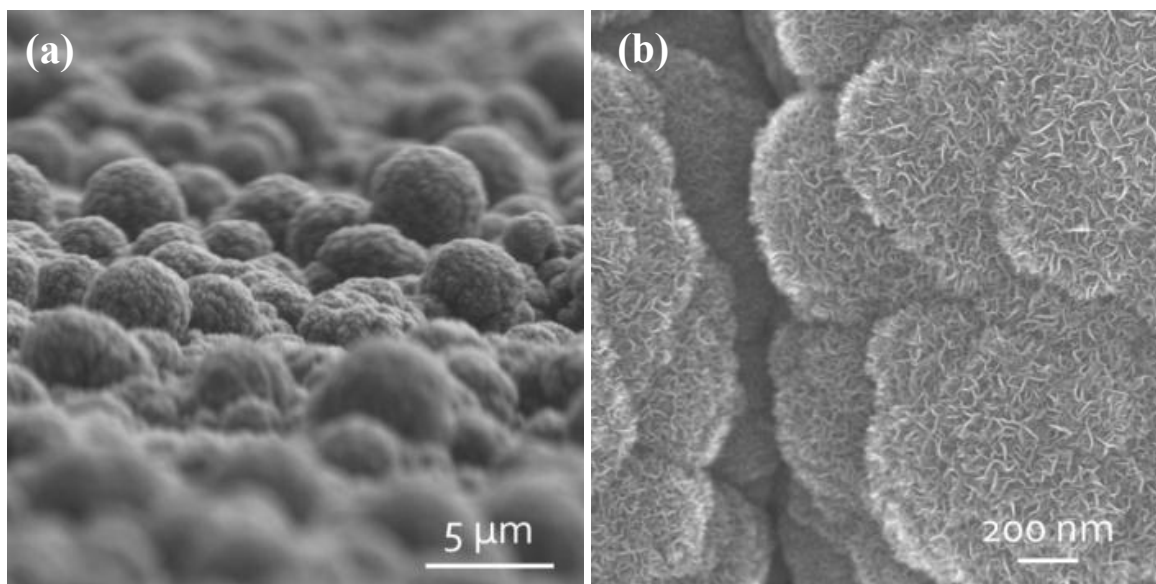


Fig. S1. Electron microscopy characterization of VG grown on a stainless steel plate. (a) The VG forms dome-like structures viewed at an angle of  $5^\circ$  (SEM). (b) A close view of the VG reveals a tightly-packed and highly-ordered graphene sheet configuration (SEM).

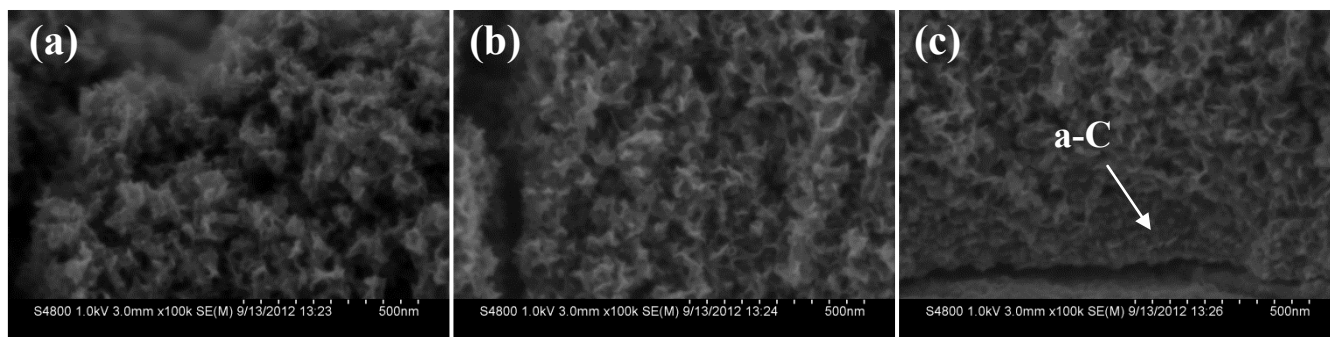


Fig S2 SEM images of the (a) top portion, (b) mid portion, and (c) bottom portion of VG-1.

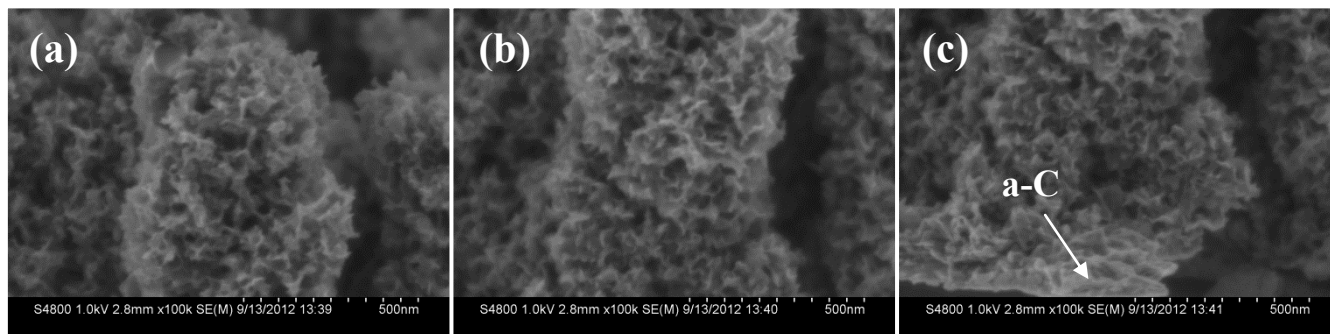


Fig S3 SEM images of the (a) top portion, (b) mid portion, and (c) bottom portion of VG-2.

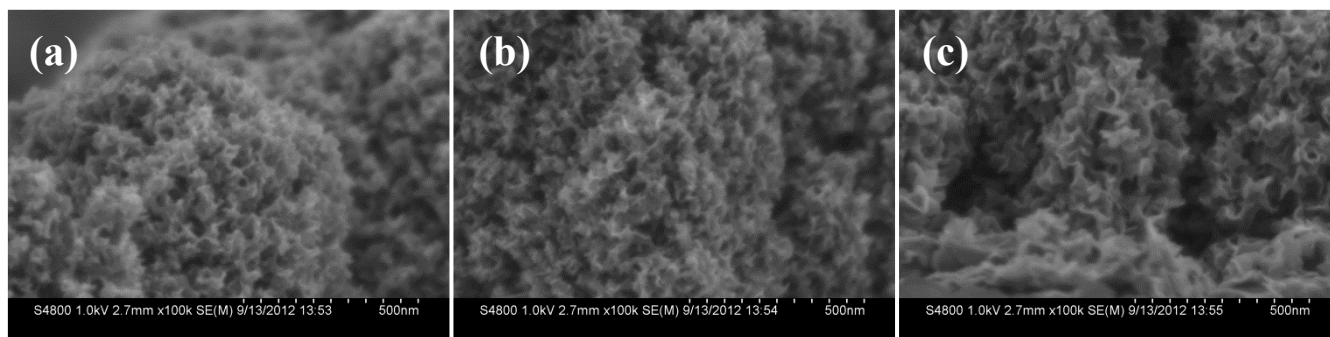


Fig S4 SEM images of the (a) top portion, (b) mid portion, and (c) bottom portion of VG-3.

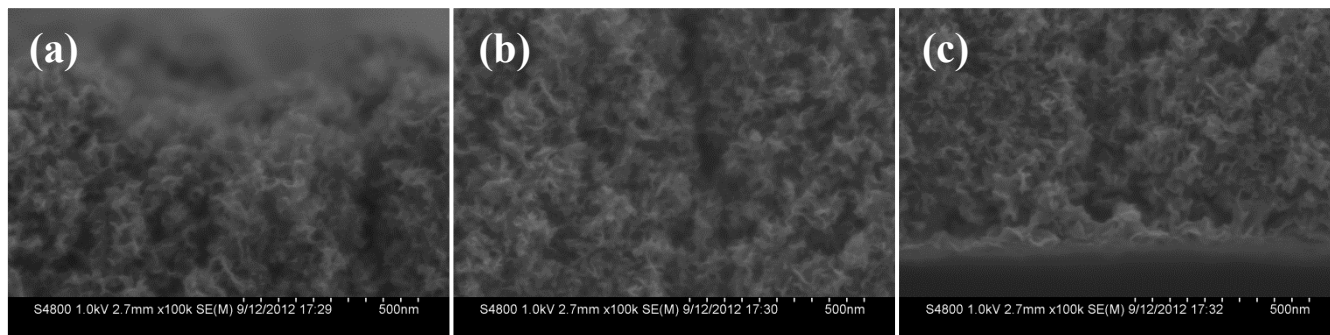


Fig S5 SEM images of the (a) top portion, (b) mid portion, and (c) bottom portion of VG-4.



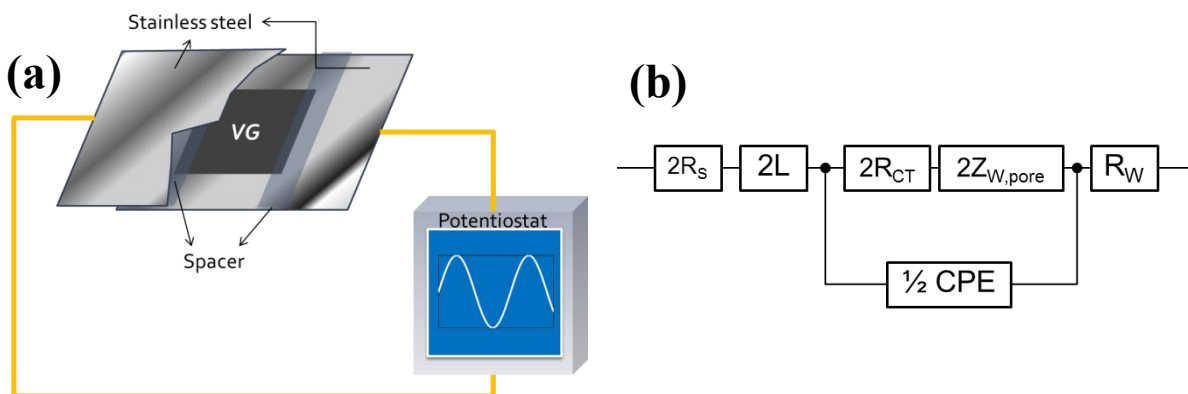


Fig. S6. (a) Schematic of a dummy cell with two identical electrodes. (b) Equivalent circuit diagram for fitting the electrochemical impedance spectra.  $R_S$  is the Ohmic serial resistance, which can be determined from the onset of the first semicircle ( $\sim 100$  kHz). A constant phase element (CPE) describing deviation from the ideal capacitance and charge transfer resistance  $R_{CT}$  gives rise to the first semicircle (mid-frequency: 100-0.1 kHz).  $Z_W$  is the Nernst diffusion impedance in the bulk electrolyte between electrodes, which is represented by the second semicircle (low frequency: less than 10 Hz).  $Z_{W,pore}$  is the Nernst diffusion impedance in the pores of carbonaceous material.

Table S1. Photovoltaic parameters of DSSCs with VG and platinum counter electrodes.

electrode	$V_{OC}$ (mV)	$J_{SC}$ (mA/cm <sup>2</sup> )	FF	$\eta$ (%)
Pt/FTO	735	8.72	0.64	4.68±0.83
VG-1	785	9.88	0.60	4.76±0.35
VG-2	769	7.75	0.66	4.14±0.24
VG-3	791	8.17	0.64	4.27±0.15
VG-4	711	12.1	0.67	5.36±0.39

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