Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Carbon black derived graphene quantum dots composited with carbon aerogel as a highly efficient and stable reduction catalyst for iodide/tri-iodide couple

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Electrode preparation for DSSCs:

TiO_2 paste is screen-printed onto an FTO glass (Nippon Sheet Glass Co., 3.1 mm, <30 Ω/cm^2) to form the photoanode layer with a working area of 0.4 x 0.4 cm^2. CA and GQD/CA pastes are prepared by adding 0.1 g CA or GQD/CA composite powders to a binder solution. The binder solution is prepared by mixing 0.025 g ethylcellulose and 1ml α-terpineol at 110 ^oC for 20 min. The CA (GQD/CA) films are formed with a spin coater and calcined at 400 ^oC for 40 min to remove the residual solvent and binder and to strengthen the adhesion between the CA (GQD/CA) layer and the FTO glass. The Pt based counter electrodes are fabricated by sputter-depositing a 50 nm thick Pt film onto an FTO glass.

Assembly and performances of DSSCs:

The photoanodes with a working area of 0.16 cm^2 are heated at 120 ^oC for 10 min to remove the trapped air and moisture. They are then soaked in a dye solution of 0.3 mM cis-bis(isothiocyanato)bis(2,20-biprydi-4.40-dicarboxylatoruthenium(II)bis-tetrabutylammonium (N719, Solaronix) for 12 h for dye adsorption. The N719 dye is dissolved in a mixture of t-butanol and acetonitrile at a volumetric ratio of 1:1. The electrolyte contains 0.6 M 1-propyl-2, 3-dimethylimidazolium iodide (99%, Aldrich), 0.1 M lithium iodide (99.9%, Aldrich), 0.05 M iodine (99.5%, Fluka), and 0.6 M tert-butyl pyridine (98%, Fluka) with acetonitrile as the solvent. To assemble the cell, a spacer of a thickness 60 μm is used to connect the counter electrode and photoanode. Note that common practices to improve the power conversion efficiency of DSSCs are not adopted in this work since the purpose is to differentiate the performances of three different counter electrodes. The current density–voltage (J–V) curves are recorded with a source meter (Kiethley 236, Kiethley) under illumination of a solar simulator (YSS-E40, Yamashita Denso; AM 1.5, 100mWcm^{-2}) calibrated by a reference Si solar cell (SN2008-152, Yamashita). EIS is conducted with a potentiostat (PGSTAT30, AUTOLAB). A dummy cell composed of two Pt electrodes is used to characterize the Pt counter electrode. Dummy cells, consisting of a Pt electrode and a

CA or GQD/CA electrode, are characterized to determine the charge transfer resistances associated with the CA or GQD/CA based counter electrodes. The EIS is conducted at zero bias with a scanning range of 10^6–0.1 Hz.

Table S1. Charge transfer resistances (R_{ct}) of Pt, CA and GQD/CA based counter electrodes.

	R_{ct} (Ω cm^2)
Pt	2.1
CA	11.2
GQD/CA	3.4

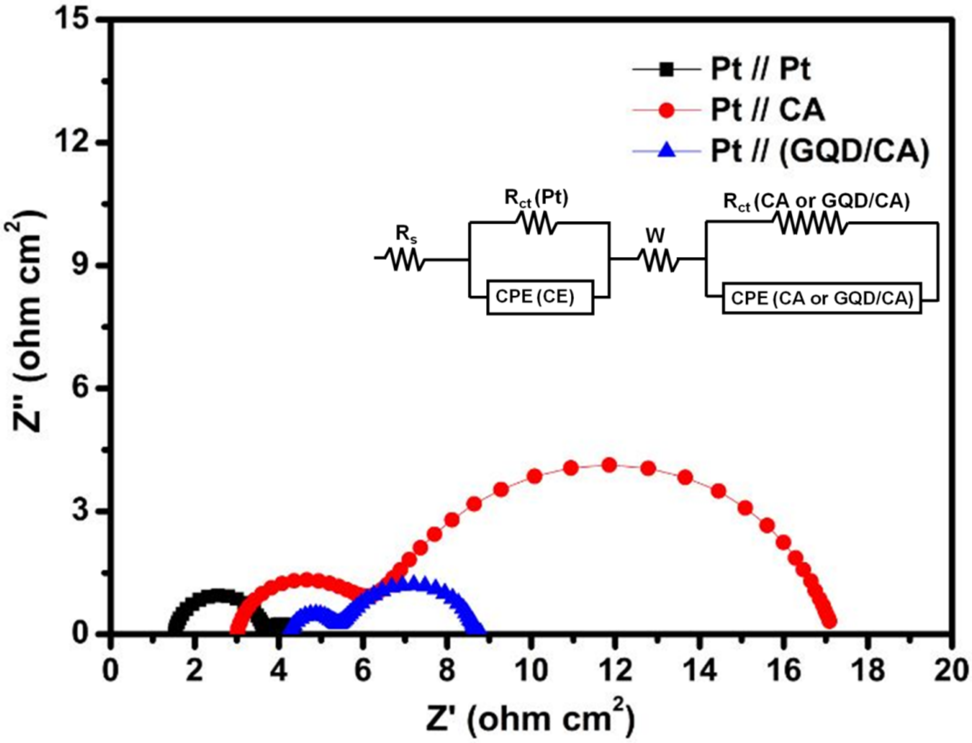

Fig. S1 EIS spectra of Pt, CA and GQD/CA based counter electrodes. Inset is an equivalent circuit model for data fitting of the spectra.

The equivalent circuit used to fit the impedance data is depicted as an inset of Fig. S1. Here, R_s is the serial resistance accounting for the external circuit resistances; W is the Warburg diffusion impedance for the diffusion resistance between the two counter electrodes; R_{ct}(Pt) is the charge transfer resistance at the reference Pt counter electrode; CPE(CE) is the constant phase element associated with the reference Pt counter electrode; R_{ct}(CA or GQD/CA) is the charge transfer resistance at the tested counter electrode; and CPE(CA or GQD/CA) is the constant phase element associated with the tested counter electrode. Here, we focus on R_{ct} (Pt, CA or GQD/CA) to investigate the catalytic efficiencies of the Pt, CA, and GQD/CA counter electrodes. The result is summarized in Table S1.

Table S2. Open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), power conversion efficiency (η), of Pt, CA and GQD/CA based cells.

	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
Pt	0.73	12.69	0.7	6.53
CA	0.78	9.99	0.62	4.85
GQD/CA	0.79	11.36	0.67	5.97

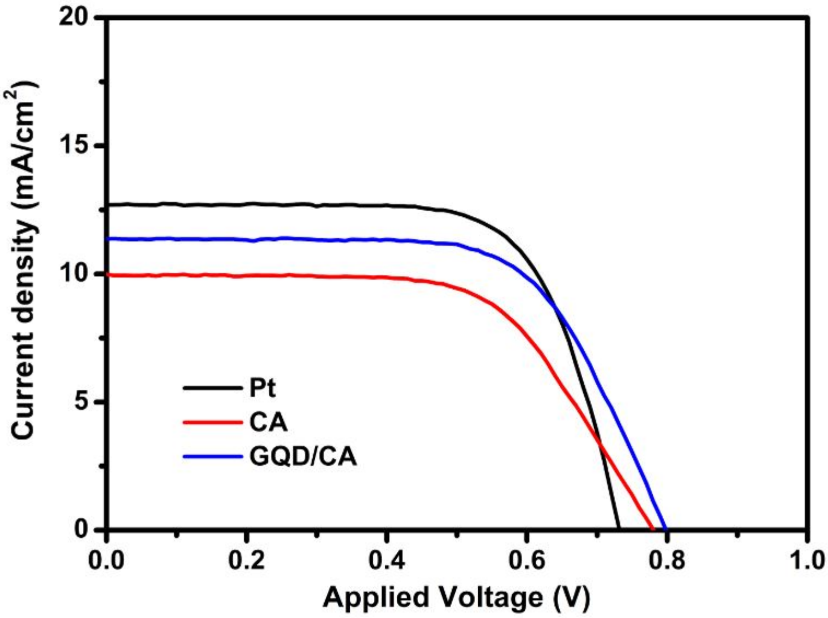

Fig. S2 J–V curves recorded for Pt, CA and GQD/CA based cells.