

Supplementary information for

**Quantum-confined bandgap narrowing of TiO₂ nanoparticles by graphene quantum dots
for visible-light-driven applications**

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1. Experimental

Synthesis of GQDs from carbon black

50mg carbon black (Spuer P, Alfa Aesar) was put inside a 50ml round flask. 6ml concentrated HNO₃ (70%, Chem-Supply) was then introduced to the round flask followed by adding 18ml H₂SO₄ (98%, Chem-Supply) slowly and carefully under magnetic stirring (350rpm). Upon the completion of adding the materials, the round flask was placed into a silicon oil bath with temperature set as 160°C. A condenser was subsequently applied to reflux the vaporized acids and acids decompositions (majorly HNO₃ decompositions since gas with brown colour were generated inside round flask) and the reflux is quite critical as without it nitric acid would fully decompose soon resulting in termination of reaction. Upon completion of reaction for targeted duration, the reacted materials were poured slowly into 200ml of DI water under vigorous stirring. NaOH (Chem-Supply) pellets were added slowly and prudently till PH=5. Then the PH of the solution was further tuned to 7 via a NaOH solution (100mg/ml). The final solution

was subsequently concentrated to 100ml before subject to dialysis with a 500Da tube membrane (SpectrumLabs) for 3 days.

Preparation of GQDs sensitized P25 films

3g powder of TiO₂ nanoparticles (P25, Degussa) were introduced to a glass vial. 70mg of polyethylene glycol (Mn~1500, Sigma-Aldrich) were then added to the vial followed by sufficient DI water addition to form a viscous paste with volume around 20ml. Square TiO₂ films (1cm*1cm) were fabricated via doctor blade printing the TiO₂ paste on glass slides (Citoglass). After dried at room temperature overnight, the as fabricated TiO₂ films were subjected to annealing in a furnace at 450°C for 30min. Upon completion of annealing, the TiO₂ films were immersed in solutions (0.1mg/ml) of as-prepared GQDs including G20, G30, G60, G100, G150, G210 and left for 96hrs. The GQDs/P25 films were then rinsed with DI water bottle to remove unattached excessive GQDs.

Fabrication of graphene quantum dots sensitized solar cells

Square TiO₂ films (0.5cm*0.5cm) were fabricated with similar procedures adopted for the GQDs/P25 films on slides of indium tin oxide (ITO) glass (1.25*3cm, Rs=~85 Ω/sq, Sigma-Aldrich). A poly-dispersed GQDs solution was prepared by mixing 2ml of each of the as synthesized GQDs' solutions (each having similar concentration 0.5mg/ml) including G20, G30, G60, G80, G100, G150, G210. The TiO₂ films were immersed in the poly-dispersed GQDs solutions for 96hrs. The GQD-sensitized TiO₂ films as the photo-anodes of the solar cell were then dried overnight in an oven at 80°C. As for the photo-cathode, a platinum film (0.5*0.5cm) was deposited onto ITO glass slide for 3min via a DC sputter system (K575x, Emitech) by applying an aluminium foil mask on top of ITO glass. A small hole (diameter~1mm) was drilled

through the photo-cathode to one of the four corners of the platinum square. For the final cell assemblage, a square Surlyn loop (0.7cm*0.7cm) were applied in between photo-anode and photo-cathode to seal the them together under thermal compression at 110°C. Iodine couple electrolyte was eventually vacuumly filled into the cell through the small hole drilled in the photocathode before the cell could be wired up for cell performance testing.

Characterization

An UV/Vis spectrometer (Agilent 8453) was applied for acquisition of the absorption spectra. Different chemical bonding conditions were qualitatively evaluated through a Fourier transformation infrared (FTIR) spectrometer (Spectrum Two, Perkin Elmer). Elemental compositions and chemical bonding status were quantitatively analysed by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra). High resolution transmission electron microscopy (HRTEM) (Philips Tecnai F20), along with AFM (NT-MDT NTEGRA Spectra) were adopted for the morphology analysis. I-V characteristics of the GQDSSCs were acquired through a solar simulator (QE-PV-S1, Newport).

2. Carbon black adopted in this research

Carbon black (CB) employed as the precursor of GQDs in this research consists of spherical particles having diameter around 30nm. These spherical particles attached together forming chain-like networks (Fig. S 1 a). Each of the spherical particles is composed of clustered sp^2 crystallites that are randomly oriented^{1, 2}. The crystallites could be seen under high magnification of high resolution transmission electron microscopy (HRTEM) images (Fig. S 1 b).

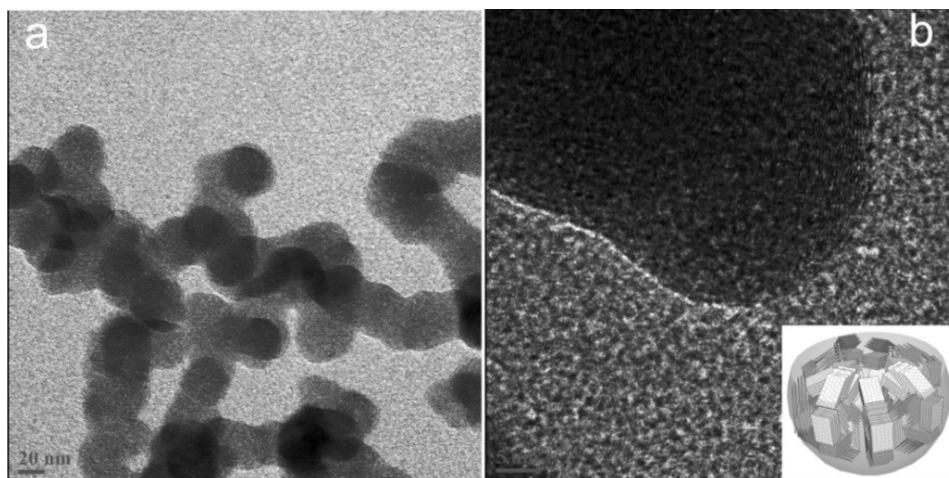


Figure S1. HRTEM images of CB adopted as precursor of GQDs: a) low magnification; b) high magnification, inset is a 3D model showing the structure of CB sphere which consists of graphitic crystallites

3. As synthesized GQDs

From the AFM height profile analysis, the as synthesized GQDs have a thickness around 1.2 nm indicating 1 or 2 layers of carbon atoms (Fig. S 2 a and b). Therefore, it is evident that exfoliation of crystallites in CB during the one-pot reaction was achieved. With the duration tuned, GQDs of different sizes could be obtained as revealed by the dynamic light scattering (DLS) measurement (Fig. S 2 c).

Figure S 3 a shows the HRTEM image of G20 (GQDs synthesized for a reaction duration of 20min). Figure S 1 b exhibits the band gaps (see section 5 for the details of band gap measurement) of the selected GQDs which possesses a gradually incremental trend with the increase of reaction duration. The increase of band gap corresponds to the decrease of particle sizes (Fig. S 2 c) which is an indication of the quantum confinement effect³. The band gaps of the as synthesized GQDs dictate their light absorption feature-as shown in Figure S 3 c, the as synthesized GQDs are excellent UV absorber regardless of the physical states (i.e. either in solution or as solid films)

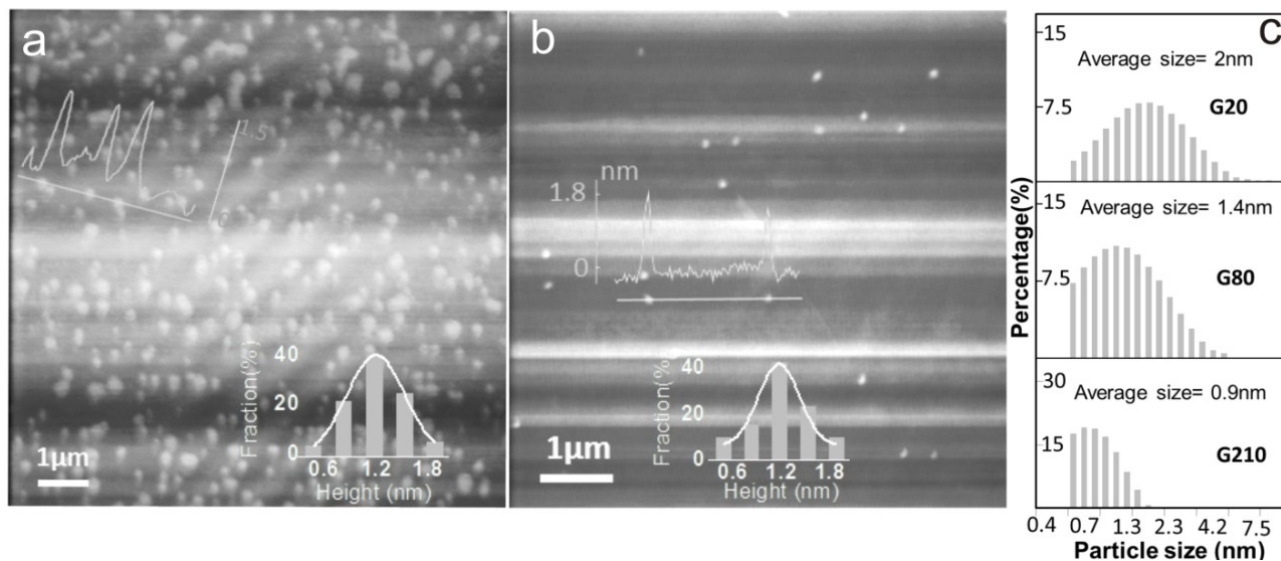


Figure S2. AFM images for G20 (a) and G210 (b) and DLS results (c). Inserted height distributions in a and b are collected over 300 dots respectively; inserted curves in a and b are the height profiles along the line markers under the curves respectively. No DLS data could be collected below the machine limit at ~ 0.6 nm as shown in c.

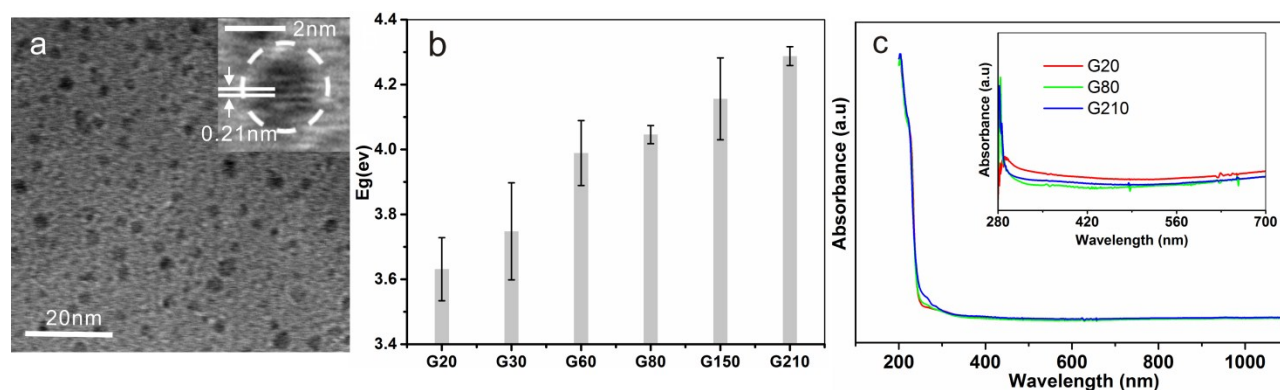


Figure S3. As synthesized GQDs: (a) HRTEM image of G20; (b) bandgaps for the as synthesized GQDs in this research; (c) UV/Vis of G20, G80 and G210. Inset is the UV/Vis spectra of solid films of the three GQDs.

4. Chemical composition analysis via XPS peak fitting

Figure S 4 are the XPS spectra measured for CB, G20, G80, G210. Typical oxygen containing functional groups represented by each of the Gaussian-Lorentzian components

(%Gaussian=30%) were identified as shown in the figure. The relative atomic assignment of each functional groups were summarized in Table.S1

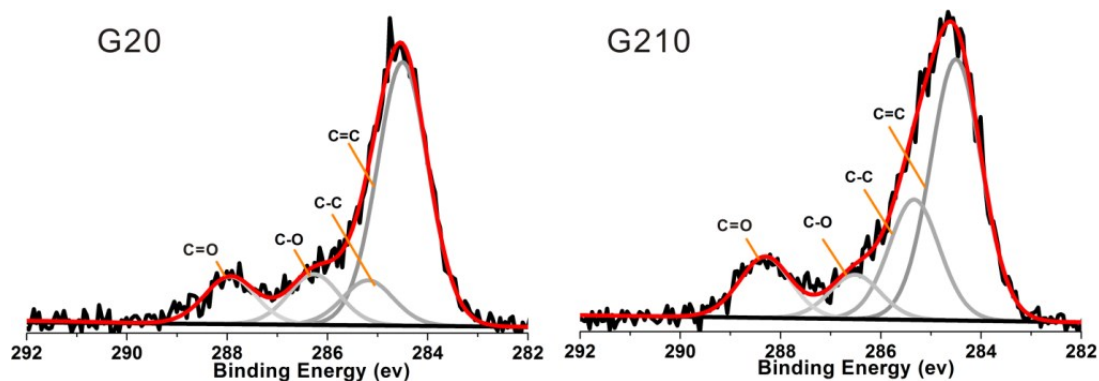


Figure S4. XPS profile fitting for two of the as synthesized GQDs

Table.S1 Atomic concentration assignment (%)

Sample	C=C	C-C	C-O	C=O
G20	64.8	11.1	12.5	11.7
G210	53.7	24.6	9.1	12.6

Due to the existence of oxygenated functional groups, the as synthesized GQDs can form very stable aqueous dispersions and the particle sizes do not significantly vary over time. As shown in Figure S 5, the particle size of a G20 sample stored over one year (average particle size~2nm) is not significantly different from the fresh prepared sample, which suggests that the risk of severe agglomeration is very low as the functional groups rendered the GQDs negatively charged causing repulsion among themselves.

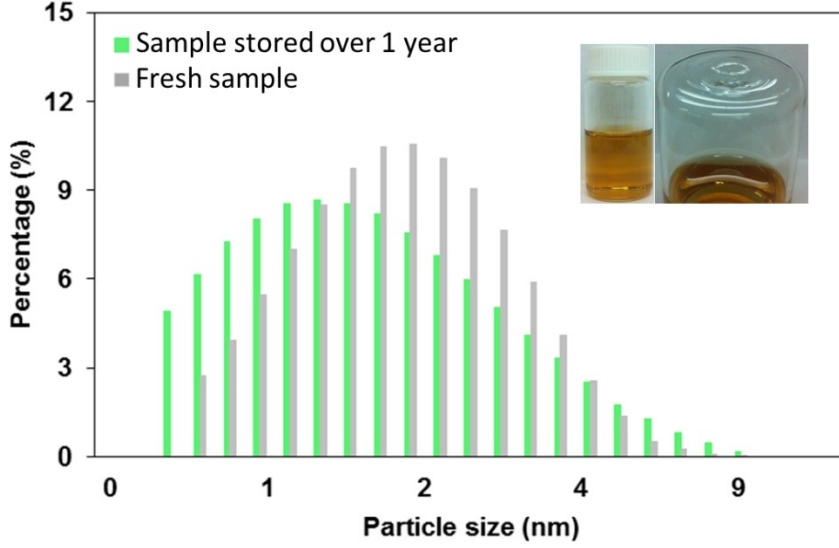


Figure S5. The stability of sizes of G20 over time (size distributions from DLS). Inset are the photos of the sample stored over 1 year without any precipitate sighted.

5. Band gap measurement

The band gaps of GQDs were measured by a modified Tauc model⁴ (Eq. S 1) according to which the band gap of semiconductor materials could be determined by an absorption spectrum fitting method. To be more specific, determination of the band gap could be translated into

extrapolating the linear region of $\left(\frac{Ab(\lambda)}{\lambda}\right)^{\frac{1}{m}}$ vs λ curve as to obtain λ_g . The band gap is then derived applying $E_g = 1239.83 / \lambda_g$.

$$Ab(\lambda) = B_1 \lambda \left(\frac{1}{\lambda} - \frac{1}{\lambda_g} \right)^m + B_2 \quad \text{Eq. S1}$$

Where, B_1 and B_2 are two constants. m is an index which could have different values (ie. 1, 1/2, 3/2, 2, 3). Figure. S 6 a presents typical cases of using this method to determine the band gap of GQDs synthesized in this research. The best fitting was acquired when $m=1/2$.

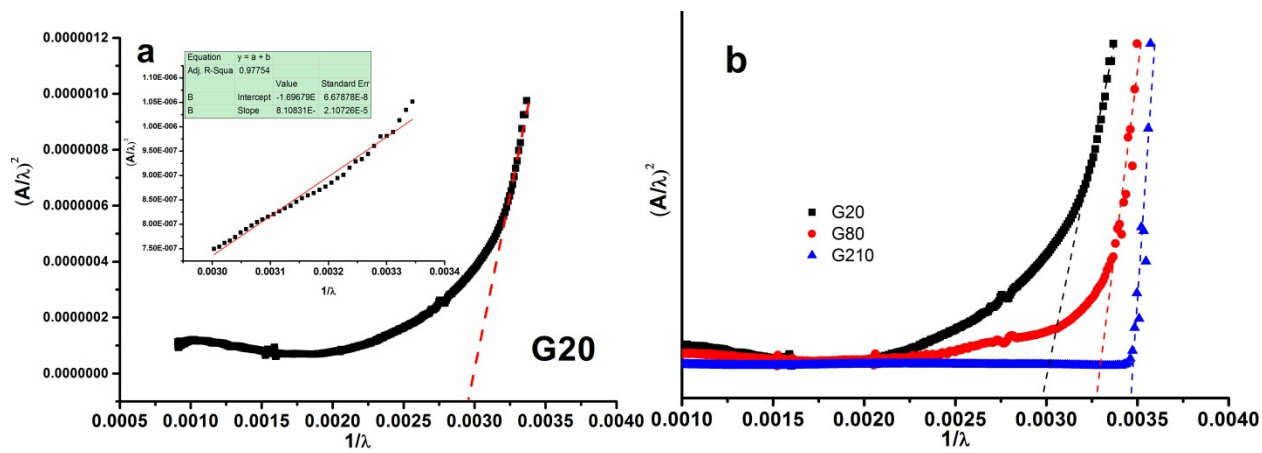


Figure S6. $\left(\frac{Ab(\lambda)}{\lambda}\right)^{\frac{1}{m}}$ vs. λ curves with their linear regions extrapolated: a), G20; b), a comparison among G20, G80, G210

6. Photoluminescence of GQDs before and after -Ti-O-C- bond formation

Formation of -Ti-O-C bond between GQDs and TiO_2 lead to the quenching of photoluminescence (PL) of GQDs (Fig. S 7). In addition to the PL intensity quenching, the PL spectra of the as synthesized GQDs also blue shifted.

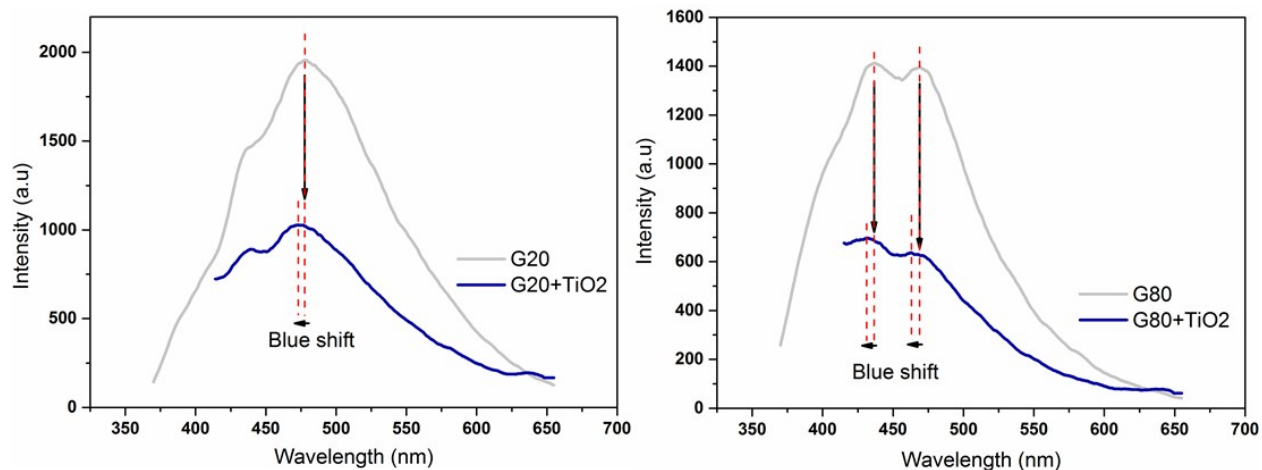


Figure. S7 Photoluminescence of GQDs before and after -Ti-O-C- bond formation

7. TiO_2 films for graphene quantum dots sensitized solar cells and process of cell fabrication

The thickness of the TiO_2 films fabricated in this research is around $2\mu\text{m}$. The TiO_2 films have porous structure as shown in Figure S 8. Figure S 9 is the process of fabrication for the solar cell. Similar approach was adopted for the well-known dye-sensitized solar cells (DSSCs). Table S 2 summarizes the main performance parameters of the as synthesized solar cells.

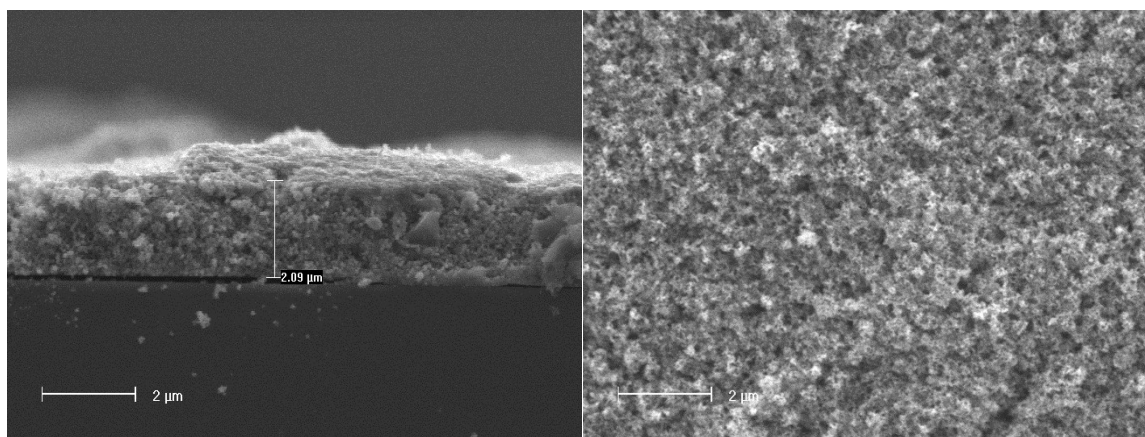


Figure S8. SEM images of TiO_2 films: cross section (left) and porous surface (right)

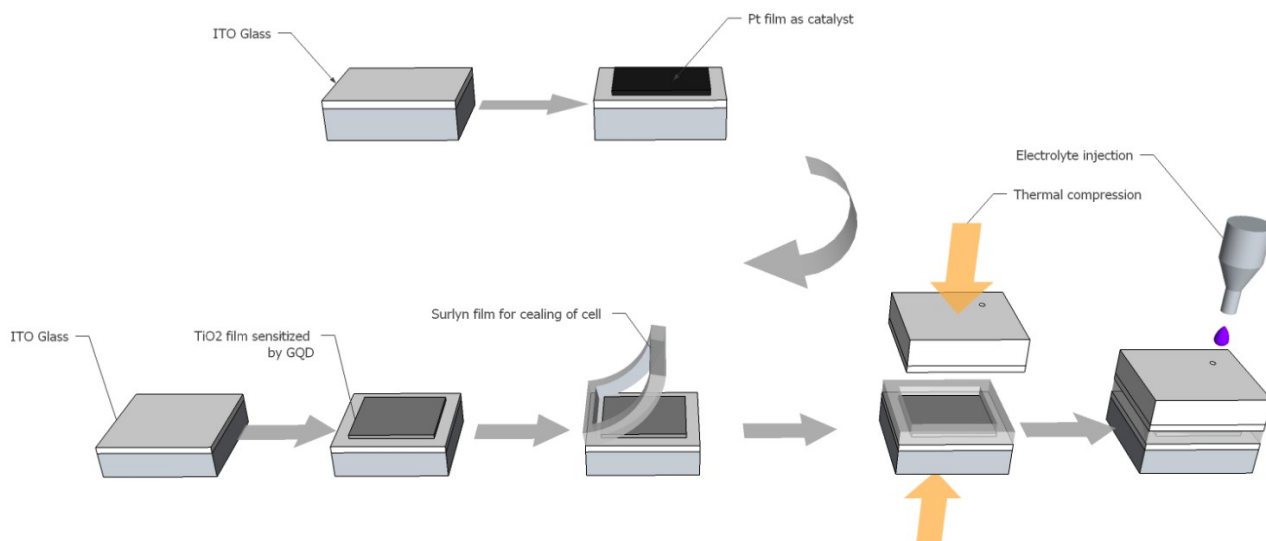


Figure S9. Fabrication process of solar cells

Table S2. Summary of performance parameters of cells

Cells	t(μm)	R_s (Ω/sq)	VOC(V)	JSC ($\mu\text{A}/\text{cm}^2$)	FF
As tested	2	~85 (ITO)	0.44	135	0.50
In Ref. 5	10	~8 (FTO)	0.48	200	0.58

8. Visible light photocatalytic performance of GQDs-TiO₂ photocatalyst

3mL of the poly-dispersed GQDs solution similar to the solution used for solar cell test was diluted to 15ml with DI water and the pH of the solution were tuned to 5 at the same time. After adding 200mg of P25 powder into the solutions, the mixture was magnetically stirred (350rpm) for 96 hrs. The mixture was then subject to several centrifugation rounds at 11500rpm with abundant water (pH=6) to remove the excessive unattached GQDs and any other possible impurities. The final sedimented photocatalyst were collected and dried in oven at 60°C overnight.

For a typical photocatalytic test, 20mg of the as prepared GQDs/P25 photocatalyst was dispersed into 40mL of methylene blue (Chemsupply) solution (10ppm) facilitated by 1 min ultrasonication in dark. The mixture was then kept in dark for 30min with magnetic stir (350rpm) to obtain the absorption-desorption equilibrium. A 300W xenon lamp (PLS-SXE300CUV, Perfectlight) with a 460nm cut off filter installed was applied for the photo-degradation. The distance between the lamp and the mixture (stored in a double wall beaker) was keep at 25cm and the temperature of the mixture was keep at 25°C with water flux applied. 6ml of the mixture was withdrawn from the beaker at each duration. The photocatalyst was removed by

centrifugation at 11500rpm. The supernatant liquid was collected. A UV/Vis spectrometer was adopted for measuring the absorbance intensity of the collected liquid at 660nm (the absorption peak of MB) which was applied for calculating the concentration change (C/C_0). The control tests on P25 facilitated photo-degradation of MB was conducted with the same loading and following same procedure with the tests on GQDs/P25 photocatalyst. Same illumination conditions and reaction durations were also applied for self-degradation of MB.

The GQDs-P25 photocatalyst (Insert in Figure S 10) shows brownish colour in stark contrast to the white colour possessed by P25, which is an indication of improved absorption toward visible light. The photocatalytic performance was demonstrated with the photo-degradation tests of an organic dye methylene blue (MB). Figure S 10 presents the photocatalytic degradation results of MB under visible light (provided with a 300W Xenon lamp to which a 420nm cut off filter was applied). Due to the self-degradation of MB, the concentration of the MB solution decreased with the illumination time. When P25 was added to the MB solution, it presented a similar degradation trend to the bare MB self-degradation upon illumination suggesting that P25 is not an effective visible photocatalyst that could facilitate the photo-degradation of MB, which is consistent with the light absorption feature of P25. However, in stark contrast to self-degradation and P25 facilitated degradation of MB, when the GQDs-P25 photocatalyst was added into the MB solution, the photo-degradation efficiency of MB was significantly improved, near half of the dissolved MB could be degraded within 30min. Therefore, the band narrowing mechanism discovered in this study enables two UV absorbers, GQDs and TiO_2 , to absorb visible light thereby rendering GQDs- TiO_2 composite an efficient visible light photocatalyst.

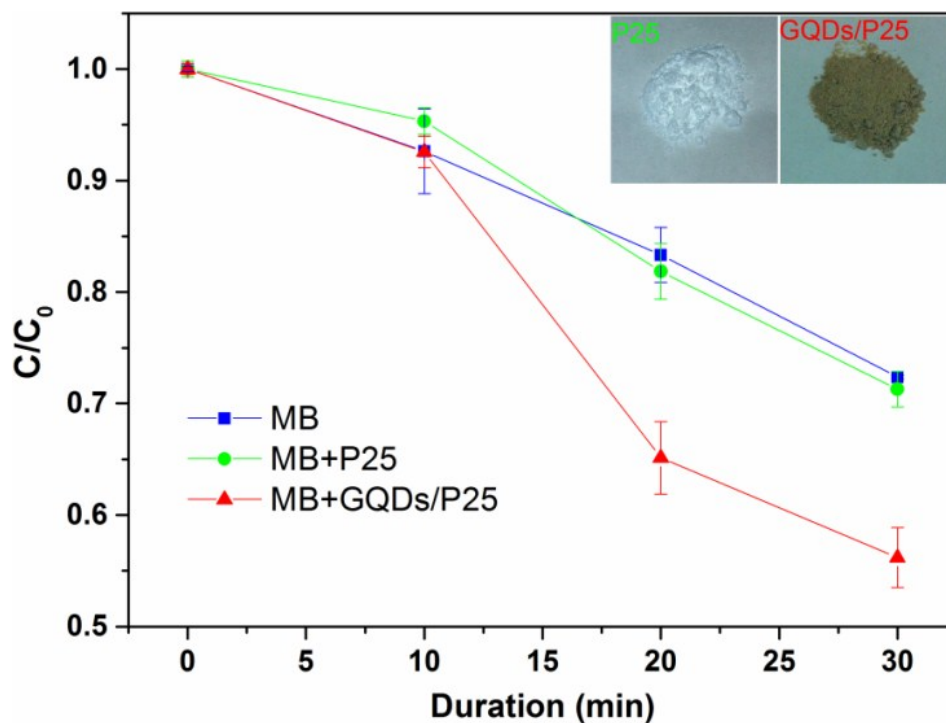


Figure S10. Photocatalytic performance test of the as prepared GQDs/P25 photocatalyst under visible light. Inserts are the photos of P25 powder and GQDs/P25 photocatalyst.

In addition to efficiency, the stability of a photocatalyst is also of great importance for its practical use. Figure S 11 a compares photocatalytic performance of an 11 months old composite stored at room temperature with that of the fresh ones (which have been presented in Figure S 10). It is obvious that the old sample perform as well as the fresh samples in degradation of MB with similar efficiency. The durable photocatalytic performance could be attributed to the sturdy Ti-O-C bonding between GQDs and TiO₂. The FTIR spectra of composites stored over 1 year as shown in Figure S 11 b exhibit similar blue shift of the Ti-O-Ti bands at 450cm⁻¹ to that of the fresh samples presented in the main article, which suggests that the risk of deterioration of the Ti-O-C bond over time is very low. As a result, the photocatalytic capability of the GQD-TiO₂ composite is also well preserved over time.

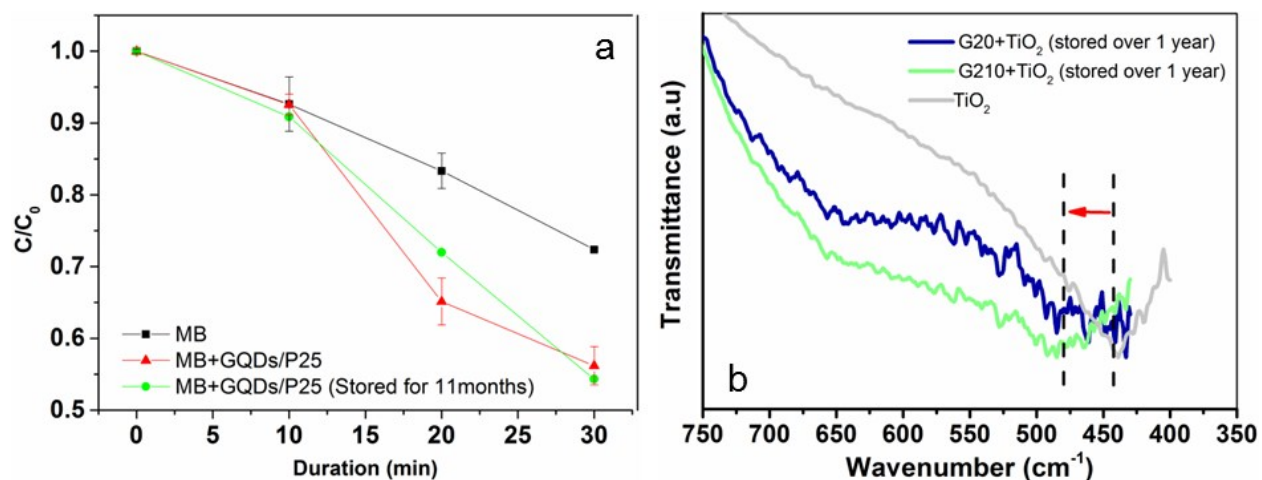


Figure S11. Stability of the GQD-TiO₂ composites: (a), Comparison of the photocatalytic performance of a composite sample store for 11 months with freshly prepared ones (as shown in Figure S 10) under visible light; (b), FTIR spectra of composite samples stored over 1 year showing the blue shift due to the Ti-O-C bond.

Reference

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