# Carbon Quantum Dots and Carbon Layer Double Protected Cuprous Oxide for Efficient Visible Light $CO_2$ Reduction

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## Experimental Section

*1. Preparation of $Cu_2O$, CQD/$Cu_2O$ and CL@CQD/$Cu_2O$ composite:*

All chemicals were purchased from Sigma-Aldrich and analytical grade, used without further purification. We use a mild, single-step ultrasonic approach to produce $Cu_2O$/CQD by developing our former reported work. The preparation of $Cu_2O$ and $Cu_2O$/CQD composites in this experiment applied their method with modifications. Firstly, 75ml of NaOH solution (1M) is added into 75mL of $CuSO_4$ solution (0.1M) drop by drop to form suspension. After ultrasonically treated for 15min, 10ml of polyvinylpyrrolidone (50g/L, molecular weight~30000) followed by 50mL of glucose solution (1M) is added into the mixture with continuous stirring. Then further 1-hour ultrasonic treatment is carried out for the mixture. Afterward, some of the precipitate is directly taken out for washing, while some precipitate is transferred into a Teflon-lined autoclave to be heated at 150℃ for 18hr (for CL@CQD/$Cu_2O$). The rest precipitate is kept in the beaker for 18-hours ageing (for CQD/$Cu_2O$). Finally, the products are respectively washed and centrifuged with deionized water followed by ethanol, and oven dried at 60℃ for 12hr. Final obtained products are $Cu_2O$, $Cu_2O$/CQD and CL@CQD/$Cu_2O$, respectively.

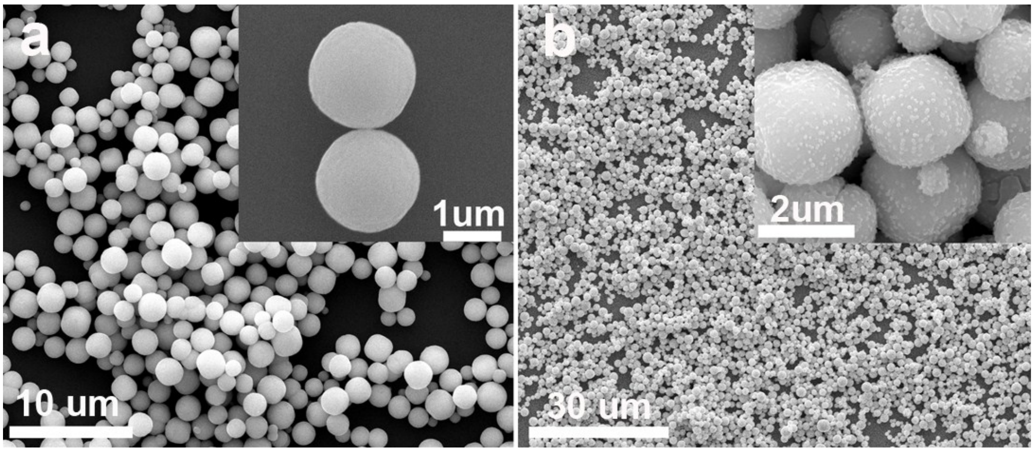


*Figure S1 (a) The SEM image of the obtained $Cu_2O$ and (b) CQDs/$Cu_2O$ from ultrasonic method*

Based on the former research and this work the formation of CL@CQD/$Cu_2O$ can be divided into 3 steps: Firstly, the substrate solution of glucose, NaOH and $Cu_2SO_4$ is given a ultrasonic treatment, the small $Cu_2O$ particles will be formed in a short time in the solution, meanwhile, due the excessive glucose and NaOH in the solution, the small amount of CQDs are formed; Secondly, with ultrasonic treatment time going, more CQDs formed and the small $Cu_2O$ particle grows bigger; Thirdly, the mixture is moved to a autoclave to be treated by hydrothermal method, then the glucose will form a carbon layer on the surface of $Cu_2O$ particle, also the CQDs near the $Cu_2O$ are capsuled by the carbon layer.

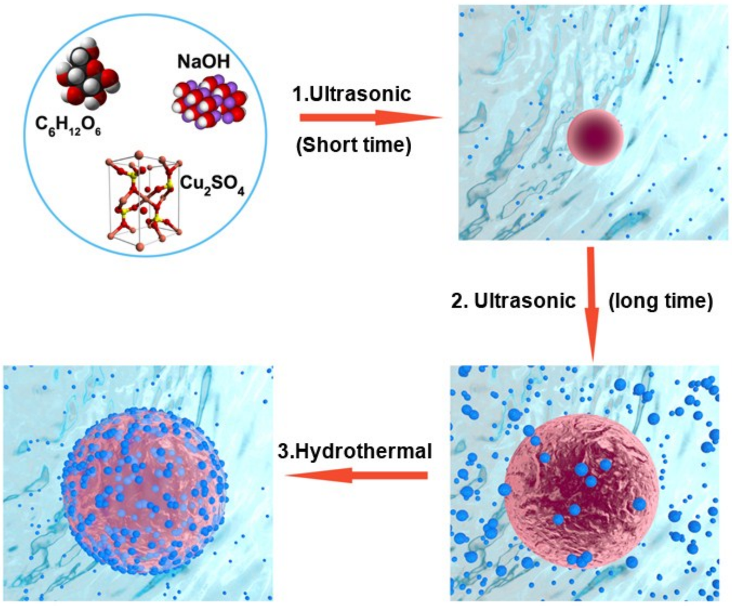


*Figure S2 The formation process of the CL@CQDs/$Cu_2O$ particle*

## 2. *Material characterization*

Scanning electron micrograph (SEM) images and energy-dispersive X-ray (EDS) element analysis were achieved by using Zeiss Ultra while transmission electron micrographs (TEM) and high-resolution TEM (HRTEM) images were taken on JEOL 2200FS Transmission Electron Microscope. X-ray powder diffraction (XRD) was recorded on Shimadzu S6000 X-

Ray Diffractometer which using Cu Kα (λ=0.154nm) radiation with resolution of 0.02°. Shimadzu UV-3600 Spectrophotometer and Renishaw inVia Raman Microscope was used to obtain the UV/Vis spectra and Raman spectroscopy, respectively. Photoluminscence spectra were tested in Horiba Fluo-Max 4.

### 3. *Photocatalytic activity test*

The photocatalytic performances of as-obtained catalysts for the $CO_2$ reduction were tested. Initially, 20mg of prepared photocatalyst and 10ml of deionised water was added into the high-pressure photocatalytic reactor (YANZHENG INSTRUMENT YZPR-100(S)). Then 1ml of triethanolamine as a hole scavenge is added into the solution to further reduce recombination and partly prevent the hole to react with $H_2O$ to produce $O_2$. After air removal and $CO_2$ saturation in the reactor by purging with $CO_2$ for 10 times, a pressure of 2 bars was given to the close reactor by injecting a certain amount of $CO_2$. Afterward, a 300W Xe lamp (YANZHENG INSTRUMENT YZXBO-PE300) was used as excitation source to irradiate the mixture from topside of reactor. The lamp gave continuous light output with intensity of about 100mW/cm$^2$ in the visible range by using an AM1.5 filter. It is noted that the solution in the reactor was continuously stirred during the irradiation. After 2.5-hours light irradiation, gaseous products in the reactor was sampled and injected into a gas chromatography (VARIAN Inc. CP-4900 Micro Gas Chromatography), which equipped with a MolSieve 5A and a PoraPLOT Q column, for composition analysis. The experimental apparatus of the photocatalytic reaction is shown in Figure in supporting information.

### 4. *Photoelectrochemical measurements*

To investigate the photoelectrochemical(PEC) activity of the photocatalysts, the CL@CQDs/ $Cu_2O$ modified electrodes was obtained as following method: Firstly, the indium tin oxide glass (ITO, 2.5 cm × 1 cm) was washed in 1 M NaOH water solution and acetone for 20 mins under ultrasonic condition, respectively. Then washed the ITO with water and dried before using. Secondly, put 3mg of catalyst into a mixture of ethanol (0.3 ml) and ethylene glycol (0.3ml) to form a suspension, followed with ultrasonic treatment to obtain uniform colloidal dispersion. Take 30μl of solution to drop onto a piece of ITO slice with fixed area of 0.5 $cm^2$ and dried in air naturally at room temperature to obtain the electrode. All the PEC tests were conducted at a constant potential and used the phosphate buffer solution as electrolyte. The tests were performed on a CHI660E which used Pt wire as counter electrode, ITO as working electrode and Ag/AgCl as reference electrode. A 300W Xe lamp supplied the light source on the measurement.

### *5.Experimental setup and bandgap calculation:*

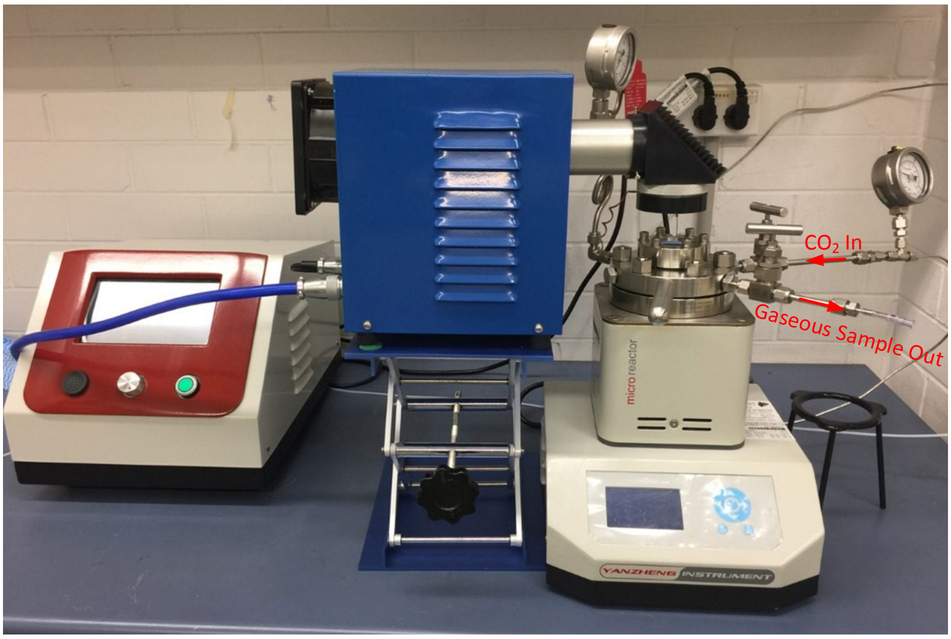
With above UV-Vis spectrum, Kubelka-Munk equations shown below is normally used to estimate the bandgap of samples.

$$(\alpha hv)^n = A(hv - E_g)$$

$$\alpha = \frac{(1-R)^2}{2R}$$

$$hv = \frac{hc}{\lambda}$$

Where α is the optical absorption coefficient; R is reflectance obtained from the UV-Vis reflectance spectrum of $Cu_2O$ and $Cu_2O$/CQD; A is a constant; n is equal to 2 for allowed direct transition of $Cu_2O$; h is Planck’s constant; c is the speed of light; hc is calculated as a constant, 1240eV.



*Experimental set-up of photocatalytic reaction tests*

### 6. *Charge transfer characterization:*

As Fig.2d shown, CL@CQD/$Cu_2O$ shows a lower PL emission peak than CQDs/$Cu_2O$ and pure $Cu_2O$ under 400 nm excitation. Such significant quenching indicates that CL@CQD/$Cu_2O$ catalyst has a much lower recombination rate of photoexcited electron/hole pairs during light irradiation, which proves that CL@CQD act as excellent electron reservoirs and can prevent the recombination of photo-induced carriers in $Cu_2O$. We also tested the electrochemical impedance spectroscopy (EIS) of pure $Cu_2O$ and CL@CQDs/$Cu_2O$, as Fig. S8 shown, the Nyquist plot of CL@CQDs/$Cu_2O$ has an obviously smaller radius than the pure $Cu_2O$ one. The semicircle in a Nyquist plot at high frequencies is characteristic of the charge transfer process, and the diameter of the semicircle is an indicator of the charge transfer resistance. The smaller resistance of CL@CQDs/$Cu_2O$ material further confirms that the CL@CQDs can improve the conductivity, also does not block electron transfer but facilitates electron migration.

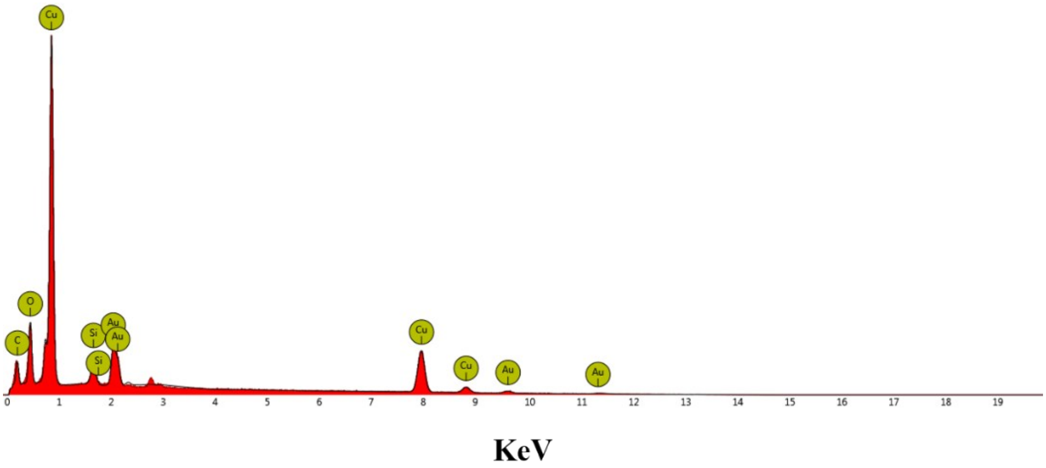


*Figure S3 The EDX spectrum of the CL@CQDs/$Cu_2O$ (use Si chip as substrate and coat the sample with Au particle)*

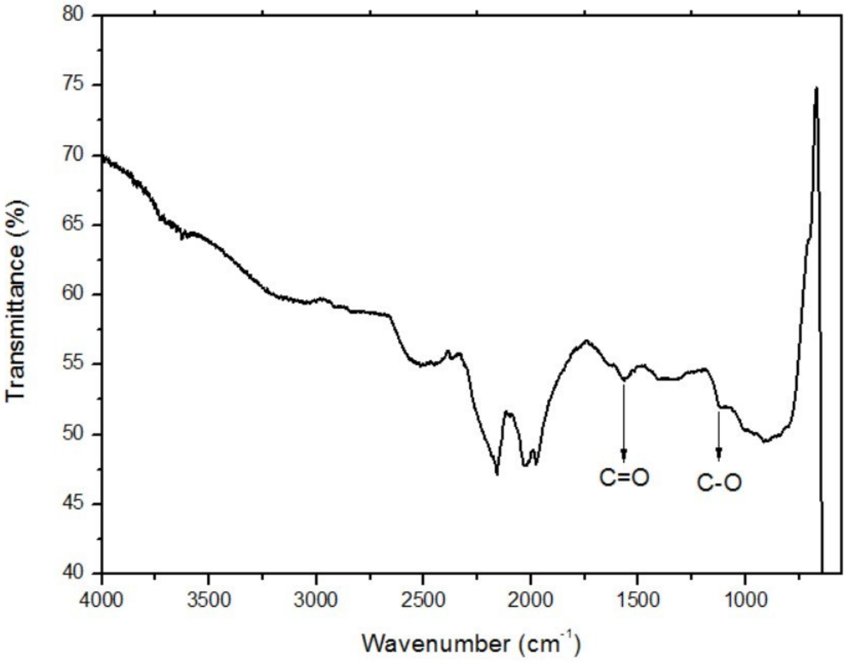


*Figure S4 FT-IR spectrum of CQDs/Cu2O after ageing*

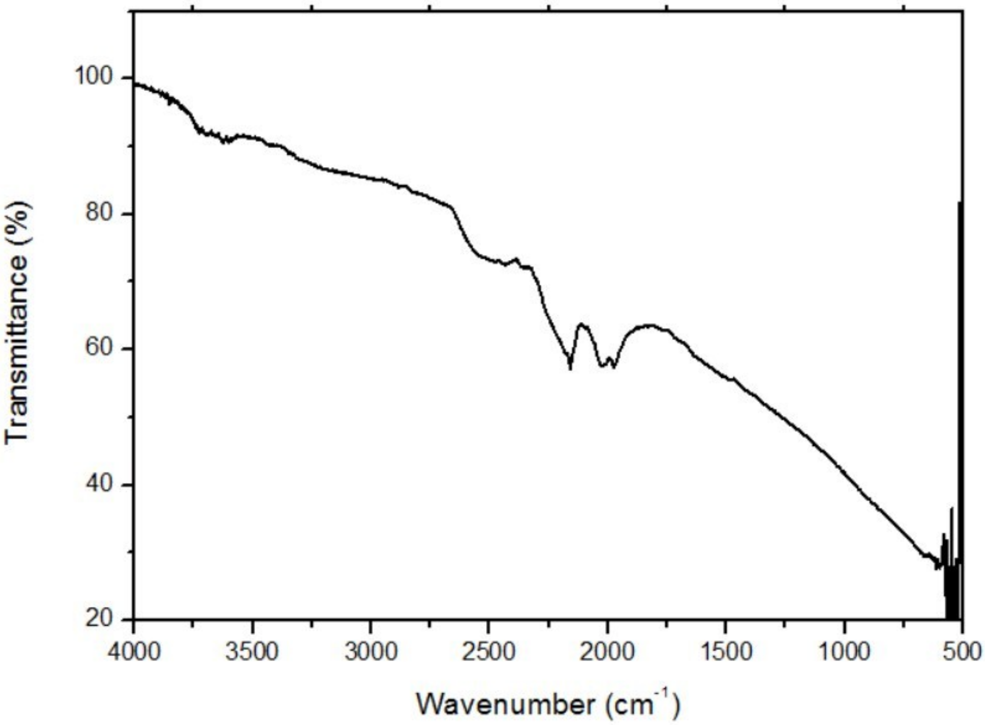


*Figure S5 FT-IR spectrum of CL@CQDs/Cu2O after hydrothermal treatment*

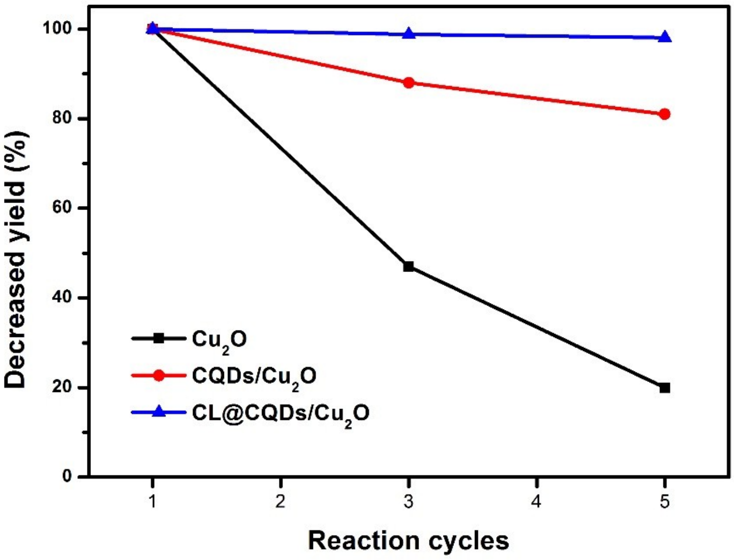


*Figure S6 The decreased methanol yield change of different catalysts for $CO_2$ reduction in 5 cycles.*

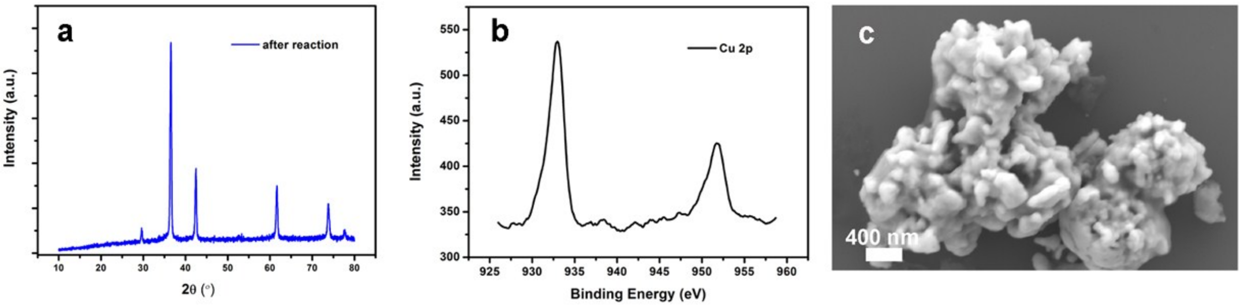


*Figure S7 The XRD, XPS (Cu 2p) and SEM of the CL@CQDs/$Cu_2O$ catalyst after 3rd reaction*

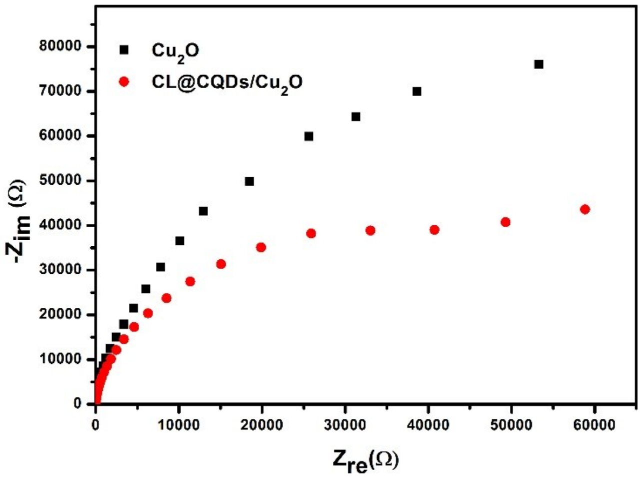


*Figure S8 The EIS of pure $Cu_2O$ and CL@CQDs/$Cu_2O$ decorated electrodes*

Table S1 The results of photocatalytic $CO_2$ reduction by using CQDs, CL@CQDs, CL@CQDs/$Cu_2O$

| Catalysts (including C element) | CQDs | CL@CQDs | CL@CQDs/$Cu_2O$ |
|---|---|---|---|
| Products from reducing reaction | Not detected | Not detected | Not detected |

*Table S2 The comparison of different Cu-based materials for $CO_2$ reduction*

| Catalyst | Light source | System | Yield of main products | Ref |
|---|---|---|---|---|
| CQDs/$Cu_2O$ | Xe Lamp(300W) | Dry ice (1g), high pressure | $CH_3OH$, 56μmol/g·h | [1] |
| Cuboid-$Cu_2O$ | Xe lamp (300 W) | $CO_2$ saturated $H_2O$ with scavenger | CO,up to 20 ppm/g·h,<br>$H_2$, up to 133 ppm/g·h, | [2] |
| Foam-like $Cu_2O$ | Hg lamp, with filters to tune λ | Purified $CO_2$(g) with moisture | $CH_3CHO$, 8.2 μmol/g·h,<br>$CH_4$, 19.2 μmol/g·h, | [3] |
| C-doped $Cu_2O$ mesoporous nanorod | Xe lamp (350 W, λ>420 nm) | $CO_2$ purged through $KHCO_3$(aq) (0.1 M) | $CH_4$, 0.0133 μmol/g·h,<br>$C_2H_4$, 0.0167 μmol/h, | [4] |
| Cu/$C_3N_4$ | Xe lamp (350 W) | $KHCO_3$(aq) (0.1 M), 0.2 bar $CO_2$ with moisture, 100 °C | $CH_4$, 109 μmol/g·h,<br>$CH_3OH$, 20 μmol/g·h,<br>$C_2H_4$, 1.5 μmol/g·h,<br>$C_2H_6$, 0.65 μmol/g·h | [5] |
| c-$Cu_2O$/g$C_3N_4$ | LED lamp (8 W) | ~1 bar $CO_2$ with moisture | CO, 0.002 μmol/g·h | [6] |
| $Cu_2O$/reduced GO | 150 W Xe lamp | sodium sulphite(0.7M) as scavenger | CO, 50ppm/ g·h | [7] |
| $Cu_2O$/C-nanoparticle | Xe lamp (300 W) | $CO_2$ purged through NaOH(aq) (1M) | $CH_3OH$, 19.40 μmol/g·h | [8] |
| CL@CQDs/$Cu_2O$ | Xe lamp (300 W) | $CO_2$, 2 bar, scavenger | $CH_3OH$, 99.60 μmol/g·h | This work |

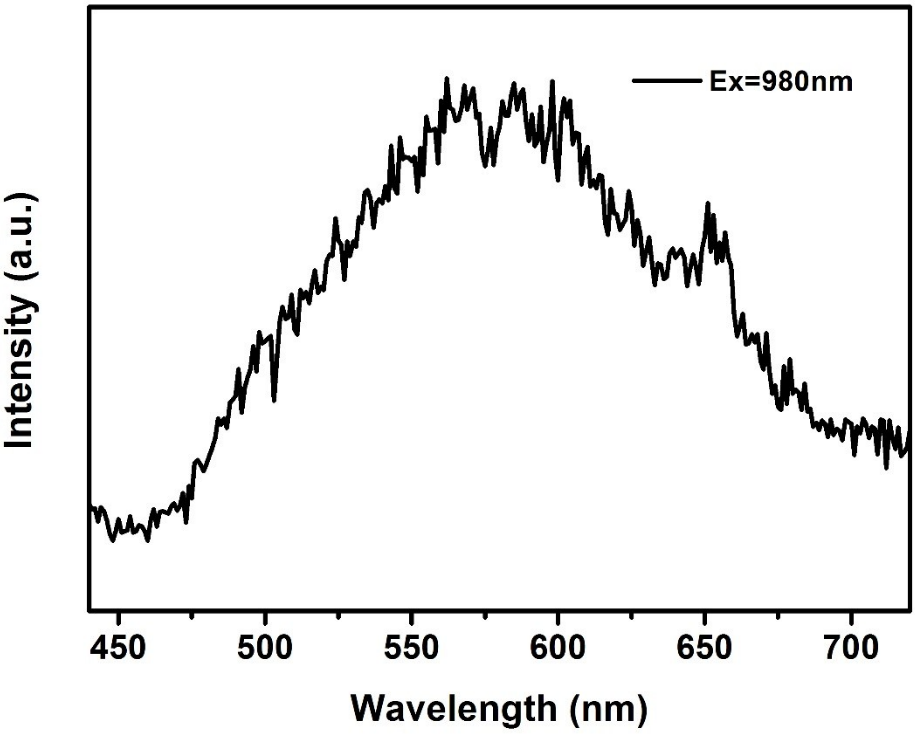


*Figure S9 The Up-conversion PL spectrum of CQDs excited under 980nm*

**Reference:**

[1] H. Li, X. Zhang, D. R. MacFarlane, *Advanced Energy Materials* **2015**, *5*, 1401077.

[2] A. D. Handoko, J. Tang, *International Journal of Hydrogen Energy* **2013**, *38*, 13017-13022.

[3] M. L. Ovcharov, A. M. Mishura, N. D. Shcherban, S. M. Filonenko, V. M. Granchak, *Solar Energy* **2016**, *139*, 452-457.

[4] L. Yu, G. Li, X. Zhang, X. Ba, G. Shi, Y. Li, P. K. Wong, J. C. Yu, Y. Yu, *ACS Catalysis* **2016**, *6*, 6444-6454.

[5] B. Tahir, M. Tahir, N. A. S. Amin, *Applied Surface Science* **2017**, *419*, 875-885.

[6] P.-Y. Chang, I. H. Tseng, *Journal of $CO_2$ Utilization* **2018**, *26*, 511-521.

[7] X. An, K. Li, J. Tang, *ChemSusChem* **2014**, *7*, 1086-1093.

[8] Z. Dedong, H. Maimaiti, A. Awati, G. Yisilamu, S. Fengchang, W. Ming, *Chemical Physics Letters* **2018**, *700*, 27-35.