Electronic Supplementary Material (ESI) for Nanoscale

Carbon Quantum Dots with Photo-generated Proton Property as Efficient Visible Light Controlled Acid Catalyst

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Supporting Information

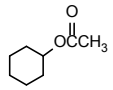
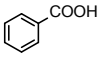
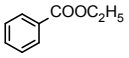
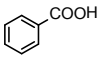
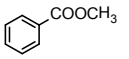
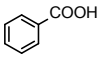
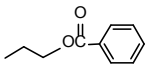
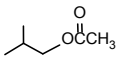
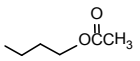
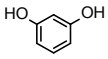
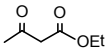
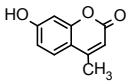
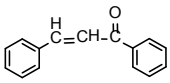
Entry	Reactants 1	Reactants 2	Products	Conv.[%] (CQDs, 1-4 nm) (light, +/-)	Conv.[%] (Graphite, 100-2000 nm) (light, +)
1	CH_3OH	CH_3COOH	CH_3COOCH_3	6.7/2.6	0.8
2		CH_3COOH		6.8/1.9	0.2
3	C_2H_5OH	CH_3COOH	$CH_3COOC_2H_5$	7.7/2.9	0.4
4	C_2H_5OH			6.3/1.3	0.3
5	CH_3OH			6.5/1.9	0.8
6				6.1/1.1	0.5
7		CH_3COOH		6.8/2.8	0.1
8		CH_3COOH		7.9/2.9	0.9
9				6.7/2.6	0.1
10				6.9/1.8	0.3

Table S1 Photocatalytic activities for different reactions (Esterification, Peckmann and aldol condensation reaction) by 1-4 nm CQDs and graphite photocatalysts with (+) or without (−) visible light ($\lambda > 420$ nm).

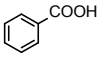
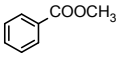
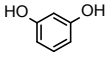
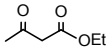
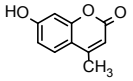
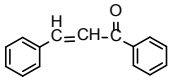
Entry	Reactants 1	Reactants 2	Products	Conv.[%] (GO) (light, +)	Conv.[%] (RGO) (light, +)
1	CH_3OH	CH_3COOH	CH_3COOCH_3	10.8	3.2
2	CH_3OH			9.5	2.9
3				10.6	2.3
4				9.3	2.1

Table S2 Photocatalytic activities for different reactions (Esterification, Peckmann and aldol condensation reaction) by GO and RGO with (+) visible light (λ > 420 nm).

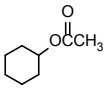
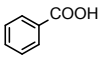
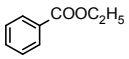
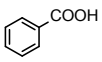
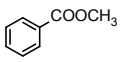
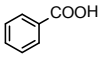
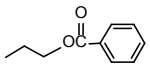
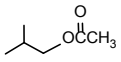
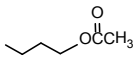
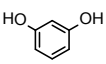
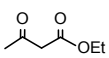
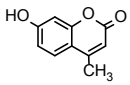
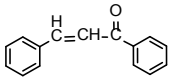
Entry	Reactants 1	Reactants 2	Products	Conv.[%] (chemical reduced 5-10 nm CQDs)
1	CH_3OH	CH_3COOH	CH_3COOCH_3	8.9
2		CH_3COOH		7.2
3	C_2H_5OH	CH_3COOH	$CH_3COOC_2H_5$	8.8
4	C_2H_5OH			8.1
5	CH_3OH			7.6
6				6.8
7		CH_3COOH		9.8
8		CH_3COOH		9.2
9				8.1
10				8.4

Table S3 Photocatalytic activities for different reactions (Esterification, Peckmann and aldol condensation reaction) by chemical reduced 5-10 nm CQDs photocatalyst with visible light (λ > 420 nm).

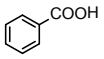
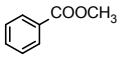
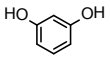
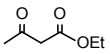
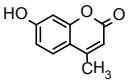
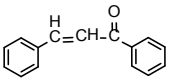
Entry	Reactants 1	Reactants 2	Products	Conv.[%] (CQDs after plasma treatment) (light,+)
1	CH_3OH	CH_3COOH	CH_3COOCH_3	5.8
2	CH_3OH			6.5
3				8.6
4				6.3

Table S4 Photocatalytic activities for different reactions (Esterification, Peckmann and aldol condensation reaction) by 5-10nm CQDs (after plasma treatment) with (+) visible light ($\lambda > 420$ nm).

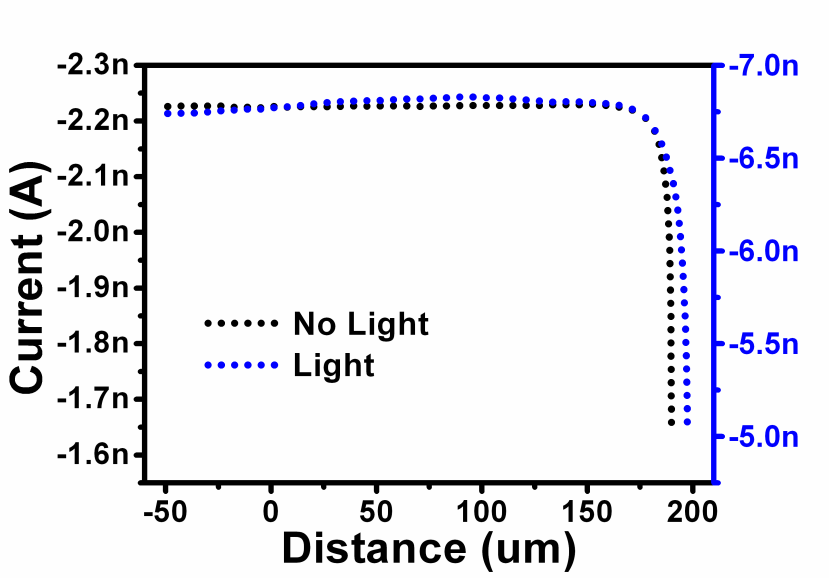


Figure S1 The two approach curves after treatment (double Y model) which the starting current are on the same height level.

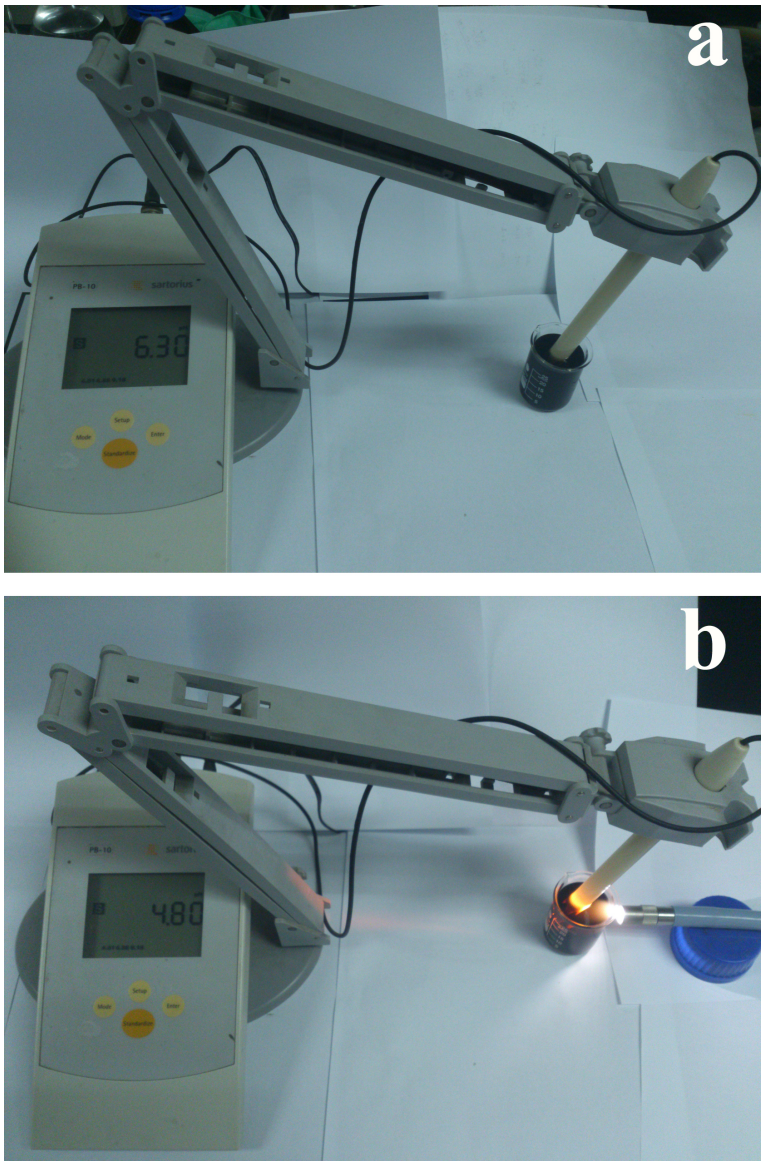


Figure S2 The pH value of 5-10nm CQDs solution (a) without light irradiation or (b) under light irradiation (35℃, 100% illumination intensity)

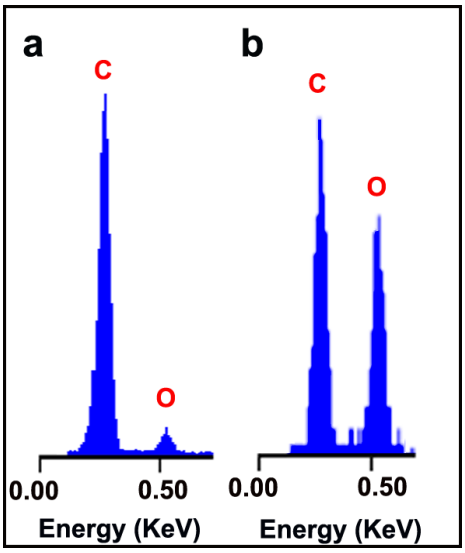


Figure S3 EDX spectra of 5-10nm CQDs (a) after chemical reduced and (b) without chemical reduced process.

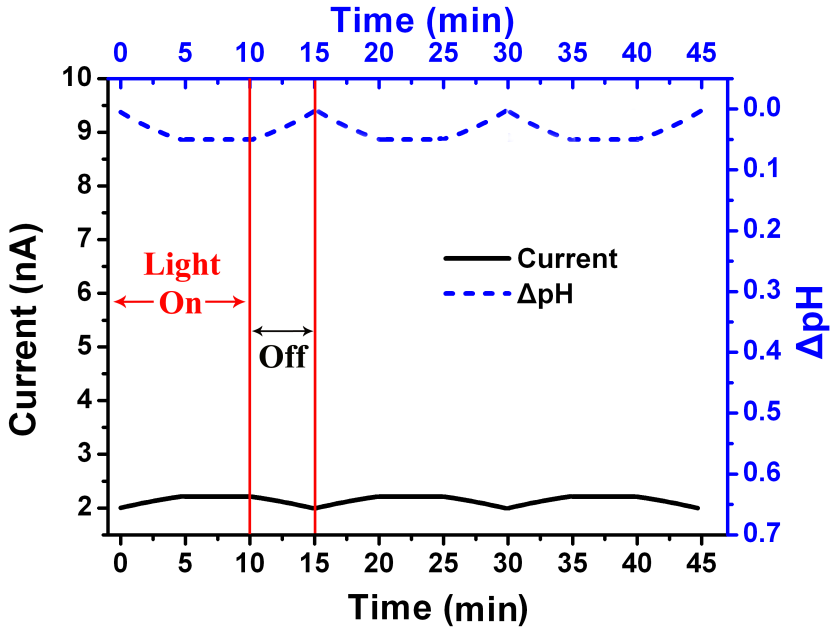


Figure S4 Photocurrent and pH value responses of 5-10 nm chemical reduced CQDs under visible light.

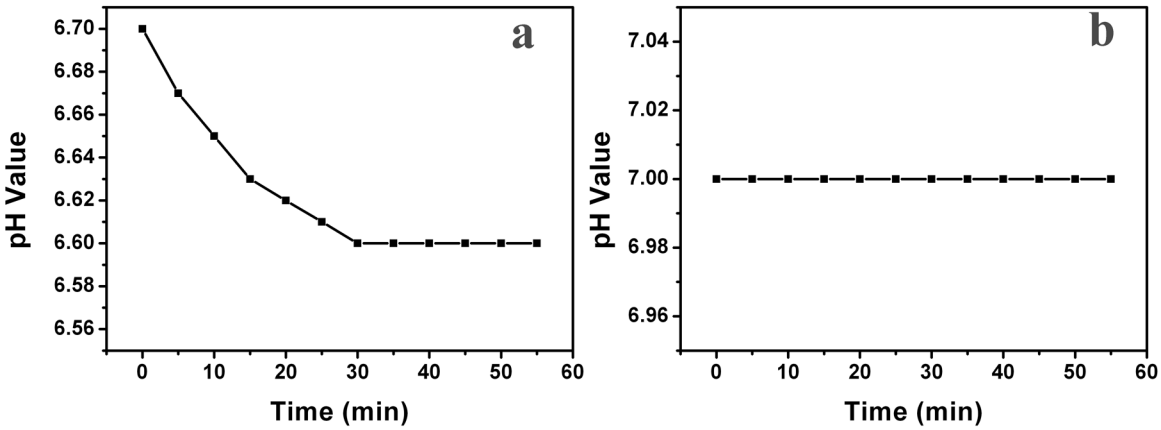


Figure S5 The pH value's changes of (a) CQDs (1-4 nm) and (b) graphite solution (1mg/ml, 100% illuminatioin, 25 ℃) under visible light irradiation.

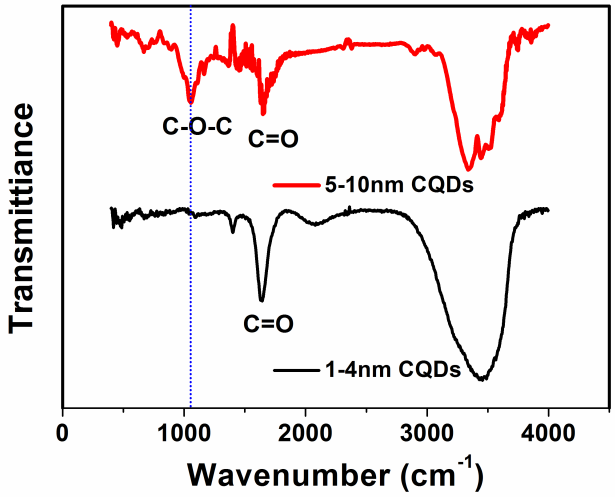


Figure S6 The FT-IR spectra of 5-10nm CQDs and 1-4nm CQDs after visible light irradiation.

The Stern-Volmer kinetic relationships:

This term applies broadly to variations of quantum yields of photophysical processes (e.g. fluorescence) or photochemical reactions (usually reaction quantum yield) with the concentration of a given reagent which may be a substrate or a quencher. In the simplest case, a plot of ϕ^0/ϕ (or M^0/M for emission) vs. concentration of quencher, [**Q**], is linear obeying the equation:

$$\frac{\Phi^0}{\Phi} \text{ or } \frac{M^0}{M} = 1 + K_{sv}[Q] \quad \textbf{(1)}$$

In equation (1) is referred to as the Stern–Volmer constant. Equation (1) applies when a quencher inhibits either a photochemical reaction or a photophysical process by a single reaction. ϕ^0 and M^0 are the quantum yield and emission intensity radiant exitance, respectively, in the absence of the quencher Q, while ϕ and M are the same quantities in the presence of the different concentrations of Q. In the case of dynamic quenching the constant K_{sv} is the product of the true quenching constant k_q and the excited state lifetime, τ^0, in the absence of quencher. k_q is the bimolecular reaction rate constant for the elementary reaction of the excited state with the particular quencher Q. Equation (1) can therefore be replaced by the expression (2):

$$\frac{\Phi^0}{\Phi} \text{ or } \frac{M^0}{M} = 1 + k_q \tau^0 [Q] \quad \textbf{(2)}$$

When an excited state undergoes a bimolecular reaction with rate constant k_T to form a product, a double-reciprocal relationship is observed according to the equation:

$$\frac{1}{\Phi_p} = \left(1 + \frac{1}{k_r \tau^0 [S]}\right) \frac{1}{A \cdot B} \quad \textbf{(3)}$$

Where ϕ_p is the quantum efficiency of product formation, A the efficiency of forming the reactive excited state, B the fraction of reactions of the excited state with substrate **S** which leads to product, and **[S]** is the concentration of reactive ground-state substrate. The intercept/slope ratio gives $k_T \tau^0$. If **[S]** = **[Q]**, and if a photophysical process is monitored, plots of equations (2) and (3) should provide independent determinations of the product-forming rate constant k_T. When the lifetime of an excited state is observed as a function of the concentration of **S** or **Q**, a linear relationship should be observed according to the equation:

$$\frac{\tau^0}{\tau} = 1 + k_q \tau^0 [Q]$$

Where τ^0 is the lifetime of the excited state in the absence of the quencher **Q**.

In the manuscript, τ^0 is $\tau_F{}^0$.