

Electronic Supplementary Information

Synthesis of Carbon Quantum Dots/SiO₂ Porous Nanocomposites and Their Catalytic Ability for Photo-enhanced Hydrocarbon Selective Oxidation

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Experimental Details.

1. Catalysts Preparation

All chemicals were purchased from Sigma–Aldrich.

Preparation of SiO₂ nanospheres: SiO₂ nanospheres were prepared according to Stöber synthesis.¹ 2 mL 98% tetraethyl orthosilicate (TEOS) was dissolved in 50 ml 95% ethanol with magnetic stirring at room temperature. After 5 min equilibration, 3 mL 25% NH₃·H₂O was dripped into the solution. After 20 min, the solution turned white. Aging overnight, the resulting white precipitate was centrifuged at 5000 rpm for 5 min and washed three times with 95% ethanol, the opaque white SiO₂ nanospheres of average sizes 100 nm were obtained.

Preparation of CQDs/SiO₂ nanocomposites: The CQDs were synthesized by using the electrochemical method developed by our research group.² Then CQDs/SiO₂ nanocomposites were prepared through a facile hydrolytic process. Firstly, 10 mL CQDs solution and 20 mL 95% ethanol were added to 50 mL beaker under vigorous stirring at room temperature. Then 1 mL 25% NH₃·H₂O was added to the above mixture to achieve a uniform solution. The hydrolytic process was carried out by dropwise adding 0.5 mL 98% TEOS to the solution with continuous magnetic stirring. After aging overnight, the CQDs/SiO₂ nanocomposites with diameter about 100 nm were centrifugal separated from the solution and washed three times with 95% ethanol, then dried at 80 °C for 5h.

In order to prepared 250 nm CQDs/SiO₂ nanocomposites, 5 mL CQDs solution was used in above process.

Preparation of SiQDs/SiO₂ nanocomposites: Hydrogen-terminated SiQDs were prepared by using the electrochemical method developed by our group.³ SiQDs/SiO₂ nanocomposites were produced in the same manner by using SiQDs in place of CQDs.

2. Catalytic selective oxidation of *cis*-cyclooctene

The catalytic selective oxidation of *cis*-cyclooctene was carried out in a 50 mL round bottom flask with water condenser and continuous magnetic stirring. 0.1 g as-fabricated catalyst and 0.12 g *tert*-butyl hydroperoxide (TBHP) were put into 10 mL *cis*-cyclooctene (95%). At last, the mixture was stirred under illumination of a 150 W Xenon lamp for 24 h at 80°C. Different samples were collected every 4 hours. After filtering off the catalyst, the oxidation products were analyzed by gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS).

The control experiments were performed in dark with the same as other reaction conditions.

3. Characterization

Scanning electron microscopy (SEM) images were taken on a FEI-quanta 200 scanning electron microscope with acceleration voltage of 20 kV. The transmission electron microscopy (TEM) images were obtained with a FEI/Philips Tecnai 12 BioTWIN transmission electron microscope operated at 200 kV with EDX analyses. While

HRTEM images were obtained with a CM200 FEG TEM. The normal TEM samples were prepared by dropping the solution onto a copper grid covered with carbon film and dried in air. Raman spectrum was collected on an HR 800 Raman spectroscope (J Y, France) equipped with a synapse CCD detector and a confocal Olympus microscope. The spectrograph uses 600 g mm^{-1} gratings and a 633 nm He-Ne laser. The Fourier Transform Infrared (FTIR) spectrum was obtained with a Nicolet 360 spectrometer. DRS absorption spectra were obtained with a PerkinElmer Lambda 750 UV-Vis Spectrophotometer. Brunauer–Emmett–Teller (BET) specific surface areas and pore size distributions were calculated by plotting the adsorption isotherm of N_2 at liquid N_2 temperature (77 K). These measurements were made on a Micromeritics ASAP 2050 porosimeter. The GC measurements were performed in a Varian 3400 GC column with a cross-linked 5% PhMe silicone column ($25 \text{ m} \times 0.20 \text{ mm} \times 0.33 \text{ }\mu\text{m}$) and a FID detector under the following conditions: carrier gas (N_2) at 140 K; temperature program 60 °C, 1 min, 15 °C/min, 180 °C, 15 min; split ratio, 10 : 1; injector, 300 °C; detector, 300 °C.

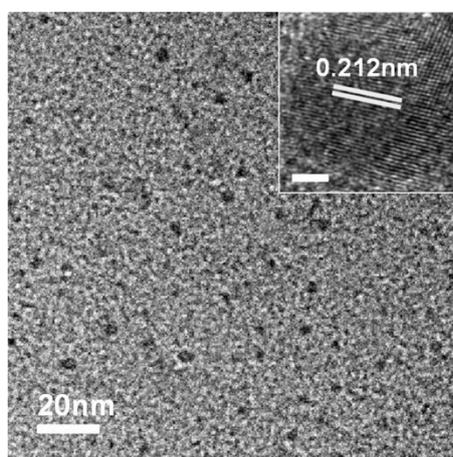


Fig. S1 TEM image of CQDs. Inset is the corresponding HRTEM image (Scale bar: 1 nm).

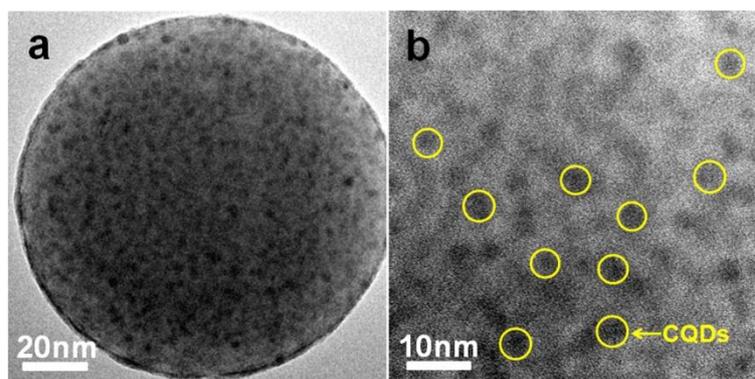


Fig. S2 TEM images of CQDs/ SiO_2 nanocomposites.

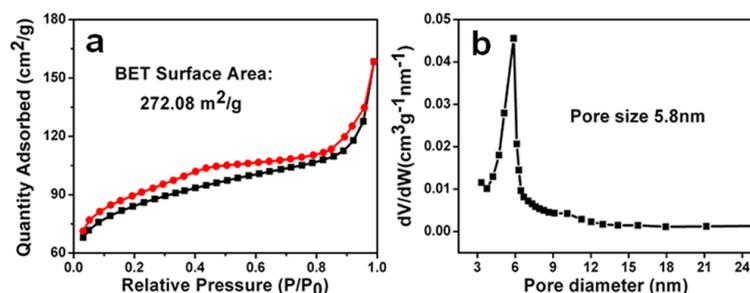


Fig. S3 (a) Nitrogen adsorption–desorption isotherm and (b) pore size distribution curve of 100 nm CQDs/SiO₂ nanocomposites.

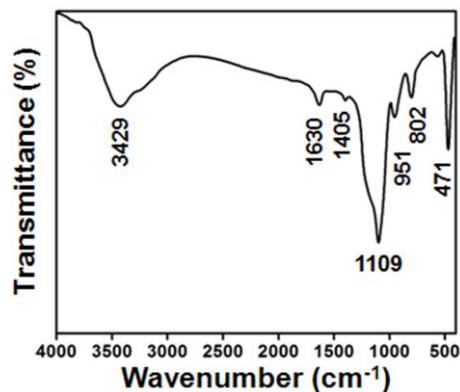


Fig. S4 FTIR spectrum of CQDs/SiO₂ nanocomposites.

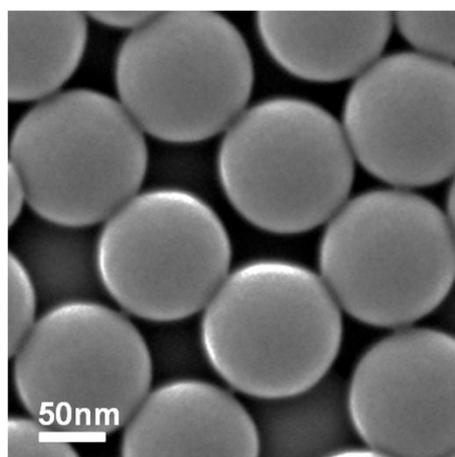


Fig. S5 SEM image of SiO₂ nanospheres.

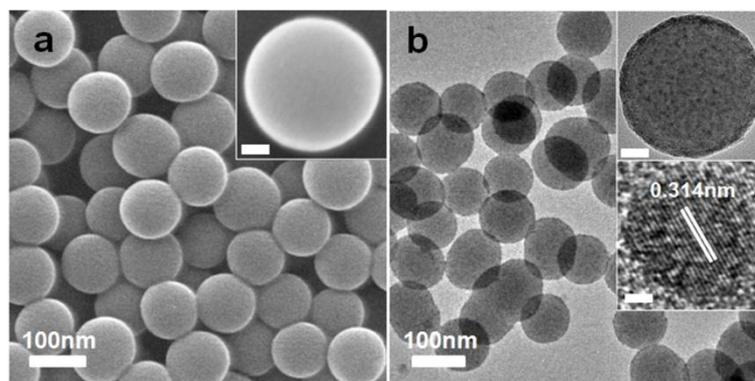


Fig. S6 (a) SEM and (b) TEM images of SiQDs/SiO₂ nanocomposites. Insert in (a) is SEM image of typical single particle of SiQDs/SiO₂ nanocomposites (scale bar: 20 nm). Inserts in (b) are TEM image of typical single particle (scale bar: 20 nm) and HRTEM image of SiQDs on SiQDs/SiO₂ nanocomposites (scale bar: 1 nm).

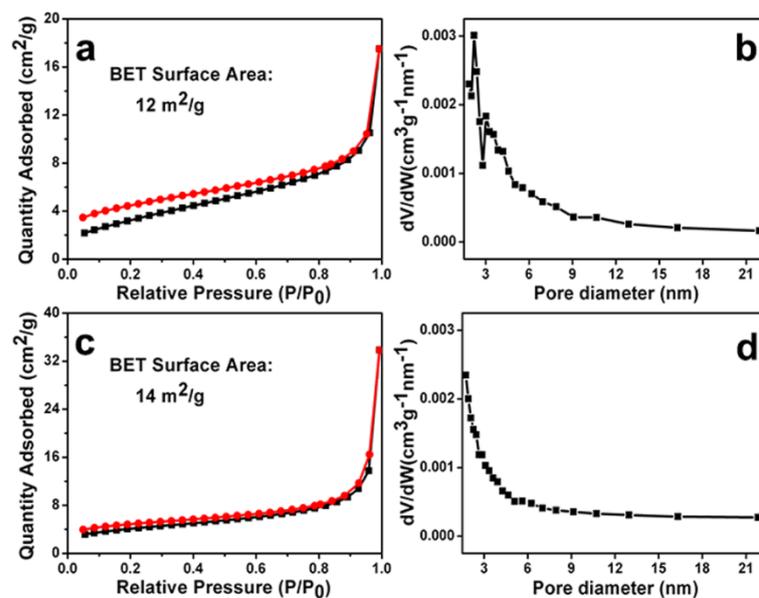


Fig. S7 Nitrogen adsorption–desorption isotherm of (a) SiO₂ nanospheres and (c) SiQDs/SiO₂ nanocomposites. Pore size distribution curve of (b) SiO₂ nanospheres and (d) SiQDs/SiO₂ nanocomposites.

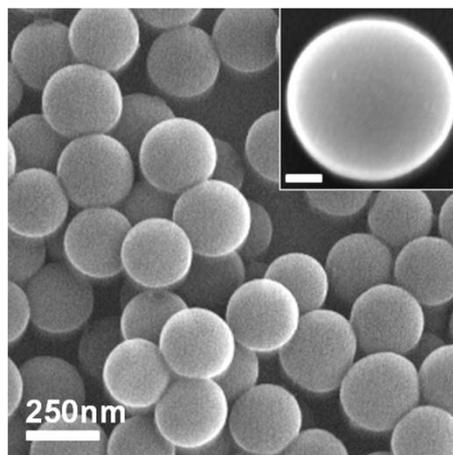


Fig. S8 SEM image of CQDs/SiO₂ nanocomposites. Inset is the corresponding SEM image of typical single particle (scale bar: 50 nm).

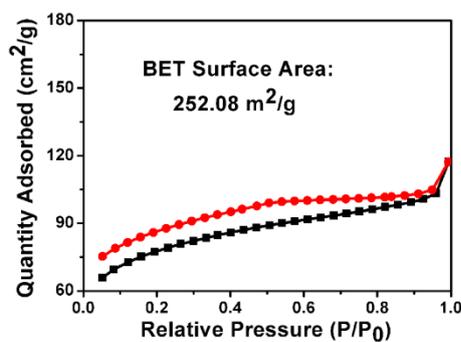


Fig. S9 Nitrogen adsorption–desorption isotherm of 250 nm CQDs/SiO₂ nanocomposites.

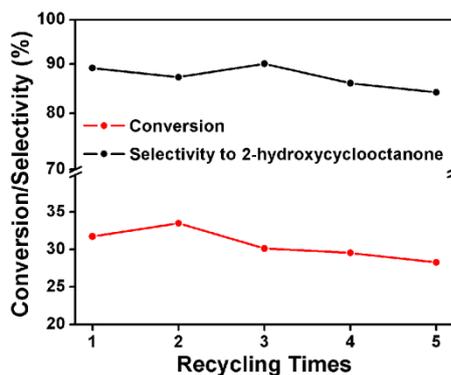
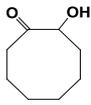
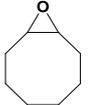
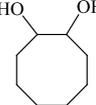


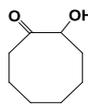
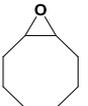
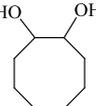
Fig. S10 The relationship between the conversion of *cis*-cyclooctene/selectivity of 2-hydroxycyclooctanone and recycling times with CQDs/SiO₂ nanocomposites as catalyst.

Table S1. Effect of reaction time on selective oxidation of *cis*-cyclooctene using 100 nm CQDs/SiO₂ nanocomposites as catalyst under visible light irradiation.^a

Reaction time (h)	Product Selectivity (%)			Conversion (%)	$\Sigma_{\text{sel}}\text{C}_8^{\S}$
					
0	0	0	0	0	0
4	57.44	15.89	26.67	7.54	100
8	65.03	12.92	21.97	11.02	99.92
12	70.94	10.43	18.40	15.21	99.77
16	76.45	9.15	13.94	19.59	99.54
20	83.24	7.37	8.64	25.06	99.25
24	89.13	5.95	4.05	31.73	99.13

^aReaction conditions: 100 nm CQDs/SiO₂ nanocomposites (0.1 g), *cis*-cyclooctene (10 mL), TBHP (0.12 g), 80 °C, under visible light irradiation. §Total selectivity to C₈ partial oxidation products.

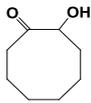
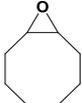
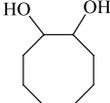
Table S2. Effect of different sizes of CQDs/SiO₂ nanocomposites as catalysts on selective oxidation of *cis*-cyclooctene.^a

Size	Product Selectivity (%)			Conversion (%)	$\Sigma_{\text{sel}}\text{C}_8^{\S}$
					
100 nm	89.13	5.95	4.05	31.73	99.13
250 nm	79.52	6.09	10.85	16.69	96.46

^aReaction conditions: CQDs/SiO₂ nanocomposites (0.1 g), *cis*-cyclooctene (10 mL), TBHP (0.12

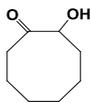
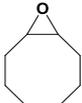
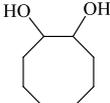
g), 80 °C, under visible light irradiation. §Total selectivity to C₈ partial oxidation products.

Table S3. Effect of different nanomaterials as catalysts on selective oxidation of *cis*-cyclooctene.^a

Nanomaterial	Product Selectivity (%)			Conversion (%)	Σ _{sel} C ₈ [§]
					
CQDs/SiO ₂	89.13	5.95	4.05	31.73	99.13
SiO ₂	77.06	7.14	7.86	9.98	92.06
SiQDs/SiO ₂	80.64	7.36	5.07	14.26	93.07

^aReaction conditions: as-synthesized catalysts (0.1 g), *cis*-cyclooctene (10 mL), TBHP (0.12 g), 80 °C, under visible light irradiation. §Total selectivity to C₈ partial oxidation products.

Table S4. Effect of different reaction conditions on selective oxidation of *cis*-cyclooctene.^a

Reaction condition	Product Selectivity (%)			Conversion (%)	Σ _{sel} C ₈ [§]
					
light	89.13	5.95	4.05	31.73	99.13
dark	82.04	7.90	8.84	11.93	98.78

^aReaction conditions: 100 nm CQDs/SiO₂ nanocomposites (0.1 g), *cis*-cyclooctene (10 mL), TBHP (0.12 g), 80 °C. §Total selectivity to C₈ partial oxidation products.

References

1. W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62–69.
2. H. Ming, Z. Ma, Y. Liu, K. M. Pan, H. Yu, F. Wang and Z. H. Kang, *Dalton Trans.*, 2012, **41**, 9526–9531.
3. Z. H. Kang, C. H. A. Tsang, Z. D. Zhang, M. L. Zhang, N. B. Wong, J. A. Zapien, Y. Y. Shan and S. T. Lee, *J. Am. Chem. Soc.*, 2007, **129**, 5326–5327.