

## Electronic Supplementary Information (ESI)

*for*

# Cu(I)-doped Carbon Quantum Dots with Zigzag Edge Structure for Highly Efficient Catalysis of Azide-Alkyne Cycloadditions

Ze Xi Liu <sup>a</sup>, Bin Bin Chen <sup>b</sup>, Meng Li Liu <sup>b</sup>, Hong Yan Zou <sup>a, \*</sup>, Cheng Zhi Huang <sup>a, b, \*</sup>

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<sup>a.</sup> Key Laboratory of Luminescent and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Pharmaceutical Science, Southwest University, Chongqing 400715, China.

<sup>b.</sup> Chongqing Key Laboratory of Biomedical Analysis (Southwest University), Chongqing Science & Technology Commission, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China. E-mail: chengzhi@swu.edu.cn,

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### 3. Notes and references

## 1. Experimental Section

### 1.1 Synthesis of carbon quantum dots

First, 0.1 g ascorbic acid (AA) and 1.6 g Na<sub>2</sub>[Cu(EDTA)] was added into 50 mL round-bottom flask and heated at 250 °C for 120 min in oil bath. The color of the solid powder turned from blue to dark brown. After cooling the powder to room temperature, 100 ml ultrapure water was added to the flask and following ultrasonic for 30 min with the power of 300 W. Then the brown solution was centrifuged for 15 min at 10000 rpm and filtered using a 0.25 µm filter membrane to remove precipitate. Small molecules in the supernatant were detached through a dialysis membrane (3000 MWCO). Solid CDs were then concentrated by freezing at -80 °C and dried under vacuum for quantitative use.

### 1.2 Characterizations

Fluorescence spectroscopy was performed with an F-2500 fluorescence spectrophotometer (Hitachi, Tokyo, Japan), and UV-vis absorption spectroscopy was performed with a UV-3600 spectrophotometer (Hitachi, Tokyo, Japan). Functional group analyses were carried out using a Fourier transform infrared spectrometer (FTIR-8400S, Toyota, Japan). The fluorescence life time was measured with FLTCSPC fluorescence spectrophotometer (Horiba Jobin Yvon Inc., France). The scanning electron microscope image was performed with a S4800 scanning transmission electron microscope (Hitachi, Tokyo, Japan).

### 1.3 Calculation of fluorescence lifetime

Average fluorescence lifetime of CDs was calculated according to Equation (S2)

$$\bar{\tau} = \frac{A_1\tau_1 + A_2\tau_2 + A_3\tau_3}{A_1 + A_2 + A_3} \quad (\text{S1})$$

Wherein  $A_i$  is the fractional contributions of time-resolved decay lifetime of  $\tau_i$ .

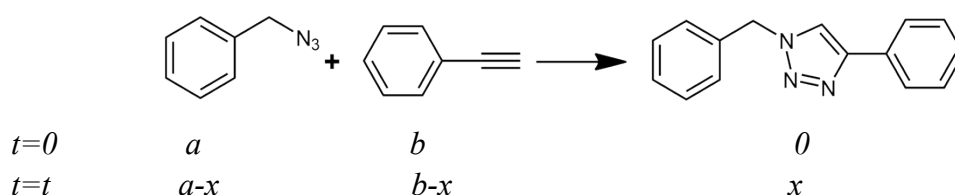
### 1.4 Performing of Huisgen 1,3-dipolar cycloaddition reaction between terminal

### azides and alkynes

In a glass vial equipped with a magnetic stir bar, 0.1 g Cu(I)-CQDs were added to 0.5 mmol of benzyl azide and 0.6 mmol of phenyl acetylene in the mixed solvent (total volume was 2 ml) of ultrapure water and ethanol with the ratio of 1:1, and the reaction mixture was stirred at 25 °C. Reaction progress was monitored by thin-layer chromatography until the azide had been completely consumed. The crude reaction mixture was worked up with dichloromethane (DCM), then centrifuged and filtered through column chromatography (silica gel column, mixture of aether petrolei/ethyl acetate=5:1 as mobile phase) to remove the catalyst and residual raw materials.

### 1.5 Kinetic study

Aliquots were taken at fixed intervals from the reaction, filtered to remove the catalyst and <sup>1</sup>HNMR employed to calculate the conversion. The equation (S2) was used for calculation of rate constant *k* as below<sup>1, 2</sup>:



a=initial concentration of benzyl azide;

b=initial concentration of phenyl acetylene;

x=concentration of the product at time t.

Thus the rate *v* of the product could be expressed as:

$$\begin{cases} v = k(a-x)(b-x) \\ v = \frac{dx}{dt} \end{cases}$$

Then

$$k(a-x)(b-x) = \frac{dx}{dt}$$

$$\int k dt = \int \frac{dx}{(a-x)(b-x)}$$

$$kt = \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)}$$

$$k = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)} \quad (\text{S2})$$

### 1.6 Cell toxicity

#### Cytotoxicity test of Cu(I)-CQDs:

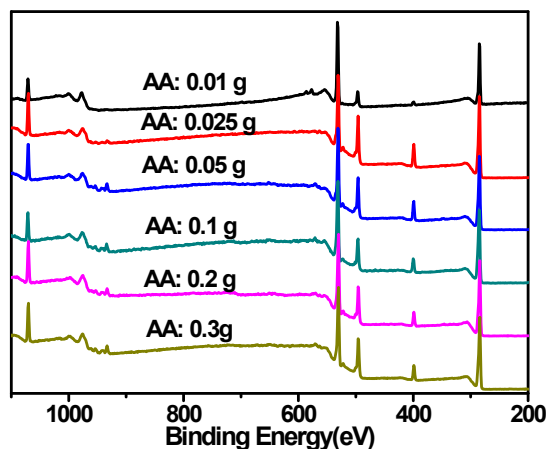
Firstly, 100  $\mu\text{l}$  human epidermoid cancer cells (Hep-2,  $1 \times 10^5$  cells/ml) in Roswell Park Memorial Institute 1640 (RPMI 1640) containing 2% fetal bovine serum (FBS) were added to each well of a 96-well plate. Then, the Hep-2 cells were maintained at 37°C in an incubator with 5%  $\text{CO}_2$  for 24 h, and continued to incubate under the same conditions after the incubation medium was replaced with 100  $\mu\text{l}$  RPMI 1640 containing 10  $\mu\text{l}$  of Cu(I)-CQDs at different concentrations. Following that, the mixture of 90  $\mu\text{l}$  RPMI 1640 and 10  $\mu\text{l}$  Cell Counting Kit-8 (CCK-8) solution was added to each well of a 96-well plate after the incubation medium was removed. The Hep-2 cells were further incubated about 20 min. Finally, the optical density (OD) was determined at 450 nm using a Microplate Reader Model. The cell viability was calculated through the following equation:

$$\text{Cell viability (\%)} = \frac{OD_{\text{treated}}}{OD_{\text{control}}} \times 100\%$$

Wherein,  $OD_{\text{control}}$  was measured in the absence of Cu(I)-CQDs, while OD treated was measured in the presence of Cu(I)-CQDs.

## 2. Results

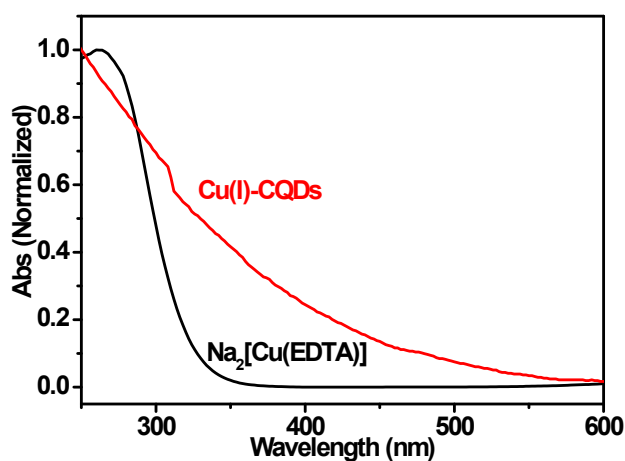
### 2.1 Figures



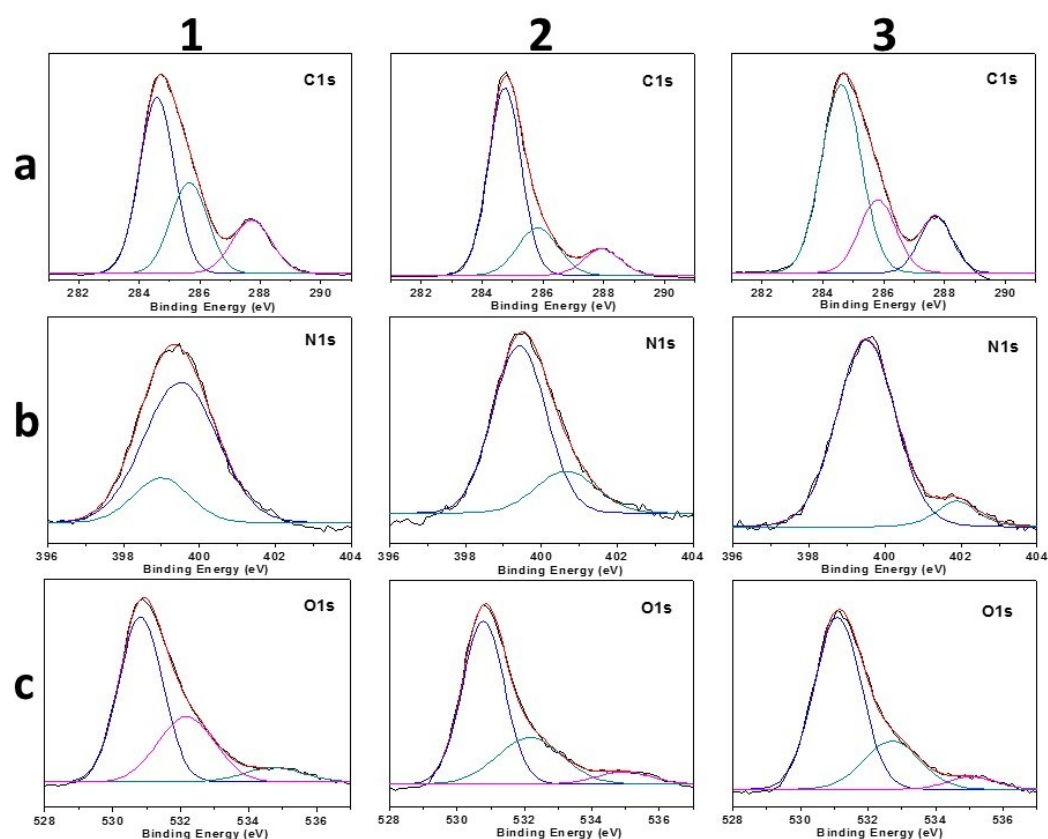
**Fig.S1** XPS spectra of Cu(I)-CQDs with the usage of AA of 0.01 g, 0.025 g, 0.05 g, 0.1 g, 0.2 g and 0.3 g.

**Table S1** Cu percentage of Cu(I)-CQDs with the usage of AA of 0.01 g, 0.025 g, 0.05 g, 0.1 g, 0.2 g and 0.3 g.

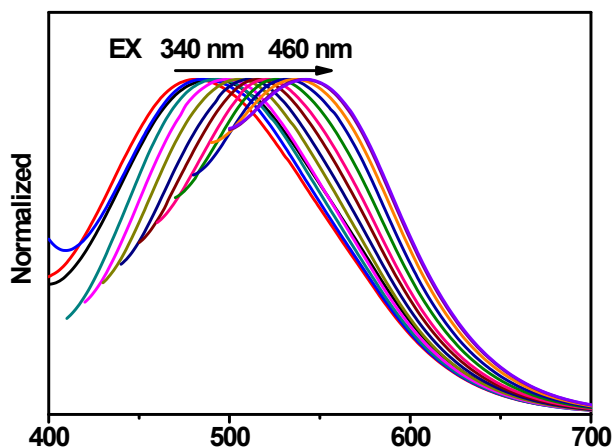
$m_{\text{Na}_2[\text{Cu}(\text{EDTA})]}/\text{g}$	$m_{\text{AA}}/\text{g}$	Cu percentage/%
1.6	0.01	0.26
1.6	0.025	0.54
1.6	0.05	1.2
1.6	0.1	1.41
1.6	0.2	1.44
1.6	0.3	1.44



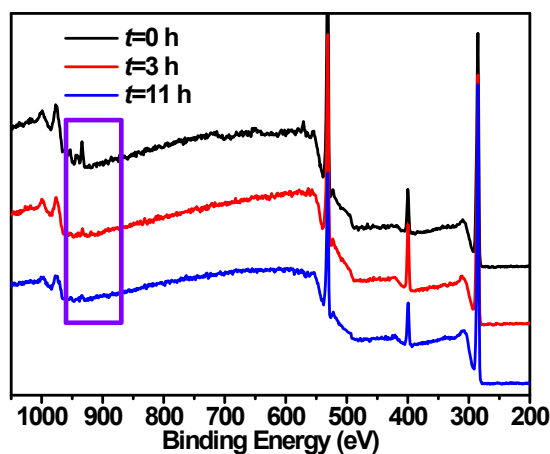
**Fig.S2** UV-vis absorption spectra of Cu(I)-CQDs and Na<sub>2</sub>[Cu(EDTA)]. The absorption intensity of Cu(I)-CQDs is much higher than Na<sub>2</sub>[Cu(EDTA)] from 300 nm to 600 nm.



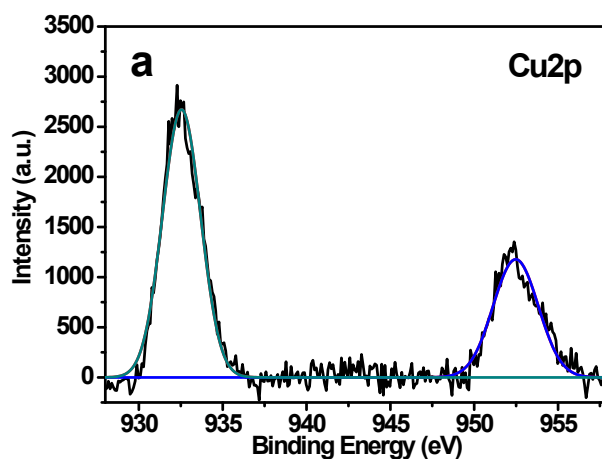
**Fig.S3** High-resolution XPS spectra of Cu(I)-CQDs before and after 3 and 11 hours' reaction. Each band were deconvoluted following the literature.<sup>3-7</sup> Row 1: before reaction. Row 2: after reaction for 3 hours. Row 3: after reaction for 11 hours. Line a: C 1s spectra and fitting peaks. Line b: N 1s spectra and fitting peaks. Line c: O 1s spectra and fitting peaks. C 1s spectra could be deconvoluted into three peaks at 284.6 eV, 285.6 eV and 287.8 eV, corresponding to C-C, C-N and C=O bonds. With the reaction continued, C-N bonds were oxidized to C=O bonds. N containing groups were oxidized from pyridinic N to -NH, and then to -NO<sub>2</sub>, gradually, while the main peak located at around 399.4 eV representing to the stable graphite N remained unchanged. At first, the abundant existence of Cu brought about a shift to higher binding energy to pyridinic N of about 0.5 eV, wherein the pyridinic N should locate at 398.5 eV as the relevant literature has reported<sup>8</sup>. Then with the reaction carried to the third hour under the irradiation of 365 nm UV light, with the release of Cu, the binding energy of -NH had shifted higher slightly<sup>3</sup>. After reacted for 11 hours, little Cu left in the CQDs, the binding energy of -NO<sub>2</sub> had little shift. What is more, the relative intensity rate of 532.2 eV/534.8 eV of the peaks in the high-resolution XPS O 1s spectra decreased, indicating the C-OH groups were oxidized to C=O bonds. All the high-resolution XPS spectra showed that CQDs was photo-oxidized during the reaction process due to 365 nm irradiation.



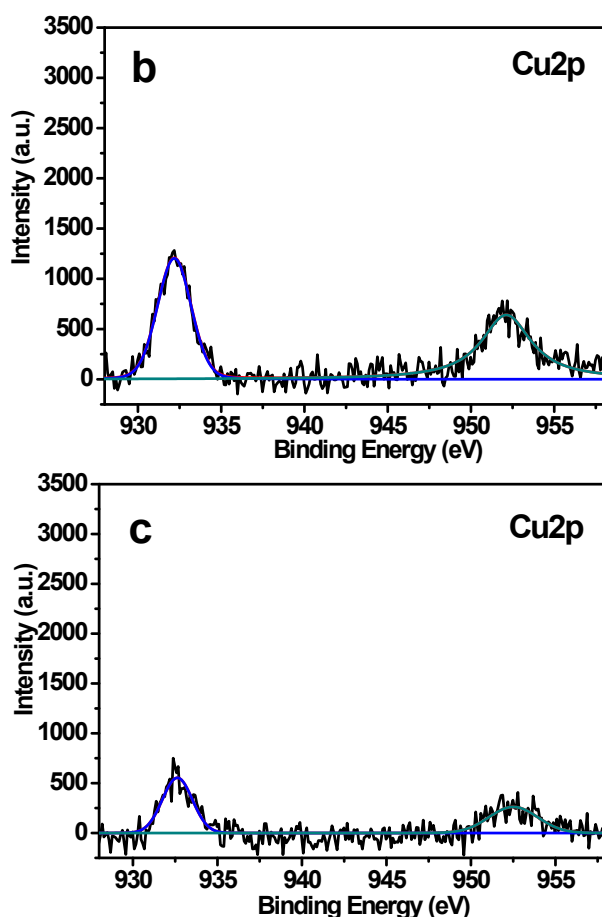
**Fig.S4** Emission spectra of CQDs recorded for progressively longer excitation wavelengths with 10 nm increments from 340 nm to 460 nm.



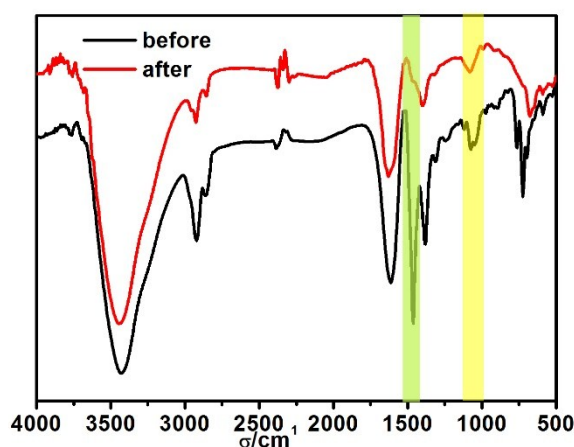
**Fig.S5** XPS spectra of Cu(I)-CQDs before and after 3 and 11 hours' reaction. The most significant change was that the content of Cu(I) decreased from 1.41% to 0.59%, and then to 0.41%, because of the UV light-induced controlling release of Cu(I) under the 365 nm irradiation. The content of Cu(I) decreased faster at the first 3 hours, which was 0.27% per hour, and slower during the later 8 hours, which was 0.023% per hour.





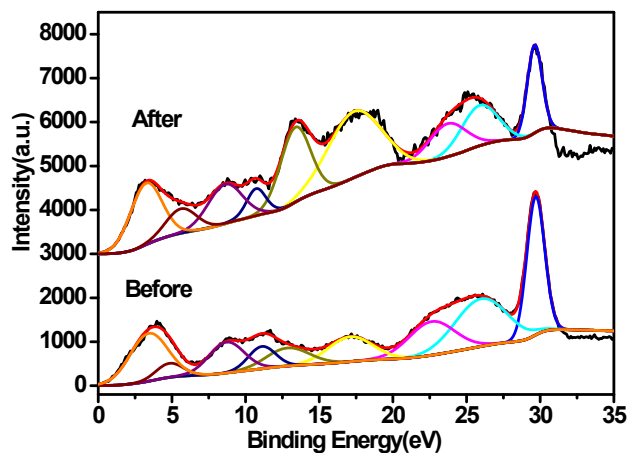


**Fig.S6** High-resolution XPS Cu 2p spectrum of Cu(I)-CQDs before and after 3 and 11 hours' reaction. a: before reaction. b: after reaction for 3 hours. c: after reaction for 11 hours. The content of Cu(I) decreased from 1.41% to 0.59%, and then to 0.41%, corresponding to the CQDs before reaction and after 3 and 11 hours reaction.

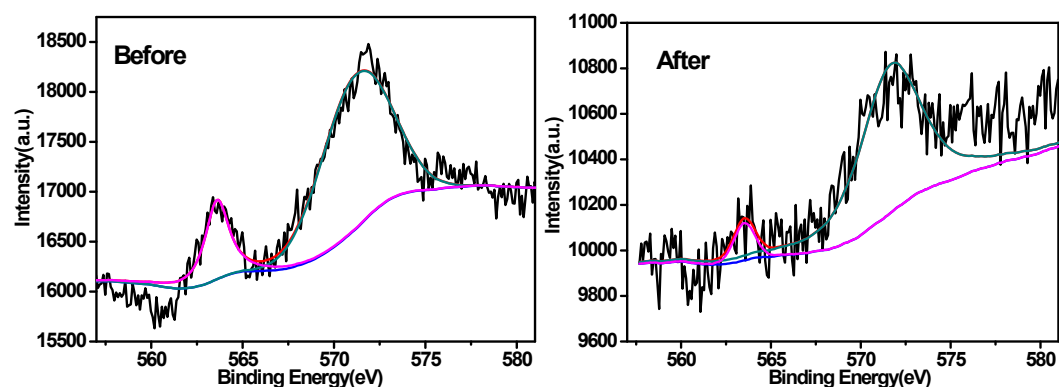


**Fig.S7** FTIR spectra of CQDs before and after catalyzing the Huisgen 1,3-dipolar cycloaddition reaction between azides and terminal alkynes under 365 nm UV light irradiation. The green and yellow bands located at around 1500  $\text{cm}^{-1}$  and 1050  $\text{cm}^{-1}$ , corresponding to C-N bond and N-Cu-N band.<sup>9</sup> After the catalyzing reaction, Cu(I) was released due to UV irradiation. The absorption peak at around 1500  $\text{cm}^{-1}$  decreased a lot indicating the decreasing of stretching vibration of C-N,<sup>10-12</sup> because

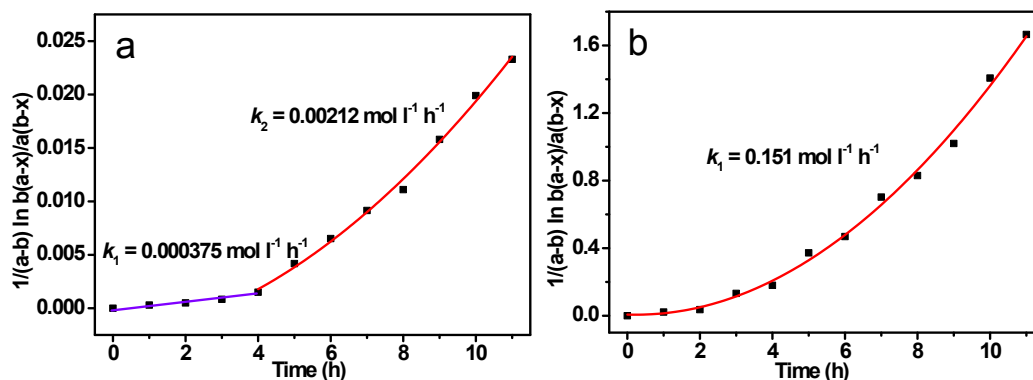
that Cu(I) was released from C-N-Cu. Similarly, disappearing of the shoulder peak at 1050  $\text{cm}^{-1}$  also showed the release of Cu(I).



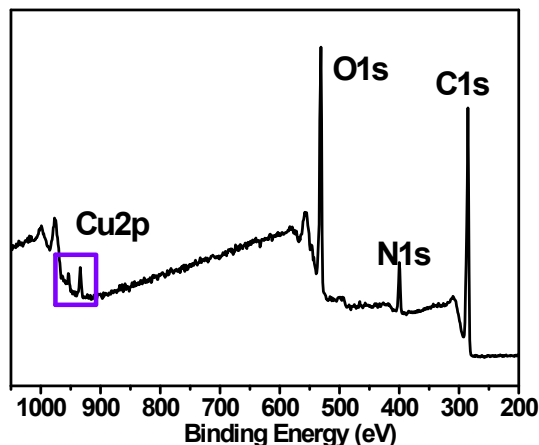
**Fig.S8** Valence spectra of the Cu(I)-CQDs before and after catalysis of azide-alkyne cycloadditions. There is little difference between the two spectrum indicating that the structure of CQDs remained unchanged during the catalysis reaction. There are some peak shifts between these two spectrum which were highly possible owing to the release of Cu(I).



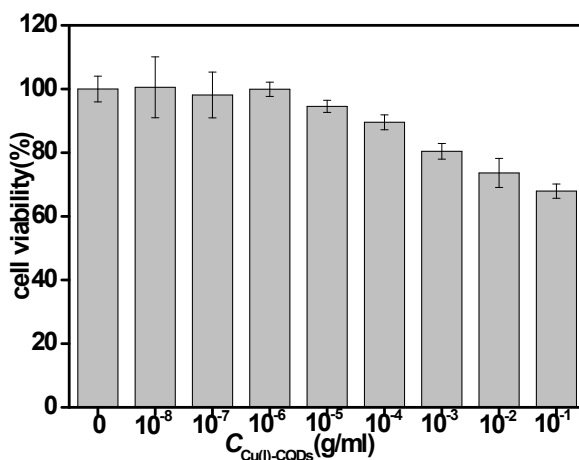
**Fig.S9** Auger electron spectroscopy (AES) spectra of Cu(I)-CQDs before and after catalysis of azide-alkyne cycloadditions. Auger electron of Cu decreased while the valence state of Cu remained unchanged which indicated the decrease of Cu(I) again.



**Fig.S10** Dynamic monitoring of the Huisgen 1,3-dipolar cycloaddition reaction between azides and terminal alkynes in the dark and under the natural light. Reaction kinetics curve of Cu(I)-CQDs catalysed CuAAC reaction. Reaction kinetics were analyzed using Eq. S2 (see *Supplementary 1.5 Kinetic study*).



**Fig.S11** XPS spectra of Cu(I)-CQDs after catalyzing the Huisgen 1,3-dipolar cycloaddition reaction between azides and terminal alkynes in the dark for 11 hours. The content of Cu was 1.21%, which had a slight decrease comparing with the CQDs before reaction.



**Fig.S12** Cell viability of Cu(I)-CQDs using Hep-2 cells as the model. (See 1.6 Cell toxicity)

### 3. Notes and references

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