

Supporting Information for

**γ -Cyclodextrin-based Metal-Organic Framework Embedded
with Graphene Quantum Dots and Modified with PEGMA via
SI-ATRP for Anticancer Drug Delivery and Therapy**

Qiaojuan Jia^a, Zhenzhen Li^a, Chuanpan Guo^a, Xiaoyu Huang^b, Yingpan Song^a, Nan
Zhou^b, Minghua Wang^a, Zhihong Zhang^{*a}, Linghao He^{*a}, and Miao Du^{*a}

^aHenan Provincial Key Laboratory of Surface and Interface Science, School of Materials
and Chemical Engineering, Zhengzhou University of Light Industry, No. 136, Science
Avenue, Zhengzhou 450001, P. R. China;

^bDepartment of Orthopedics, The First Affiliated Hospital of Zhengzhou University, No. 1,
Jianshe East Road, Zhengzhou 450052, P. R. China.

Corresponding authors:

*E-mail address: mainzh@163.com, helinghao@zzuli.edu.cn or dumiao@zzuli.edu.cn

Content

S1. Experimental Section

S1.1 Synthesis of GQDs

S1.2 Purification of CuBr

S1.3 Preparation of γ -CD-MOF-Br and GQDs@ γ -CD-MOF-Br

S2. Basic Characterizations of GQDs

S3. Chemical Structures and Components of the Samples

S3.1 Fluorescence spectra of GQDs@ γ -CD-MOF and PEGMA@GQDs@ γ -CD-MOF Composites

S3.2 XPS Survey Scan Spectra and Atomic% of Each Element in the Samples

S3.3 High-Resolution XPS Analysis

S3.4 SEM and TEM Images of γ -CD-MOF

S3.5 Stability analysis of AS1411@PEGMA@GQDs@ γ -CD-MOF composite in water

S4. UV-Vis Absorbance Standard Curve of DOX at 480 nm

S1. Experimental Section

S1.1 Synthesis of GQDs

Synthesis of GQDs was referred to the literature.[1] In brief, 1 g graphene was added into a mixture of 225 mL sulfuric acid and 75 mL nitric acid, and the mixed solution was treated by ultrasonication for 2 h. Then, the solution was heated to 90 °C in an oil bath and refluxed for 24 h and naturally cooled down to room temperature. Afterward, it was diluted with water to 800 mL and adjusted the pH to 7 by sodium bicarbonate. The final solution was filtered and dialyzed using a membrane (3500 MWCO) for 3 days to remove all nitrates and sulfates, which was stored in a refrigerator at 4 °C.

S1.2 Purification of CuBr

The purification of CuBr was referred to the literature.[2] In brief, CuBr was added into acetic acid solution in a three-necked flask and stirred at room temperature for 6 h under a high-purity N₂ atmosphere. The system was allowed to sedimentation and then, the upper layer was removed. The precipitate was dried under vacuum at 60 °C to produce the CuBr powder for further use.

S1.3 Preparation of γ -CD-MOF-Br and GQDs@ γ -CD-MOF-Br

In a typical procedure, 50 mg γ -CD-MOF or GQDs@ γ -CD-MOF was dispersed in 4.0 mL DMF by sonification. The flask was placed in ice water and then 3.8 mL triethylamine (TEA) and 2-bromoisobutyryl bromide were sequentially added with stirring. The reaction was taken at room temperature with stirring overnight. The final product (γ -CD-MOF-Br or GQDs@ γ -CD-MOF-Br) was washed with CH₂Cl₂ until the supernatant was clear and then dried at 50 °C.

S2. Basic Characterizations of GQDs

As displayed in **Figure S1a**, the PL-emission of GQDs at $\lambda = 528$ nm was observed, where its PL-excitation was at $\lambda = 474$ nm. The chemical structure of GQDs was characterized by XPS. In terms of the high-resolution C 1s spectrum of GQDs (**Figure S1b**), five clear peaks at the binding energies (BEs) of 284.6, 285.4, 285.7, 287.4, and 287.4 eV were obtained, corresponding to C-C, C-N, C-O, C=O, and N-C=O, respectively. Additionally, a weak peak at the BE of 290.7 eV was observed, due to $\pi-\pi^*$ binding in GQDs. Only two peaks at the BEs of 400.1 and 402.1 eV were deconvoluted in the high-resolution N 1s XPS spectrum (**Figure S1c**), which were ascribed to C-N and N-C=O, respectively. These results reveal that the used GQDs are rich in chemical functionality and exhibits slightly conjugated structure, which is helpful to immobilize aptamer strand.

The morphology and structure of GQDs were analyzed by transmission electron microscopy (TEM), revealing the spherical nanoparticle with a uniform distribution (**Figure S1d**). The HRTEM images of GQDs (**Figure S1e** and inset) illustrate that GQDs particles show obvious lattice fringes and an interplanar spacing of 0.213 nm, which is close to the (100) distance in graphitic carbon.[3]

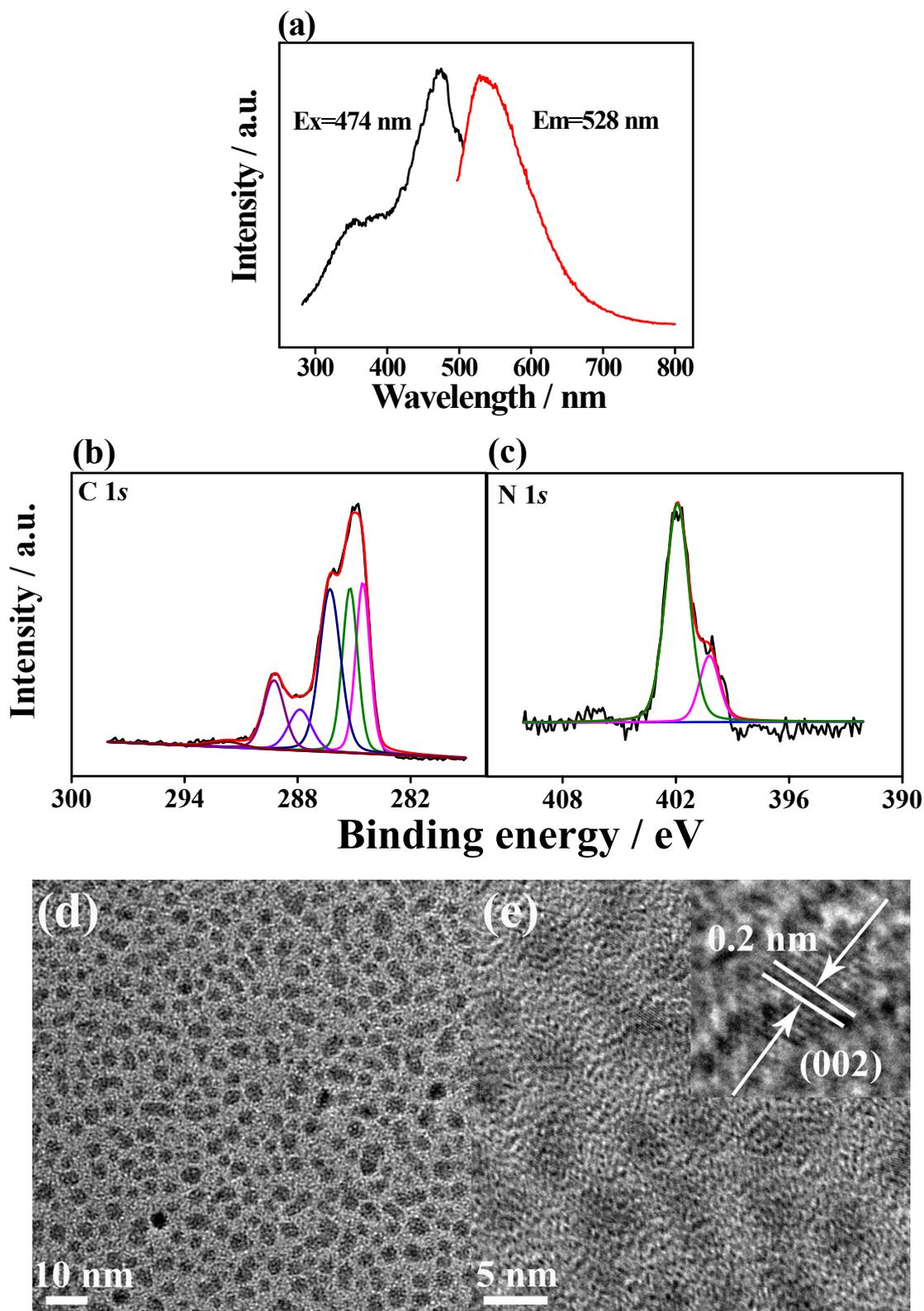


Figure S1. (a) Fluorescence spectra, the high-resolution (b) C 1s and (c) N 1s XPS spectra, and (d, e) TEM and HR-TEM images of GQDs.

S3. Chemical Structures and Components of the Samples

S3.1 Fluorescence spectra of GQDs@ γ -CD-MOF and PEGMA@GQDs@ γ -CD-MOF

Composites

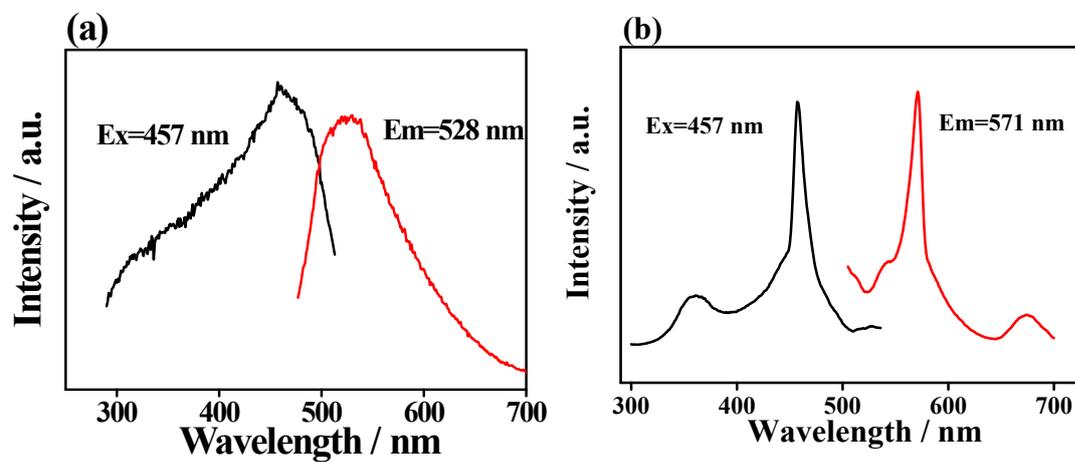


Figure S2. Fluorescence spectra of (a) GQDs@ γ -CD-MOF and (b) PEGMA@GQDs@ γ -CD-MOF composites.

S3.2 XPS Survey Scan Spectra and Atomic% of Each Element in the Samples

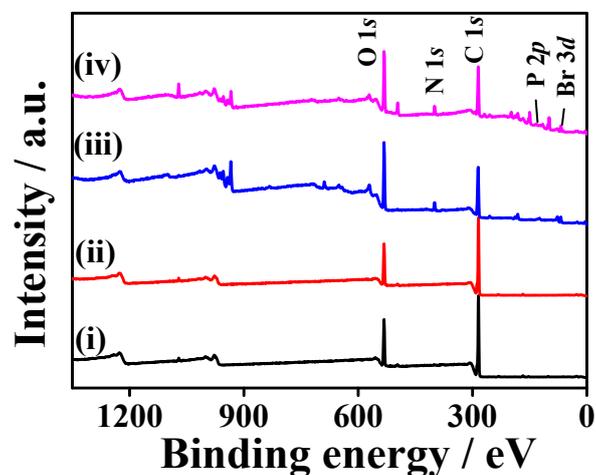


Figure S3. XPS survey scan spectra of (i) γ -CD-MOF, (ii) GQDs@ γ -CD-MOF, (iii) PEGMA@GQDs@ γ -CD-MOF, and (iv) AS1411@PEGMA@GQDs@ γ -CD-MOF.

Table S1. The Atomic% of Each Element in the Samples.

Sample	Atomic%				
	C 1s	N 1s	O 1s	Br 3d	P 2p
γ -CD-MOF	58.21	2.3	39.49	---	---
GQDs@ γ -CD-MOF	58.79	1.62	39.59	---	---
PEGMA@GQDs@ γ -CD-MOF	39.52	7.1	49.94	3.44	---
AS1411@PEGMA@GQDs@ γ -CD-MOF	37.02	6.93	48.86	4.19	3

S3.3 High-Resolution XPS Analysis

The high-resolution C 1s and O 1s XPS spectra of γ -CD-MOF were analyzed. Three peaks were deconvoluted for the high-resolution C 1s XPS spectrum at the BEs of 284.6, 260, and 288 eV (**Figure S4a**), corresponding to C-C, C-O, and -COO groups originated from the organic ligand in γ -CD-MOF. In case of the high-resolution O 1s XPS spectrum (**Figure S4a**), two peaks at the BEs of 531.6 and 533 eV were observed for C-O and C-O-C=O groups. As shown in **Figure S4b**, the same deconvoluted peaks for C 1s and O 1s high-resolution spectra were observed for GQDs@ γ -CD-MOF, further confirming their similar chemical structures.

Only after the binding of the initiator 2-bromoisobutyl bromide with γ -CD-MOF, the monomer can be polymerized over the γ -CD-MOF surface.[2] Therefore, it is necessary to make it clear if the initiator is bound with the GQDs@ γ -CD-MOF or not, which will cause the change of chemical component of GQDs@ γ -CD-MOF. As depicted in **Figure S4c**, the high-resolution C 1s and O 1s XPS spectra of γ -CD-MOF-Br were analyzed. As compared with the high-resolution C 1s XPS spectrum of parent γ -CD-MOF, two additional peaks at the BEs of 286.4 and 287.6 eV were observed for γ -CD-MOF-Br, owing to the C-Br and C=O groups originated from the initiator. However, the COOH group was disappeared for γ -CD-MOF-Br. As for the high-resolution O 1s XPS spectrum, the appearance of C=O at 532.2 eV, together with the strong Br 3d signal observed for γ -CD-MOF-Br (**Figure S5**), further confirm the successful binding of 2-bromoisobutyl bromide.

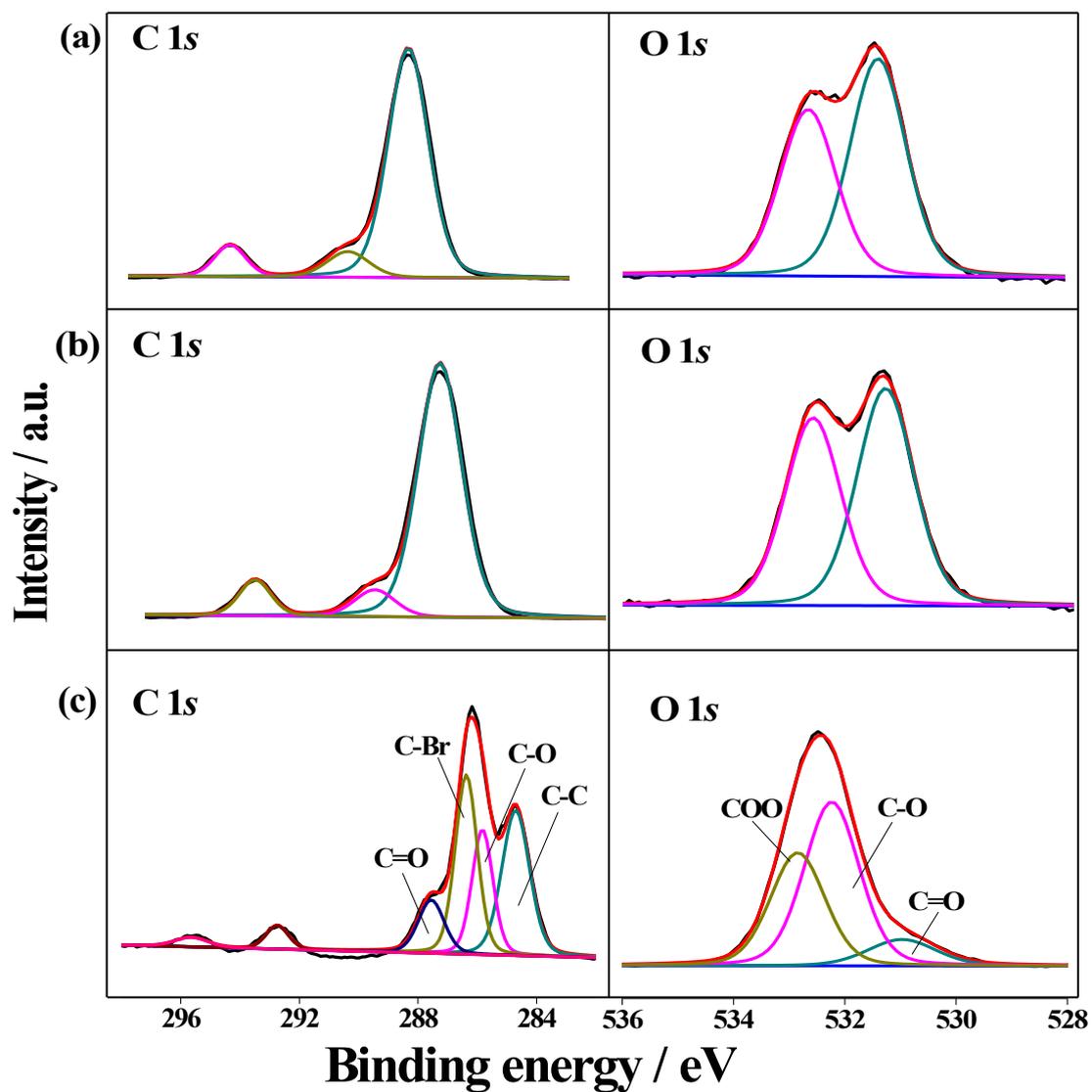


Figure S4. High-resolution C 1s and O 1s XPS spectra of (a) γ -CD-MOF, (b) GQDs@ γ -CD-MOF, and (c) GQD@ γ -CD-MOF-Br.

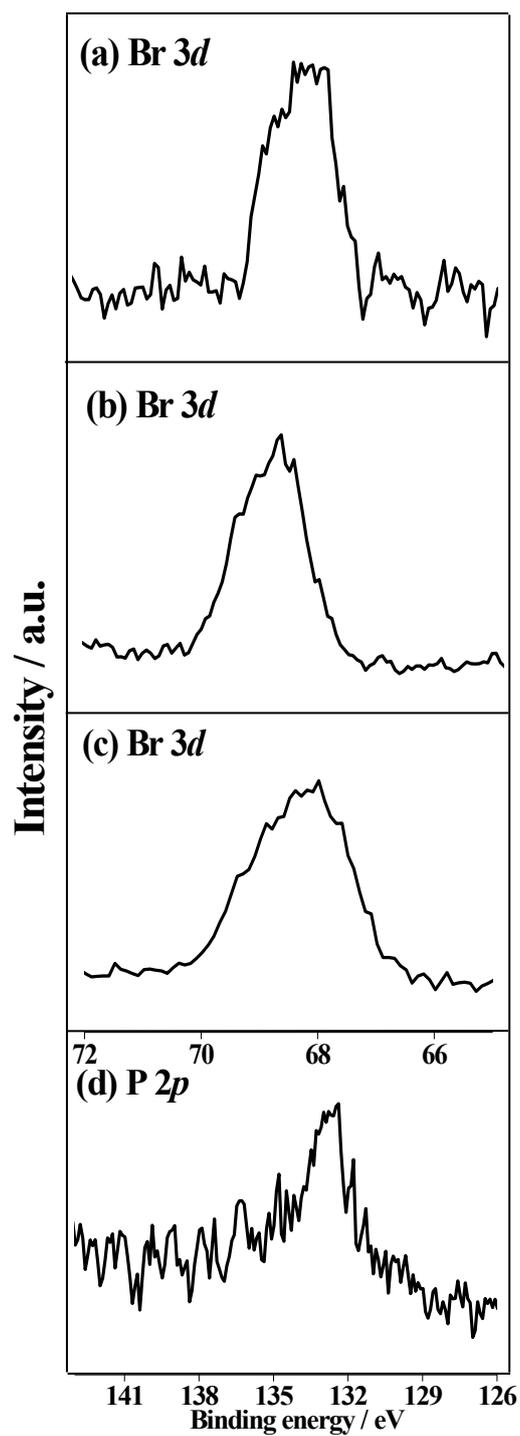


Figure S5. High-resolution of Br 3d XPS spectra of (a) GQDs@ γ -CD-MOF-Br (b) PEGMA@GQDs@ γ -CD-MOF and (c) AS1411@PEGMA@GQDs@ γ -CD-MOF. (d) High-resolution P 2p XPS spectrum of AS1411@PEGMA@GQDs@ γ -CD-MOF.

S3.4 SEM and TEM Images of γ -CD-MOF

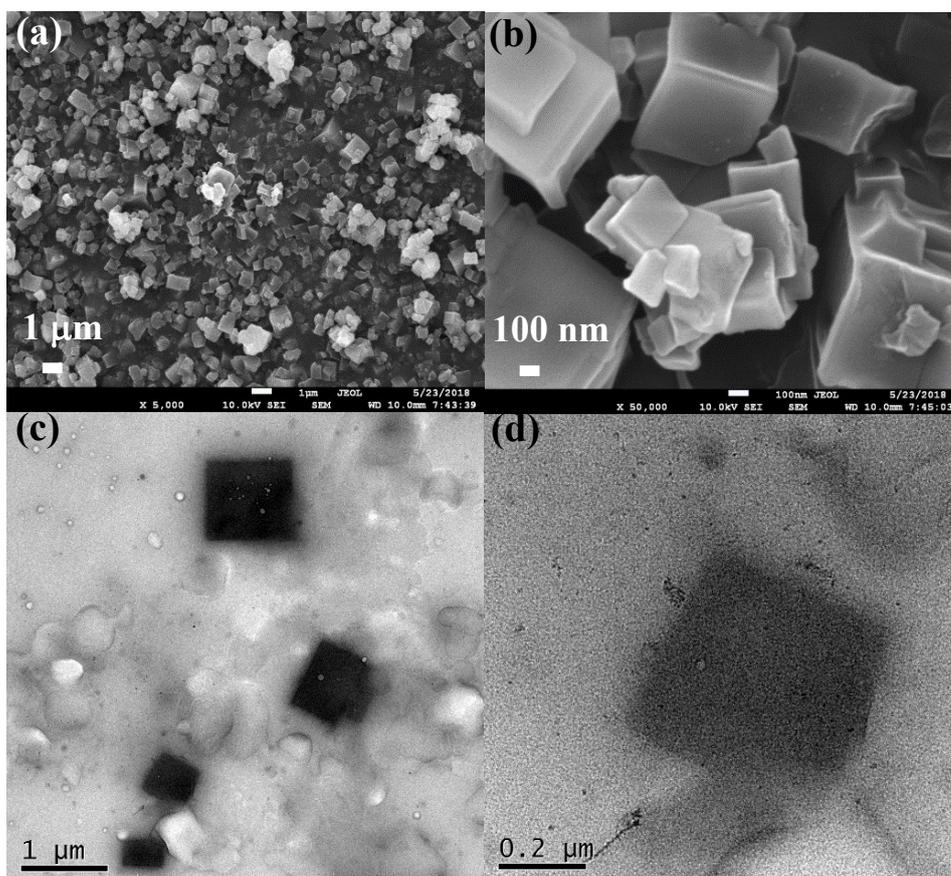


Figure S6. (a, b) Low- and high-magnitude SEM and (c, d) TEM and HR-TEM images of γ -CD-MOF.

The SEM images reveal that γ -CD-MOF is composed of nanocubes (**Figures S6a** and **S6b**), of which some nanocubes will be aggregated into even large particles. Similar result was also observed in the TEM and HR-TEM images.

S3.5 Stability analysis of PEGMA@GQDs@ γ -CD-MOF composite in water

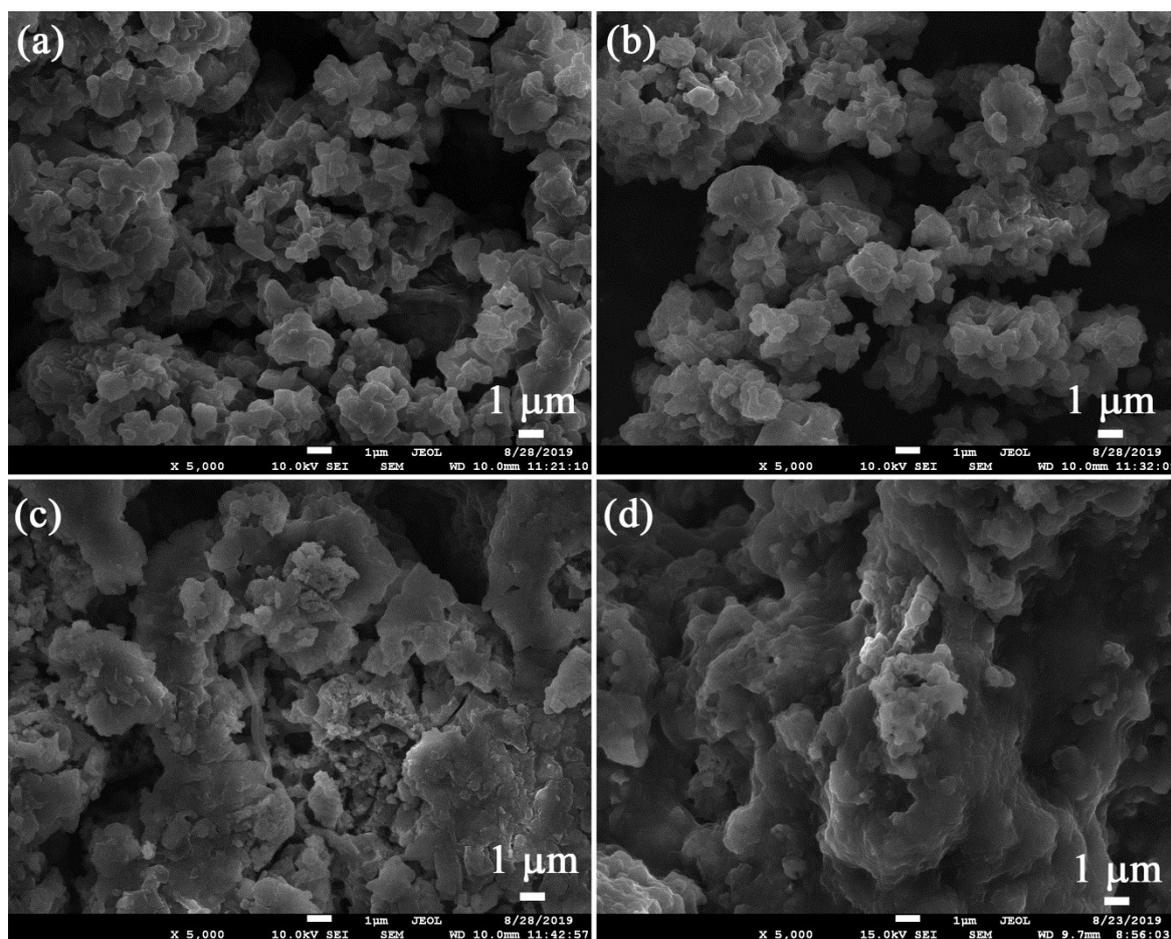


Figure S7. SEM images of PEGMA@GQDs@ γ -CD-MOF composite merged in water for (a) 0 h, (b) 1h, (c) 12 h, and (d) 24 h.

S4. UV-Vis Absorbance Standard Curve of DOX at 480 nm

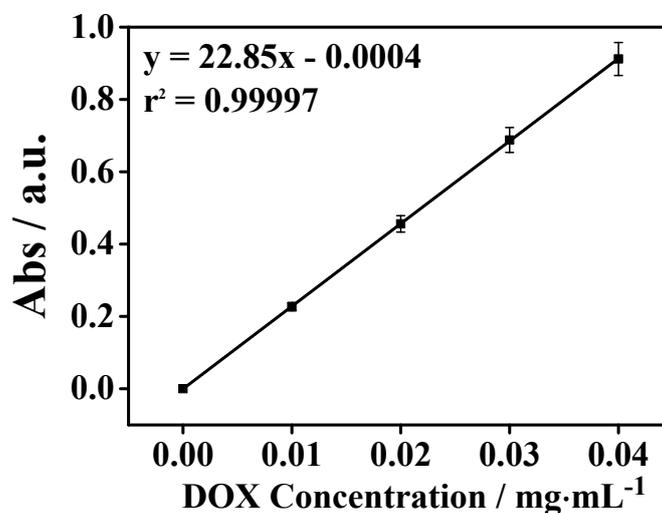


Figure S8. UV-vis absorbance standard curve of DOX at 480 nm.

References

- [1] R. Wang, H. Fan, W. Jiang, G. Ni, S. Qu, Amino-functionalized graphene quantum dots prepared using high-softening point asphalt and their application in Fe³⁺ detection, *Appl. Surf. Sci.* 467 (2019) 446-455.
- [2] S.V. Lale, R.G. Aswathy, A. Athulya, K. D Sakthi, K. Veena, AS1411 aptamer and folic acid functionalized pH-responsive ATRP fabricated pPEGMA-PCL-pPEGMA polymeric nanoparticles for targeted drug delivery in cancer therapy, *Biomacromolecules* 15(5) (2014) 1737-52.
- [3] K.M. Isaac, I.V. Sabaraya, N. Ghousifam, D. Das, A.M. Pekkanen, D.K. Romanovicz, T.E. Long, N.B. Saleh, M.N. Rylander, Functionalization of single-walled carbon nanohorns for simultaneous fluorescence imaging and cisplatin delivery in vitro, *Carbon* 138 (2018) 309-318.