## **Supporting Information**

# Ultra-fast synthesis of water soluble $MoO_{3-x}$ quantum dots with controlled oxygen vacancy and their near infrared fluorescence sensing to detect $H_2O_2$

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#### Materials

Mercaptosuccinic acid (98%+), 11-mercaptoundecanoic acid (98%) were obtained from Adamas-Beta Co. Ltd. Ammonium molybdate (98%), glutathione (98%), ethyl mercaptoacetate (98%), sodium 2-mercaptoethanesulfonate (98%), 5,5-Dimethyl-1pyrroline N-oxide (97%) and sodium hypochlorite (6-14% available chlorine) were purchased from Aladdin Co. Ltd. HCL solution (37%), hydrogen peroxide (30%), cysteine (98.5%+), ascorbic acid (99.7%), sodium nitrate (99%) and 3-Mercaptopropionic acid (98%) were obtained from Sinopharm Chemical Reagent Co. Ltd. Deionized (DI) water was achieved by a Milli-Q integral water purification system (18.2 MQ•cm resistivity at 25 °C).

#### Synthesis of MoO<sub>3-x</sub> quantum dots

0.5 g ammonium molybdate was dissolved into 20 mL deionized water to obtain the ammonium molybdate solution. A certain amount of mercaptosuccinic acid (0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6 g) as ligand was dissolved into another 20 mL deionized water as the mercaptosuccinic acid solution. Then, 2.4 mL 1 M hydrochloric acid and the mercaptosuccinic acid solution were rapidly injected into the ammonium molybdate solution, and the mixture solution was stirred with 650 rpm for 5 seconds (see a video in the supporting information), and followed by dialysis purification. The obtained QDs solutions were diluted for further characterization and sensing application as following: the 40 µL QDs solution was diluted to 3 mL by added deionized water.

#### Characterization

Transmission electron microscopy (TEM) was performed on a JEOL-2010 system operated at 200 kV. The samples for TEM examinations were prepared by dropping the suspensions on copper grids with thin carbon coating and then drying at room temperature. The Raman spectra were measured by confocal microprobe Raman spectrometer (Renishaw inVia Reflex) with a laser beam of 785 nm wavelength, 5 mW power, and 20 seconds integral time. XPS spectra were obtained on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the excitation source. X-ray diffraction (XRD) patterns were collected on a Philips X'pert Pro X-ray diffractometer using Cu K line (0.15419 nm). The optical absorption data was collected by the Shimadzu UV-2600. Fluorescence data was obtained by Horiba Fluorolog-3-21. The incubation time of  $H_2O_2$  fluorescence detection is 5 min. The electronic spin resonance

spectroscopy was obtained by Bruker EMX plus 10/12. The fluorescent lifetime spectroscopy was measured by QM400-TM.



Figure S1. The XRD patterns of 0.2g@QDs, 0.6g@QDs, 1.0g@QDs, 1.4g@QDs.

The diffractive intensity of all samples is very weak in XRD patterns, the diffraction peaks of 0.2g@QDs and 0.6g@QDs are close to the MoO<sub>3</sub>, this is consistent with previous literature of other MoO<sub>3-x</sub> QDs.



Figure S2. The Raman spectra of 0.2g@QDs, 0.6g@QDs, 1.0g@QDs, 1.4g@QDs.



Figure S3. The XPS survey spectrum of 0.2g@QDs.



Figure S4. The O 1s XPS spectra of 0.2g@QDs, 0.6g@QDs, 1.0g@QDs, 1.4g@QDs.



**Figure S5.** The optical absorption of  $MoO_{3-x}$  QDs which ligand content from 0 g to 0.3 g.



Figure S6. The optical absorption of 0.2g@QDs under different temperature .



Figure S7. The optical absorption of 0.2g@QDs under different pH value.



**Figure S8.** The optical absorption of 0.2g@QDs under different NIR irradiation time treatment.

The stability of 0.2g@QDs under different conditions was investigated (Figure S6-8). The Figure S6 exhibited the 0.2g@QDs optical absorption under different temperature, indicating that the stability of the QDs gradually became poor with increase of temperature. The Figure S7 demonstrate that QDs are very stable in acid condition, but unstable in neutral and alkaline condition (molybdenum oxide can be dissolved in alkaline condition). The stability of NIR irradiation was measured by 100 W power NIR light source (the wavelength is from 0.76  $\mu$ M to 5  $\mu$ M), the QDs showed a relative good stability (Figure S8). The NIR absorption of 0.2g@QDs just slightly decreased after 30 min irradiation, and finally kept stable.



**Figure S9**. The Optical absorption of 0.2g@QDs aqueous solution which after different amount of  $H_2O_2$  added.

The NIR absorption intensity decrease and UV absorption edge blue shift indicate the existence of oxidiation process of both oxygen vacancy and Mo-S coordination bond by  $H_2O_2$ .



**Figure S10.** a) The ESR spectroscopy of 0.2g@QDs without  $H_2O_2$  treatment b) The ESR spectroscopy of 0.2g@QDs with presence of  $H_2O_2$ .

The ESR spectra indicate that  $H_2O_2$  reacted with QD lead to formation of hydroxyl radicals, which is certified by the 1:2:2:1 characteristic peak correspond hydroxyl radicals.<sup>1</sup>



**Figure S11.** a) fluorescence lifetime spectroscopy of 0.2g@QDs with  $H_2O_2$  treatment b) fluorescence lifetime spectroscopy of 0.2g@QDs with the presence of  $H_2O_2$ .

The fluorescent lifetime was measured as shown in Figure S11, the fluorescent lifetime of 0.2g@QDs increased from 0.59 ns to 0.78 ns after H<sub>2</sub>O<sub>2</sub> adding, which caused by the decrease of LSPR absorption due to the oxidization of the oxygen vacancy.<sup>2</sup>



**Figure S12.** a) The Mo 3d XPS spectrum of 0.2g@QDs without  $H_2O_2$  treatment b) The Mo 3d XPS spectrum of 0.2g@QDs with the presence of  $H_2O_2$ .

Compared with the XPS spectrum of QDs without  $H_2O_2$  treatment, the S 2s peak and  $Mo^{5+}$  peak disappeared, which indicated the existence of oxidization process of QDs.

Probe type	Detect limit	Fluorescence region	References
dicyanomethylene-4H-pyran (DCM) (organic molecule)	79 nM	700 nm	40 ( <i>RSC Adv</i> .
			<b>2015</b> , 5, 85957-
			85963.)
CS-coumarin $\pi$ -conjugated system (organic molecule)	3.16 µM	700 nm	41 (Adv. Mater.
			<b>2016</b> , 28, 8755-
			8759.)
Mito-NIRHP (organic molecule)	26 nM	700 nm	42 (Anal. Chem.
			<b>2016</b> , 88, 8019-
			8025.)
Cy-B (organic molecule)	13 nM	710 nm	43 (J. Mat.
			Chem. B 2016,
			4, 7363-7367.)
Sulfur dope CDs	1.1 μM	770 nm	44 (Microchim.
			Acta 2017, 184,
			2055-2062.)
Cy-PFS (organic molecule)	50 nM	830 nm	45 (Anal. Chem.
			<b>2019</b> , 91, 1203-
			1210.)
MoO <sub>3-x</sub> QDs	3 nM	770 nm	This work

## Table S1. Comparison of different NIR fluorescence $H_2O_2$ sensing

### References

1. X. Li, F. Liu, D. Huang, N. Xue, Y. Dang, M. Zhang, L. Zhang, B. Li, D. Liu, L. Wang, H. Liu and X. Tao, *Adv. Funct. Mater.*, 2020, **30**, 2000308.

2. J. Li, A. V. Krasavin, L. Webster, P. Segovia, A. V. Zayats and D. Richards, *Sci. Rep.*, 2016, **6**, 21349.