Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

A sensitive colorimetric chiral recognition for thiol-containing amino acids based on NIR plasmonic MoO_{3-x} nanoparticles

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Experimental Section

Materials. Molybdenum oxide (99%), D-penicillamine (98%), L-penicillamine (98%) and acetonitrile (99%) were purchased from Aladdin Co. Ltd. D-cysteine (98%) and N-acetyl-L-cysteine (99%) were obtained from Shanghai Macklin Biochemical Co. Ltd. Ethanol absolute was obtained from Sinopharm Chemical Reagent Co. Ltd. L-cysteine (98%) was purchased from J&K Scientific. Ltd. N-acetyl-D-cysteine (97%) was obtained from Bide Pharmatech Ltd. Deionized (DI) water was achieved by a Milli-Q integral water purification system (18.2 MΩ•cm resistivity at 25 °C).

The synthesis of MoO_3 nanoparticles. This method is slightly modified based on the work of Kalantar-zadeh et al.[1] 3 g of the MoO_3 powder was ground with 0.6 mL acetonitrile for 30 min. The powder was then dispersed in a 50 vol% ethanol/water mixture (50 mL), sonicating for 120 min at the power of 100 W, and then centrifuged at 6000 rpm for 30 min at room temperature, taking the supernatant as MoO_3 nanoparticles solution.

The modification of MoO_{3-x} nanoparticles. Taking a 7 mL disposable plastic centrifuge tube as a container, 5 mg chiral thiol-containing amino acid (D/L-cysteine, D/L-penicillamine, N-Acetyl-D/L-cysteine) and 5 mL MoO_3 nanoparticles solution were added into it, then sonicating for 60 min at the power of 100 W.

The colorimetric sensing of D/L-Cys and D/L-Pen. Taking a 7 mL disposable plastic centrifuge tube as a container, 3 mL MoO_3 nanoparticles solution and a certain amount of D/L-Cys or D/L-Pen (2-40 μM for cysteine, 0.5-20 μM for penicillamine) were added into it, and sonicating for 60 min, then the optical absorption spectrum of the mix solution was measured.

The quasi in situ Raman spectroscopy. During the modification process of MoO_{3-x} nanoparticles, the sample of 100 μL solution was taken out for the measurement of Raman spectroscopy per interval 15 min (in the measurement of Raman spectrum).

The exclusion tests of solubility difference of enantiomer. Taking a 10 ml disposable plastic centrifuge tube as a container, 5 mg chiral thiol-containing amino acids (D/L-cysteine, D/L-penicillamine, N-Acetyl-D/L-cysteine) were dispersed into 5 mL of deionized water and sonicated for 2 hours to ensure that they were completely dissolved. Then 3 mL MoO_3 nanoparticles solution was added into them and sonicated for 1h, incubating at room temperature.

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. 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 were collected by the Shimadzu UV-2600. The Raman spectra were examined by confocal microprobe Raman spectrometer (Renishaw inVia Reflex) with a laser beam of 785 nm wavelength, 5 mW power, and 10 seconds integral time. The IR spectra were measured by NEXUS Intelligent Fourier Infrared Spectroscopy. The circular dichroic (CD) spectra were obtained by BRIGHTTIME Chirascan, Jasco-815.

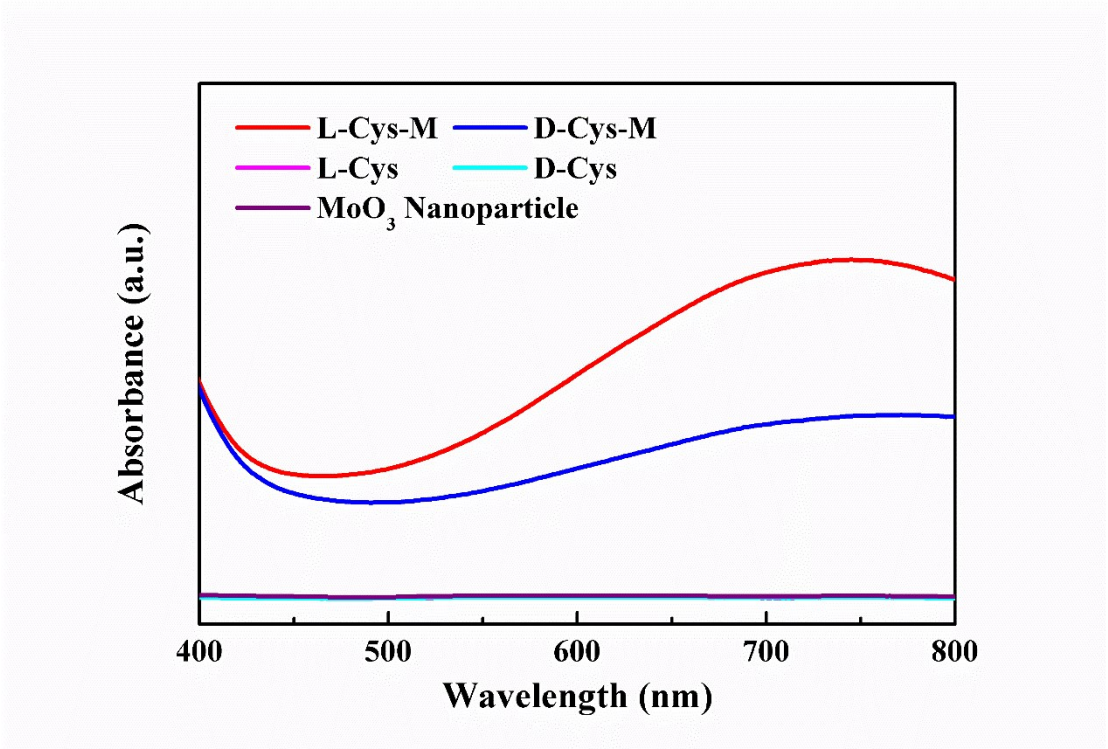

Figure S1. The optical absorption of D/L-Cys-M, D/L-cysteine, MoO_3 nanoparticle, respectively.

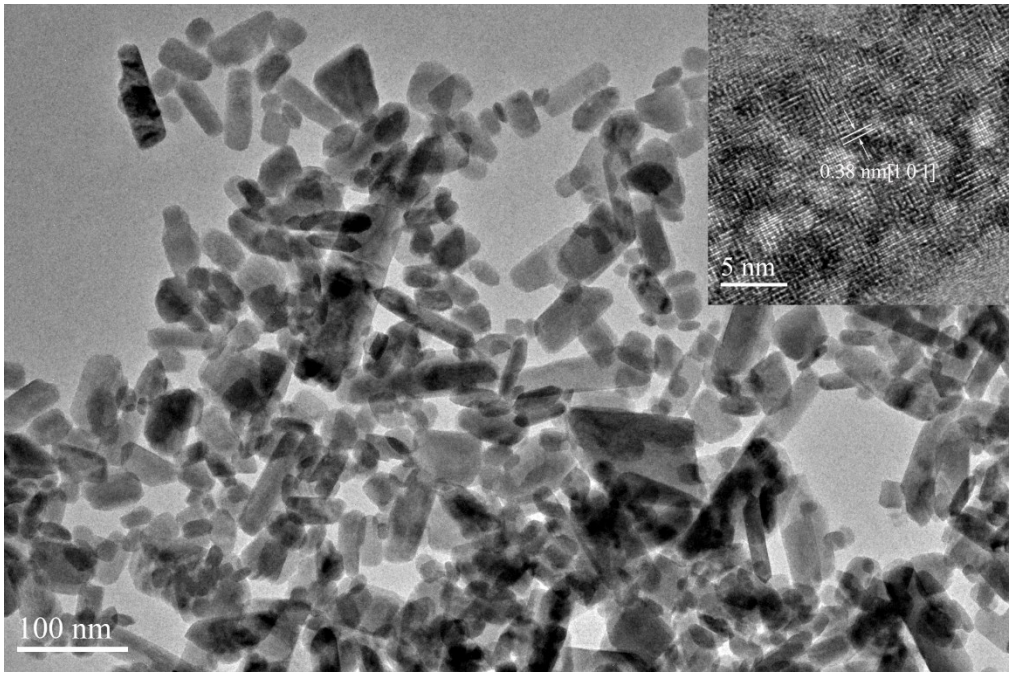

Figure S2. The TEM and HRTEM image of unmodified MoO_3 nanoparticle

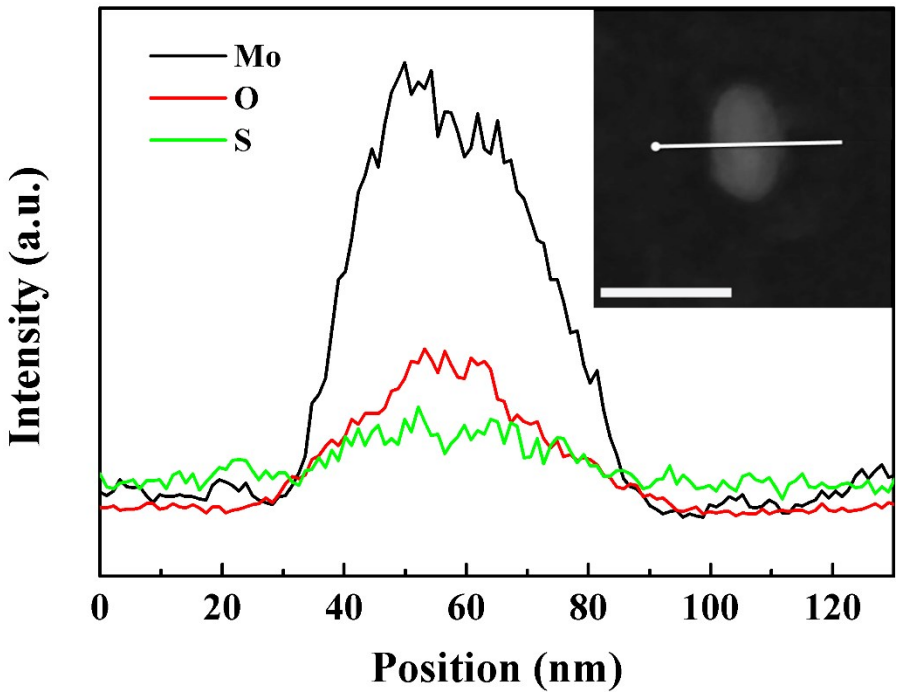

Figure S3. The EDX line scan and STEM image of cysteine modified MoO_3 nanoparticles

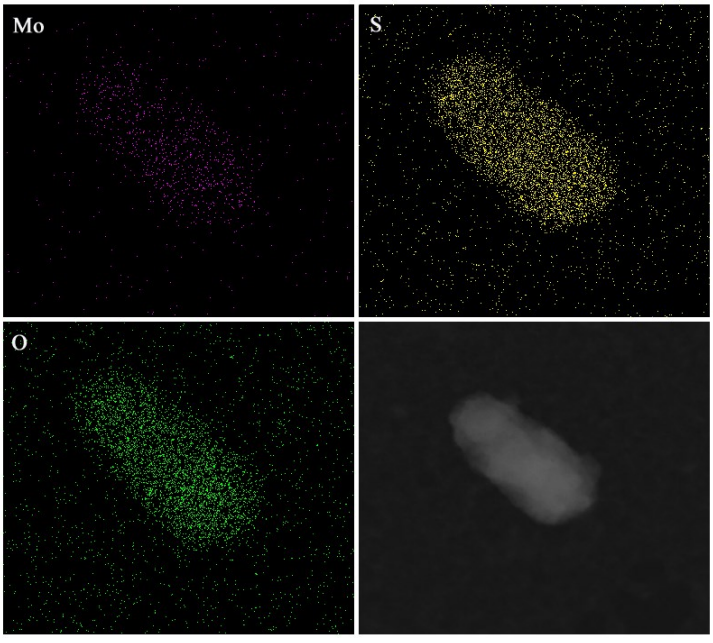

Figure S4. The EDX mapping of cysteine modified MoO_3 nanoparticles.

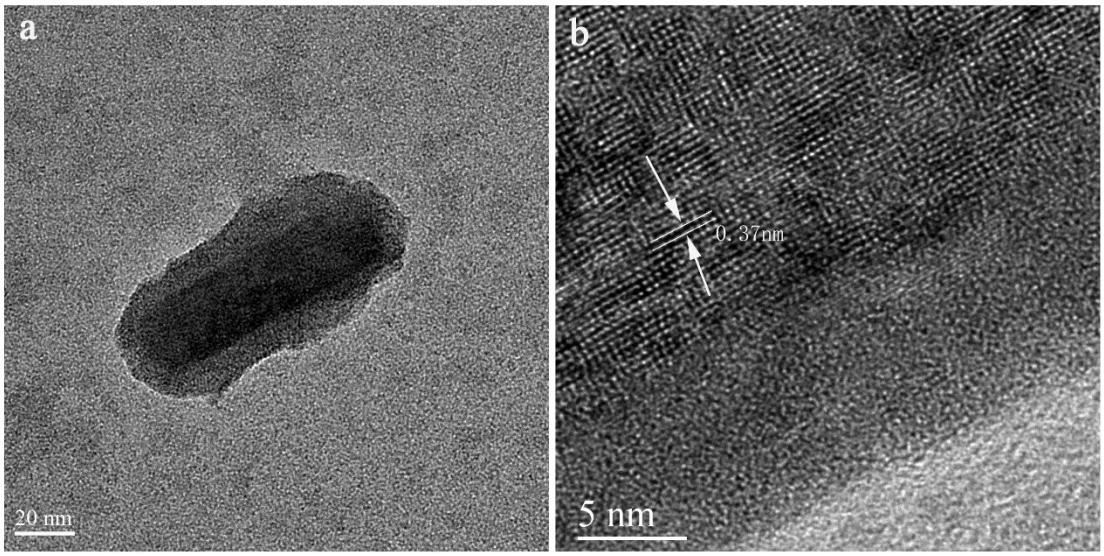

Figure S5. The TEM and HRTEM images of L-Cys-M.

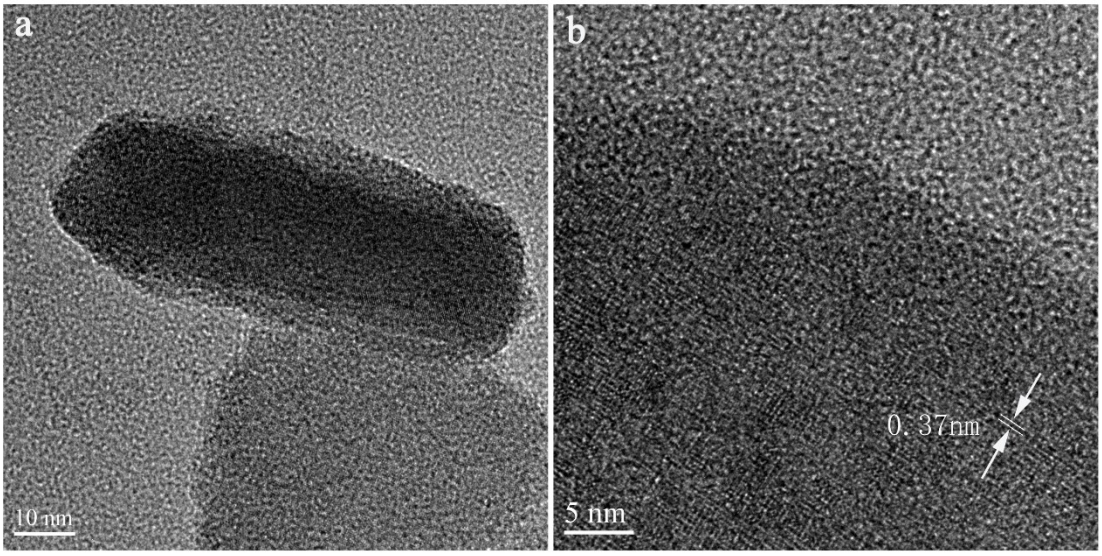

Figure S6. The TEM and HRTEM images of D-Cys-M.

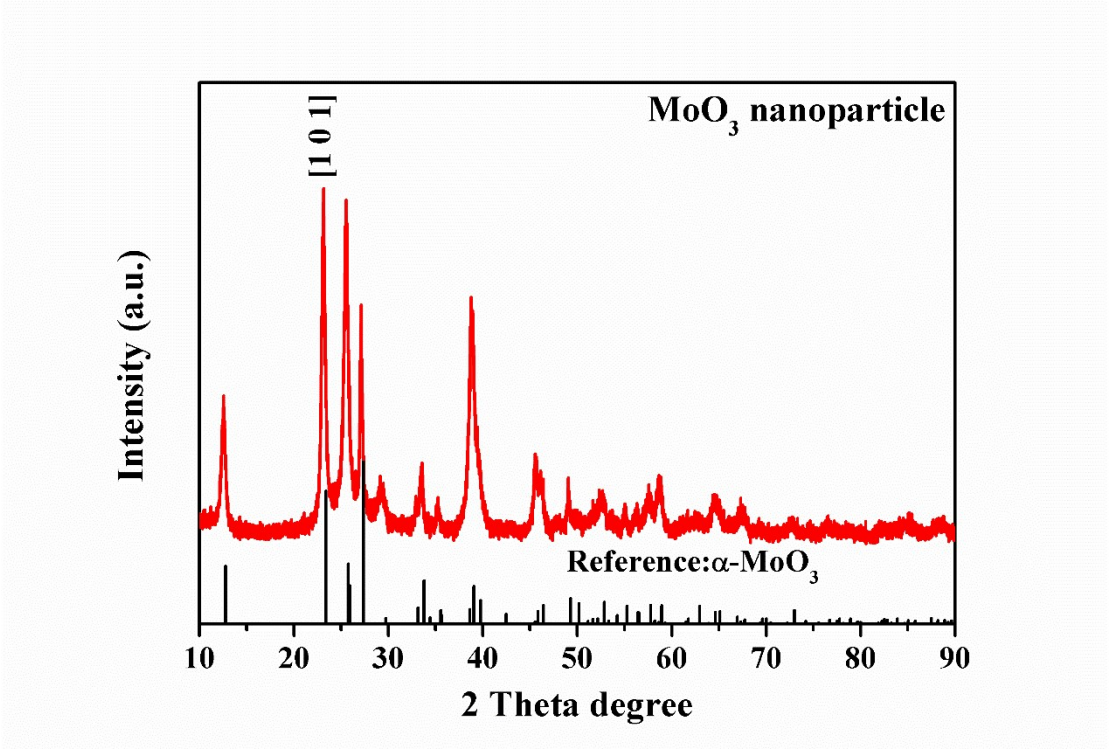

Figure S7. The XRD pattern of unmodified MoO_3 nanoparticle.

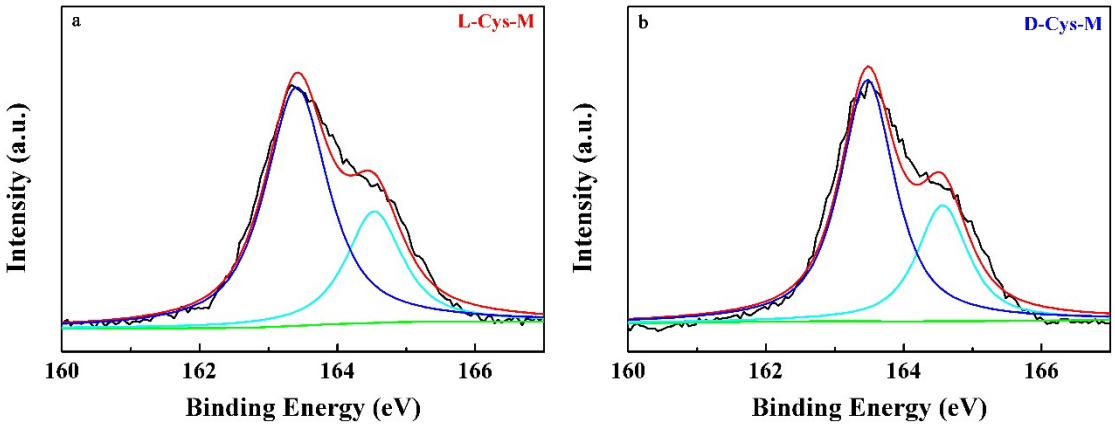

Figure S8. a) XPS spectra of S 2p core level peak regions for L-Cys-M. b) XPS spectra of S 2p core level peak regions for D-Cys-M.

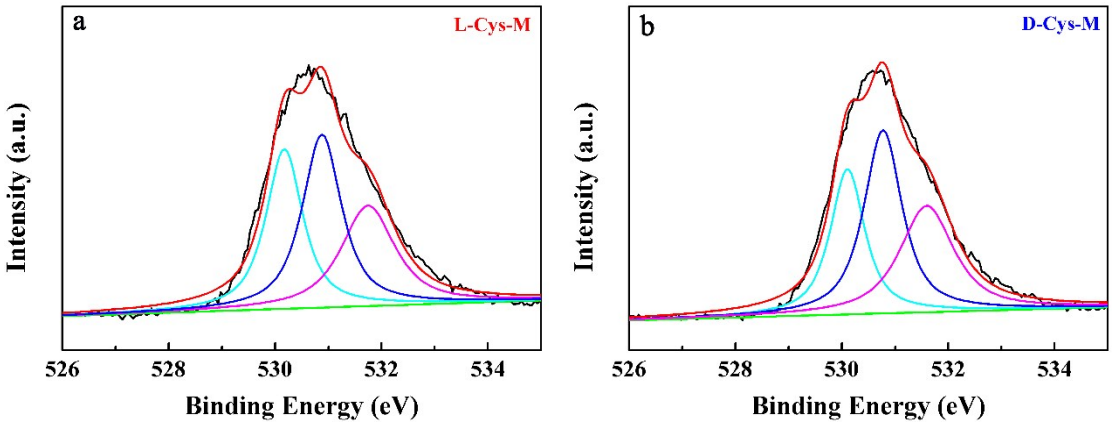

Figure S9. a) The O 1s XPS spectra of L-Cys-M. b) The O 1s XPS spectra of D-Cys-M.

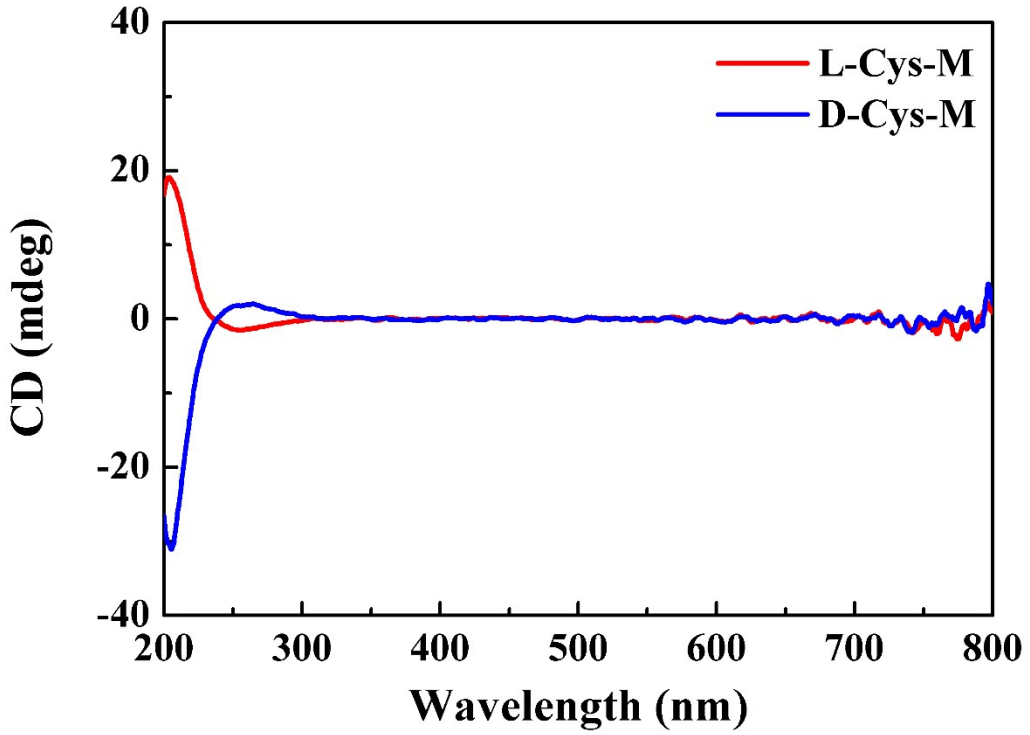

Figure S10. The Circular dichroic (CD) spectra of D/L-Cys-M.

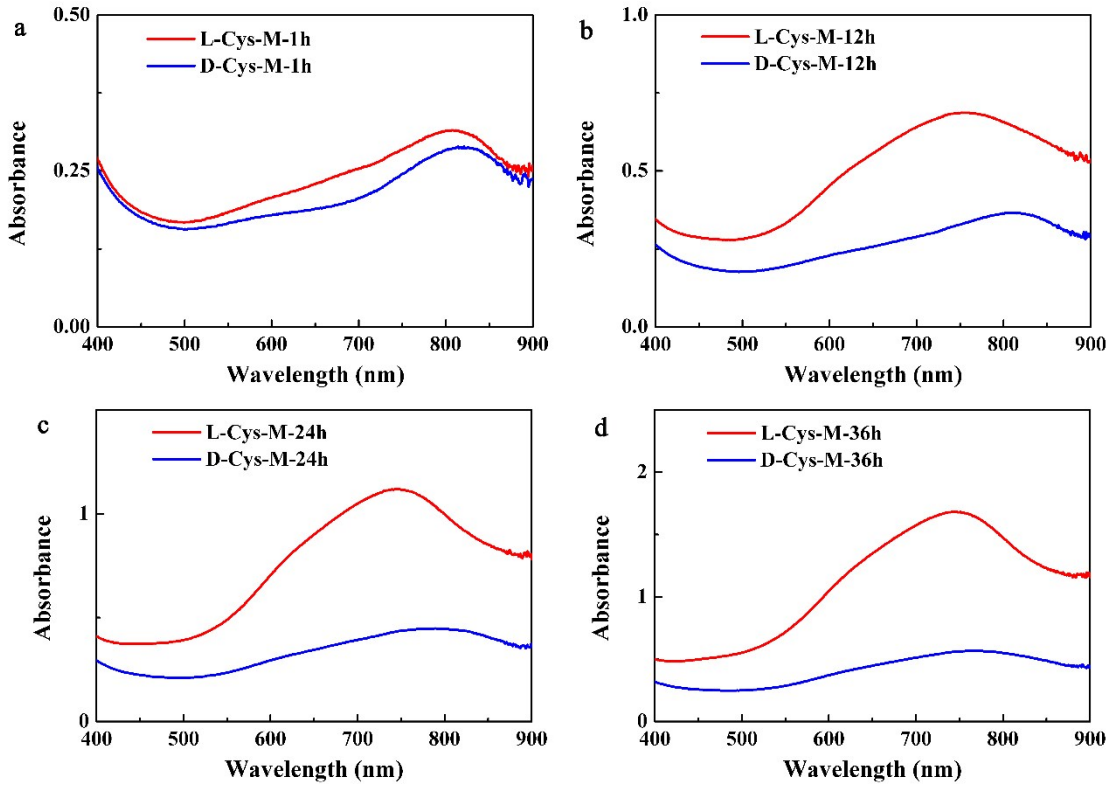

Figure S11. a) The absorption spectra of D/L-Cys-M-1h. b) The absorption spectra of D/L-Cys-M-12h. c) The absorption spectra of D/L-Cys-M-24h. d) The absorption spectra of D/L-Cys-M-36h.

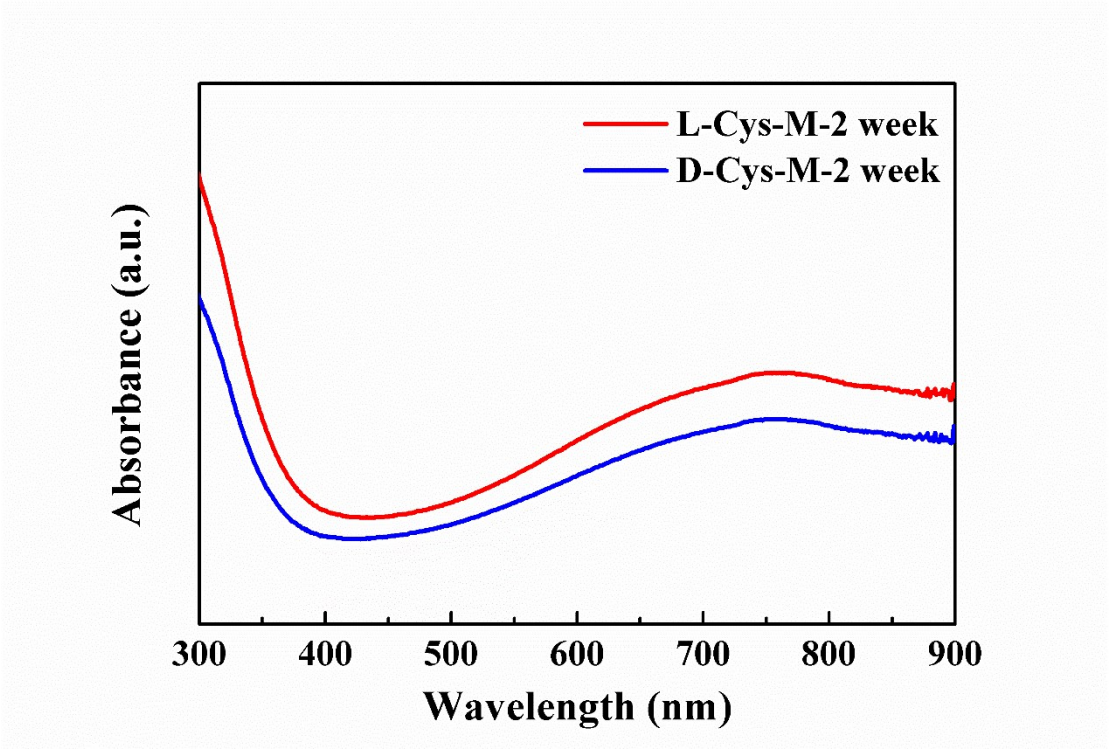

Figure S12. The absorption spectra of D/L-Cys-M-2 week.

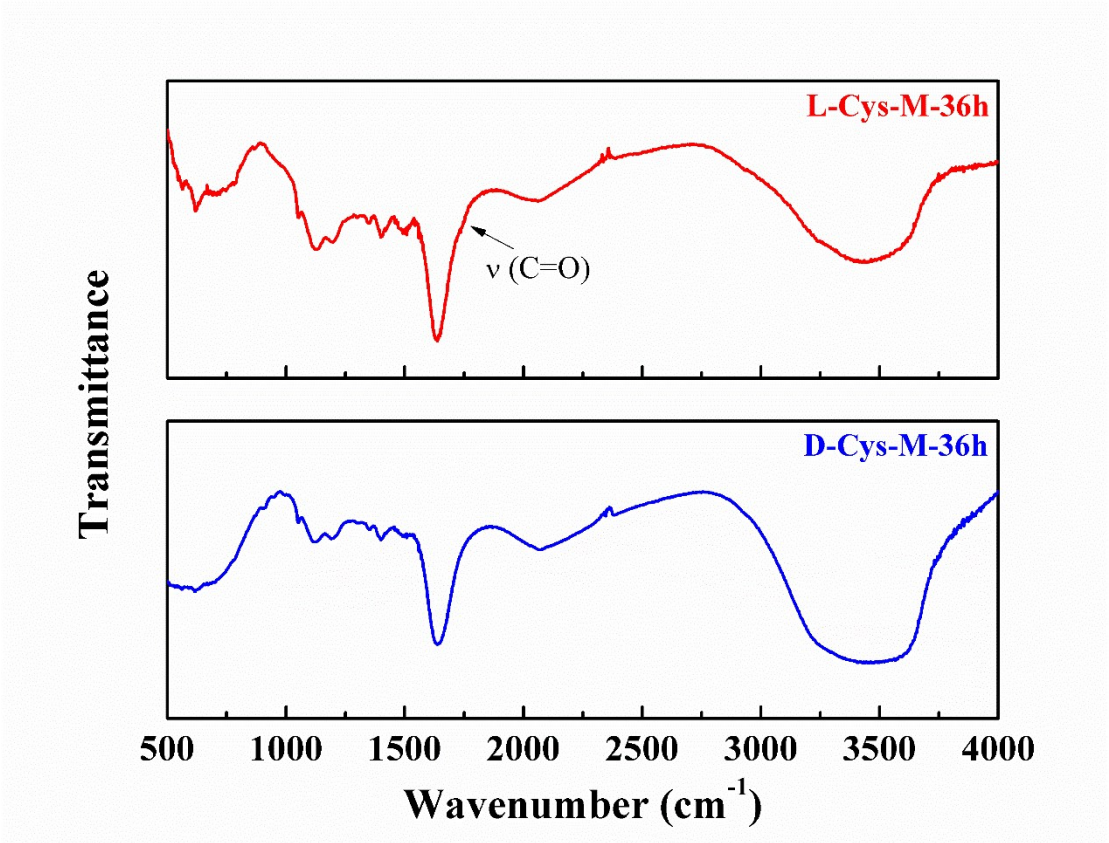

Figure S13. The IR spectra of D/L-Cys-M-36h.

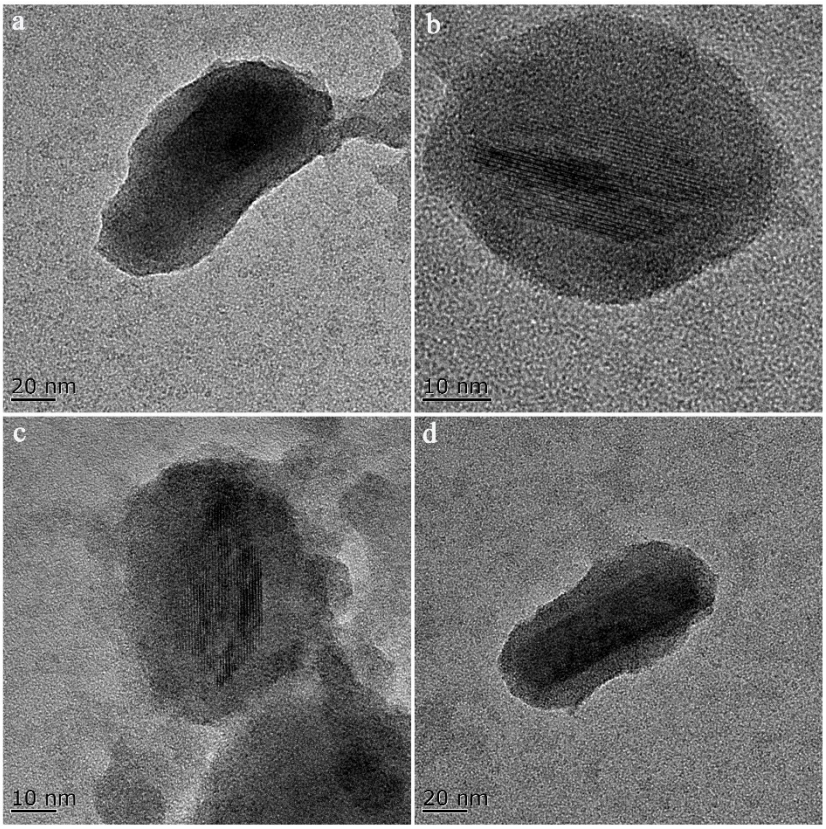

Figure S14. The TEM images of L-Cys-M-36h.

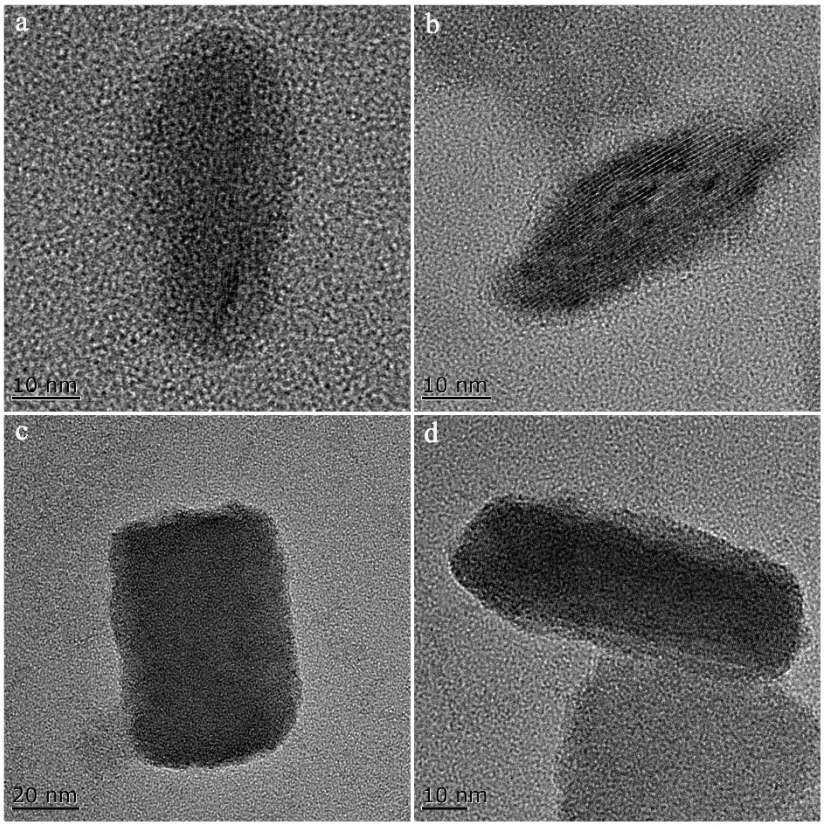

Figure S15. The TEM images of D-Cys-M-36h.

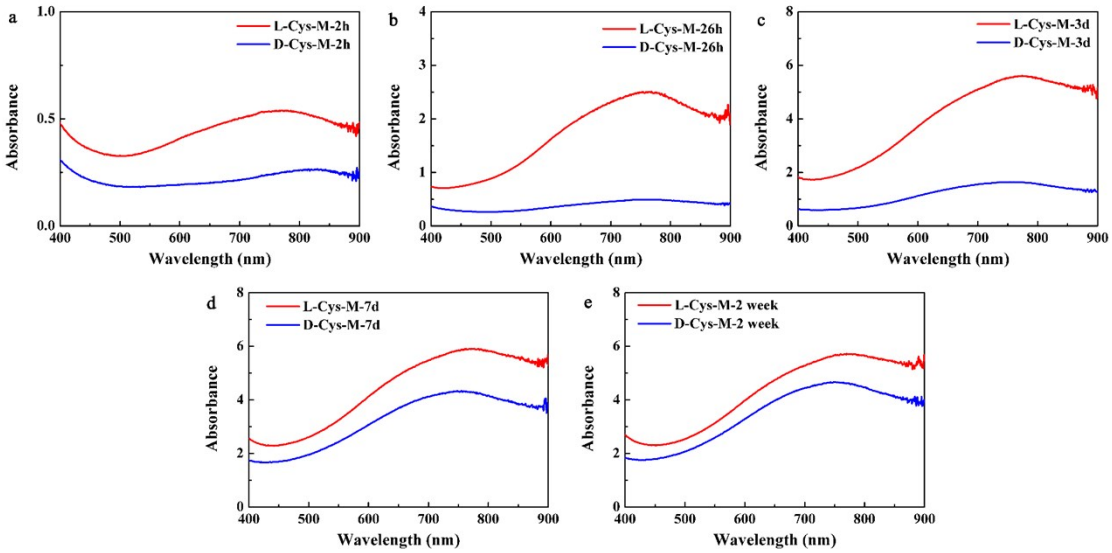

Figure S16. The absorption spectra of pre-dissolved group.

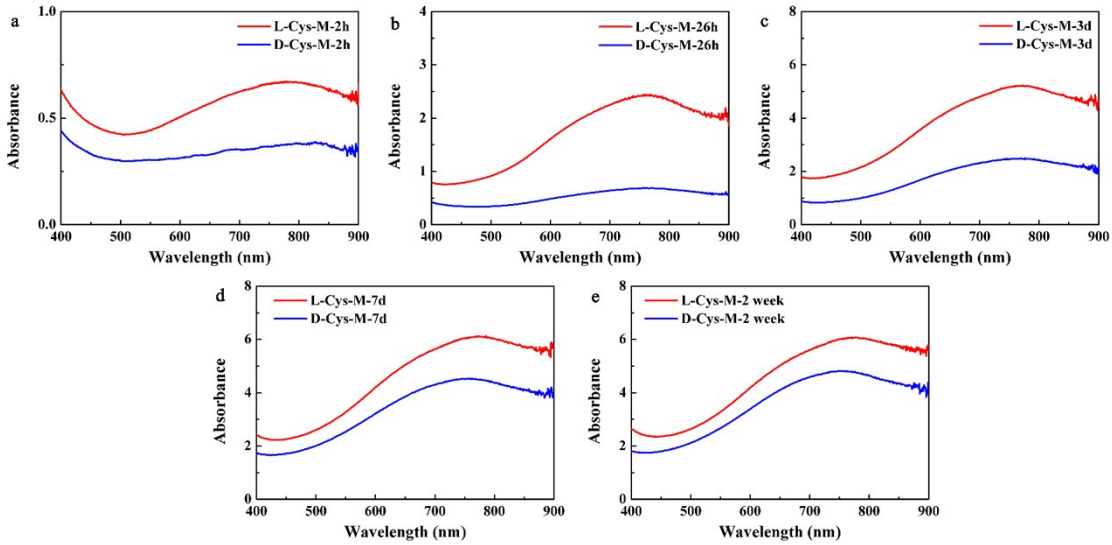

Figure S17. The absorption spectra of direct sonication group.

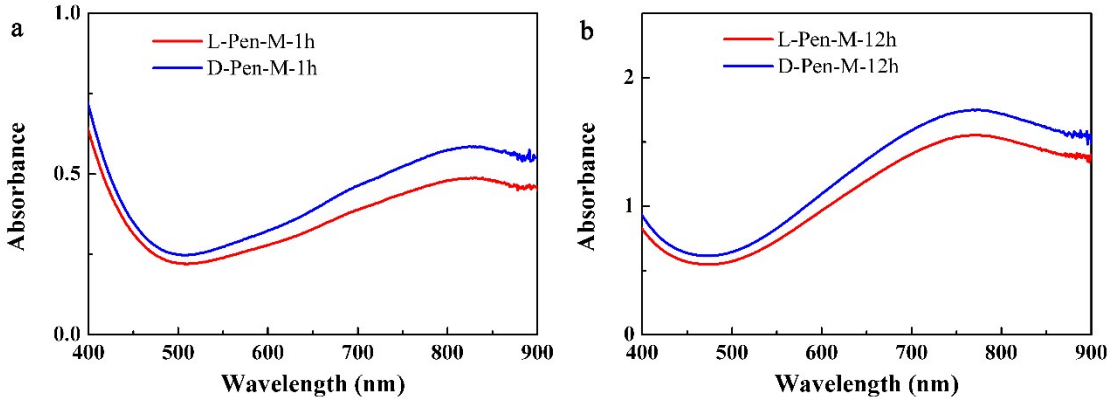

Figure S18. a) The absorption spectra of D/L-Pen-M-1h. b) The absorption spectra of D/L-Pen-M-12h.

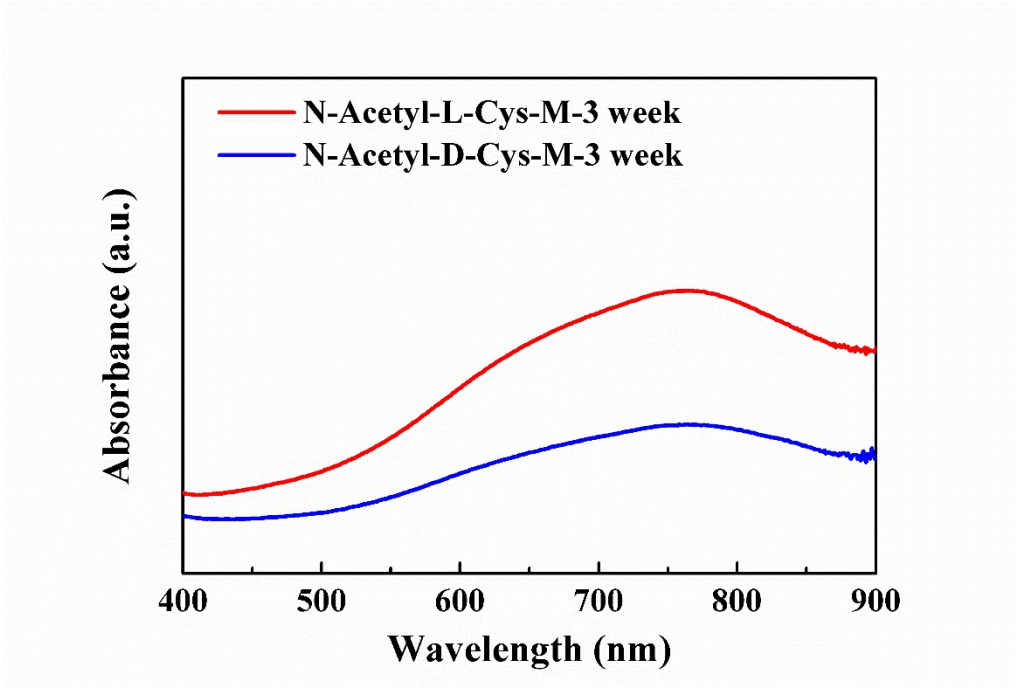

Figure S19. The absorption spectra of N-Acetyl-D/L-Cys-M-3 week.

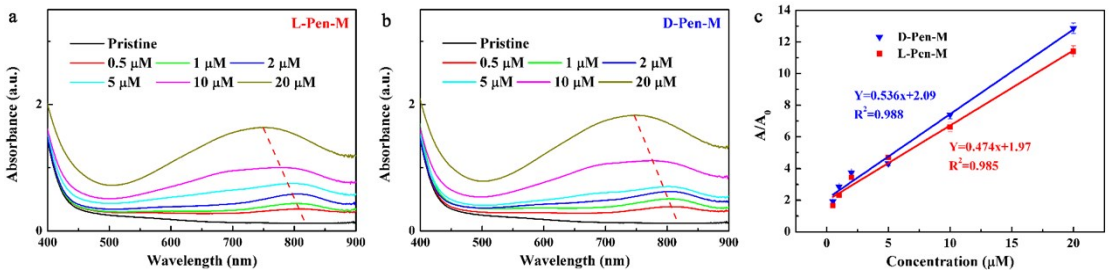

Figure S20. a, b) The optical absorption of D/L-Pen-M with the amount of D/L-Cysteine in the range from 0.5-20 μM. c) The plot of NIR optical absorption intensity (A/A_0) against the concentration of D/L-Penicillamine. A_0 is the NIR absorption coefficient maximum of pristine MoO_3 nanoparticle solution, A is the delta value of NIR absorption coefficient maximum of MoO_3 nanoparticle modified by penicillamine.

Table. S1 Comparison of different colorimetric D/L-Cys sensing

Probe type	Target molecule	Detection limit	Reference
5-triphosphate (UTP)-capped silver nanoparticles	D/L-Cys	100 nM	*Anal. Chem.*, 2011, **83**, 1504-1509.
silver nanoparticles	D-Cys	4.88 μM	*Talanta*, 2018, **184**, 149-155.
Gold nanorods	L-Cys	0.325 μM	New J. Chem., 2018, **42**, 12706-12710.

MoO_3 nanoparticles	D/L-Cys	43 nM for L-Cys/ 107 nM for D-Cys	This work

1. M. M. Alsaif, K. Latham, M. R. Field, D. D. Yao, N. V. Medhekar, G. A. Beane, R. B. Kaner, S. P. Russo, J. Z. Ou and K. Kalantar-zadeh, *Adv. Mater.*, 2014, **26**, 3931-3937.