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Top-down produced CdSe quantum dots as an ultrasensitive SERS platform for detection of uric acid

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Synthesis of silica microspheres

Silica microspheres (approximately 450 nm in diameter) were synthesized *via* a typical Stöber process[1]. In brief, 1.2 L of ethanol was added into a three-necked flask (3 L). The system was magnetically stirred and heated to 63 ℃ through an oil bath, followed by the addition of TEOS (240 mL). 20 minutes later, 240 mL of aqueous ammonia and 240 mL of deionized water were added and stirred for 3 hours. When the system was cooled down to room temperature, the silica was immediately precipitated by centrifugation (4500 rpm, 10 min) (Centrifuge, Z32 HK, HERMLE). The sediment was washed by ethanol, then collected after vacuum-dried.

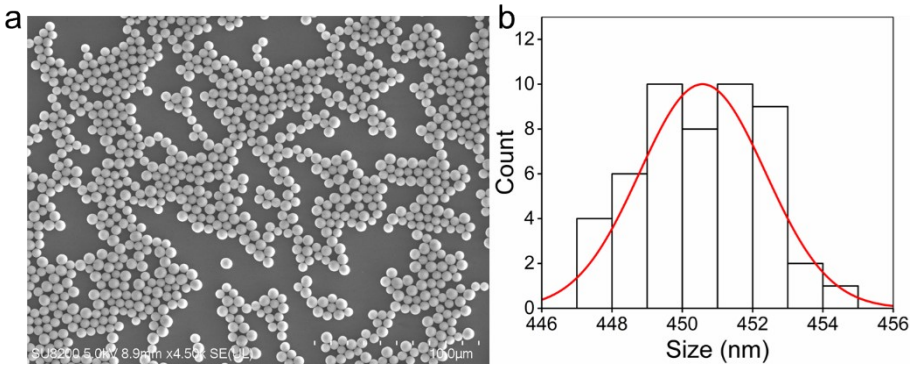

Fig. S1 (a) SEM images of SiO_2 microspheres and (b) the lateral size distributions.

SERS experiments

The SERS substrate was obtained *via* the spin-coating method. Specifically, the SiO_2/Si substrate was washed by acetone, ethanol, and deionized water in sequence. Then, 5 μL of CdSe QDs dispersion (0.5 mg mL^{-1}) was dribbled onto the surface of SiO_2/Si and formed a dense thin film after spinning. MB dye was used as probe molecule to verify the SERS properties of CdSe QDs substrate. Simply, 5 μL of MB probes with different concentrations (10^{-4}–10^{-10} M) were consecutively dropped on the surface of above substrate. The laser power was 0.5 mW with a 5 s exposure time under the 633 nm laser excitation. Furthermore, the SERS intensities of some typical Raman peaks were calculated to quantitatively describe the Raman enhancement. We calculated the enhancement factors (EF) values using the following Equation:[2]

$$EF = (I_{SERS} \cdot C_{Raman}) / (I_{Raman} \cdot C_{SERS})$$

where I_{SERS} and C_{SERS} refer to the Raman intensity and concentration of probes in

the SERS spectra, and I_{Raman} and C_{Raman} are the Raman intensity and concentration of probes in the Raman spectra.

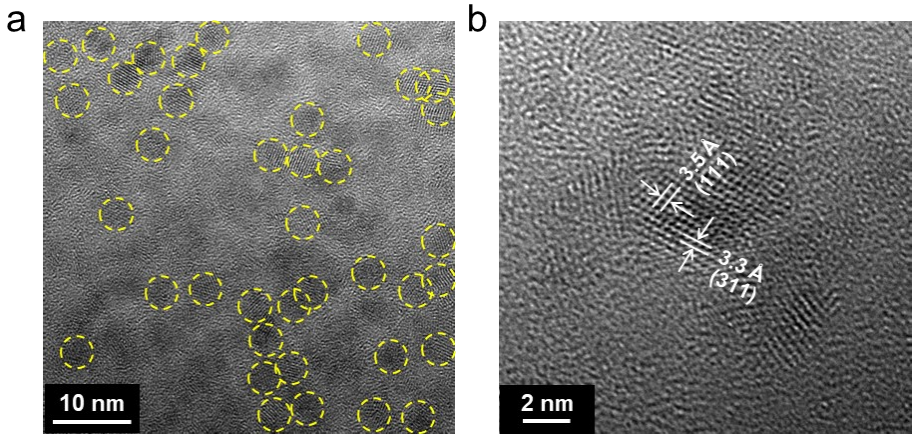

Fig. S2 (a)−(b) HRTEM images of CdSe QDs.

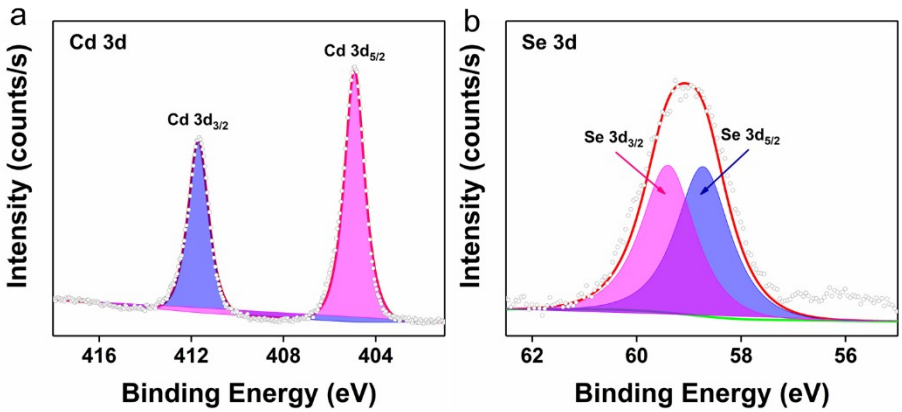

Fig. S3 High-resolution XPS spectra of (a) Cd 3d and (b) Se 3d in bulk CdSe.

Fabrication of CdSe QDs-PMMA thin films

The CdSe QDs-PMMA hybrid thin films with varying concentrations (0.1 to 1 wt%) were fabricated by solution processing. In brief, PMMA was dissolved in NMP to form a 300 mg mL^{-1} solution. Based on the pre-designed loading contents and the as-required constant total weight, the PMMA solution and QDs dispersion were mixed by vigorous stirring and sonication. The mixture with known volume was dropped into a polytetrafluoroetylene (PTFE) mold to form a 8μm thick polyimide film as the releasing layer. After complete removal of the solvent from the evenly spreading mixture by moderate heating (70 ℃) overnight on a hot plate. Finally, the

CdSe QDs-PMMA hybrid thin films were obtained.

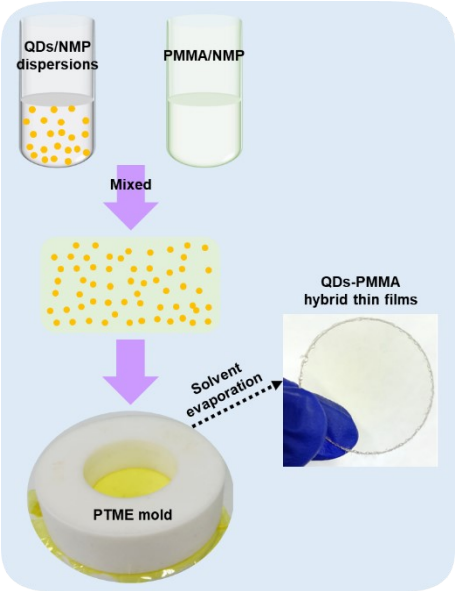

Fig. S4 Schematic illustration of the preparation of CdSe QDs-PMMA hybrid thin films.

Table S1 Enhancement factors of some typical Raman peaks of MB at different concentrations.

Concentration (mol/L)	1150 cm^{-1}	1298 cm^{-1}	1393 cm^{-1}	1495 cm^{-1}	1618 cm^{-1}
10^{-4}	39.27	41.16	51.18	40.87	37.58
10^{-5}	320.43	323.25	394.34	362.48	336.00
10^{-6}	2.11×10^{3}	2.40×10^{3}	3.73×10^{3}	3.60×10^{3}	2.86×10^{3}
10^{-7}	1.42×10^{4}	1.35×10^{4}	2.13×10^{4}	1.70×10^{4}	1.23×10^{4}
10^{-8}	1.16×10^{5}	1.16×10^{5}	1.47×10^{5}	1.44×10^{5}	1.02×10^{5}
10^{-9}	5.82×10^{5}	7.32×10^{5}	7.64×10^{5}	9.57×10^{5}	5.73×10^{5}
10^{-10}	2.95×10^{6}	4.56×10^{6}	4.37×10^{6}	5.05×10^{6}	3.43×10^{6}

UV-vis absorbance spectrum, band gap and valence band spectra of CdSe QDs^{3-}

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It is well known that the optical band gaps *Eg* have a relationship with the absorption coefficient α by the following Equation S1:

$$(\alpha h\nu)^{1/\gamma} \sim (h\nu - Eg) \qquad (1)$$

where $h\nu$ is the photo energy and γ is a constant. As for CdSe, γ=2 and Eq. (1) becomes the following Equation S2:

$$(\alpha h\nu)^{1/2} = B(h\nu - Eg) \quad (2)$$

where α is a constant, thus the optical band gap Eg of the samples can be obtained using the extrapolation of $(\alpha h\nu)^{1/\gamma}$ versus $h\nu$ curve.

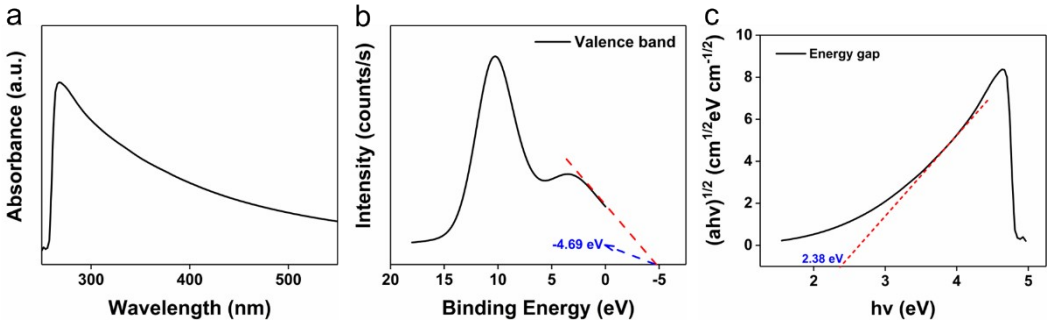

Fig. S5 (a) UV-vis absorbance spectrum of CdSe QDs (aqueous solution). (b) The valence band (VB) spectrum of CdSe QDs. (c) The band gap of CdSe QDs which evaluated from the UV-vis absorbance spectrum.

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