

## Supporting Information

### Electrochemical Gelation of Quantum Dots Using Non-Noble Metal Electrodes at High Oxidation Potentials

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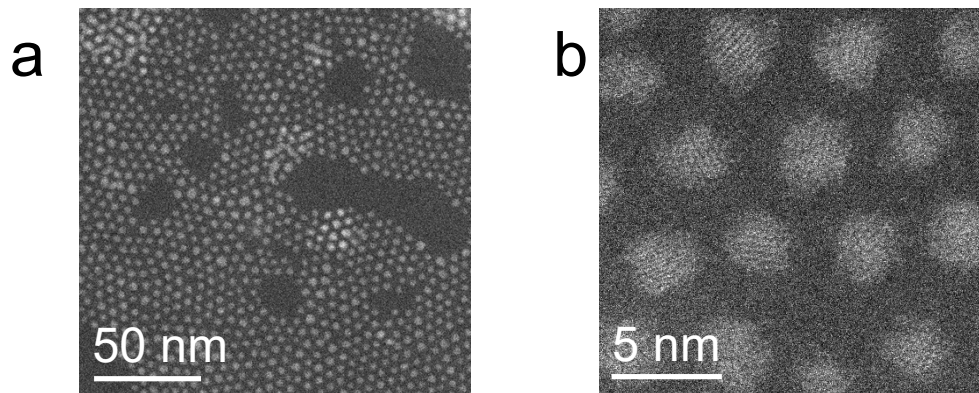
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#### Synthesis of CdS QDs.

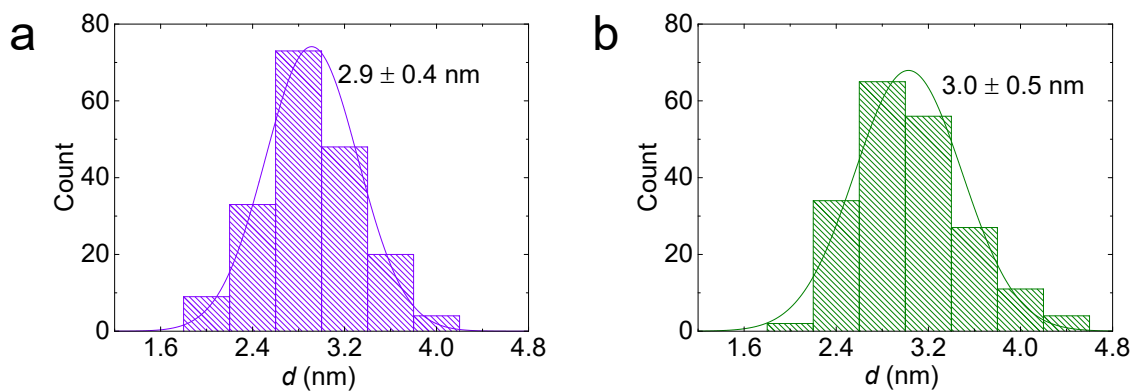
The Cd precursor mixture was first prepared in a Schlenk flask (100 mL) by weighing CdO (0.06 g, mmol), TOPO (3.0 g, 7.8 mmol), and TDPA (0.23 g, 0.83 mmol). Flask was connected to an active vacuum and heated to 150 °C with stirring to get a maroon-colored liquid. After 20 minutes, the vacuum was disconnected, and a slow Ar purge was established through the system. Next, the temperature was set to 350 °C. When the content in the flask turned colorless (~1 hour), the temperature was reduced to 320 °C. 2 mL of TOP (measured inside an Ar-filled glovebox) was injected into the mixture at this temperature. Next, the temperature was raised to 370 °C, and the S precursor mixture (2.4 mL TOP and 90 µL of TMS, measured and mixed inside an Ar-filled glovebox) was injected into the flask. After 15 minutes, the temperature was reduced to 75 °C, and the continued Ar flow through the flask was stopped. Heating and stirring were disconnected after 18 hours, and content in the flask was transferred to a vial for purification using 15 mL toluene. The content in the vial with toluene was sonicated for 10 minutes and centrifuged for 14 minutes at 3000 rpm. Insoluble contaminants were precipitated, and the clear supernatant was separated into a different vial. Next, methanol was added until turbidity. The vial was centrifuged for 14 minutes at 3000 rpm to precipitate the QDs. The supernatant containing soluble contaminants was decanted out. Precipitated QDs were redispersed in toluene. Sonication, precipitation, centrifugation, and redispersion steps were repeated one more time.

#### Exchange of capping ligand with MUA.

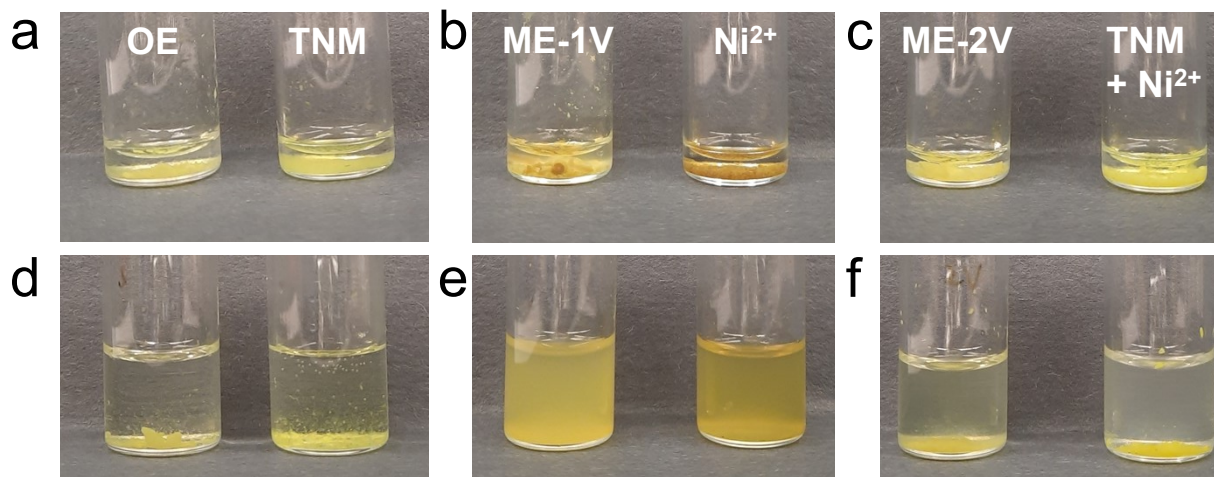
MUA solution in methanol was prepared by dissolving 0.41 g MUA (equivalent to 4 times of Cd moles used for the synthesis) in 5 mL of methanol. The pH of the MUA solution was adjusted to 10 using TMAH. At the end of the synthesis process, QDs are capped with TOPO. To exchange the ligands, prepared MUA solution was added to the QD dispersion and sonicated in the dark for 1 hour at room temperature. At the end of the sonication, ethyl acetate was added to the vial containing the QDs until turbidity. The vial was then centrifuged for 14 minutes at 3000 rpm. The supernatant was discarded, and the QDs were dispersed in methanol. Precipitation with ethyl acetate, centrifugation, and redispersion with methanol was repeated one more time. Purified samples were used to estimate the concentration using the UV-vis absorbance. QD concentration was adjusted to 40 µM and stored in the dark in an Ar-filled vial until the gelation.



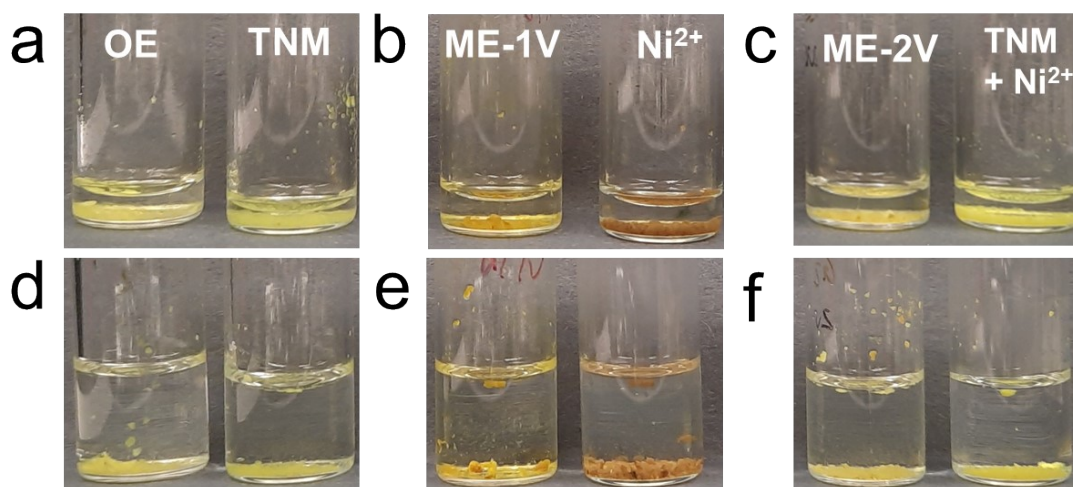
**Figure S1.** a, Low-magnification and b, high-magnification STEM images for CdS QDs.



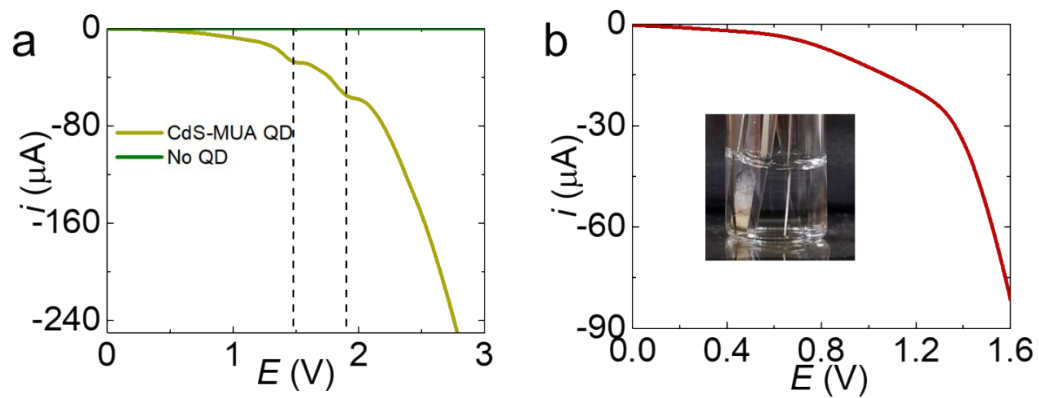
**Figure S2.** CdS QD size distribution **a**, before and **b**, after the electrogelation at 2 V. The total number of QDs in the size analysis is > 180.



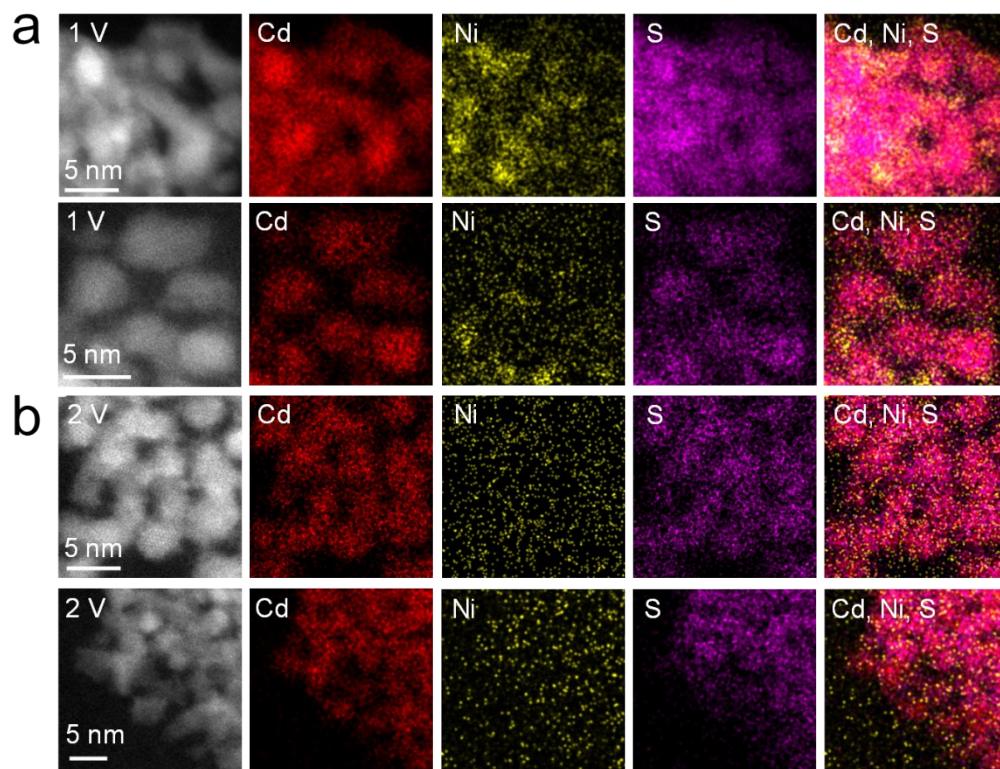
**Figure S3.** EDTA test results. **a**, Pt OE-gel and chemically prepared oxidative gel using TNM as the chemical oxidant. **b**, ME-gel prepared at 1 V using a Ni electrode and chemically prepared metal-mediated assembly using  $\text{Ni}^{2+}$ . **c**, Electrogele prepared at 2 V using a Ni electrode and chemically prepared gel in which TNM and  $\text{Ni}^{2+}$  are added simultaneously. **d**, **e**, and **f**, the corresponding solutions in **a**, **b**, and **c** after adding 2 mL of EDTA.



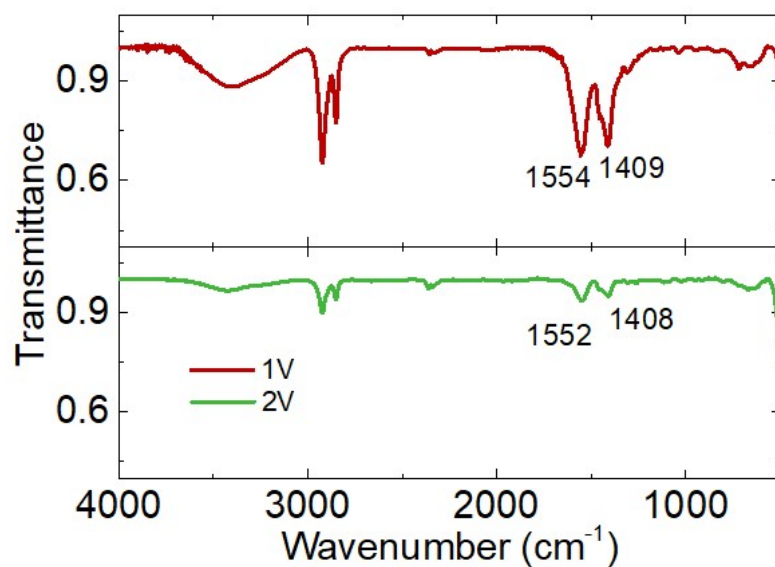
**Figure S4.** EDTA blank test results. **a**, Pt OE-gel and chemically prepared oxidative gel using TNM as the chemical oxidant. **b**, ME-gel prepared at 1 V using a Ni electrode and chemically prepared metal-mediated assembly using  $\text{Ni}^{2+}$ . **c**, Electrogele prepared at 2 V using a Ni electrode and chemically prepared gel in which TNM and  $\text{Ni}^{2+}$  are added simultaneously. **d**, **e**, and **f**, the corresponding solutions in **a**, **b**, and **c** after adding 2 mL of water.



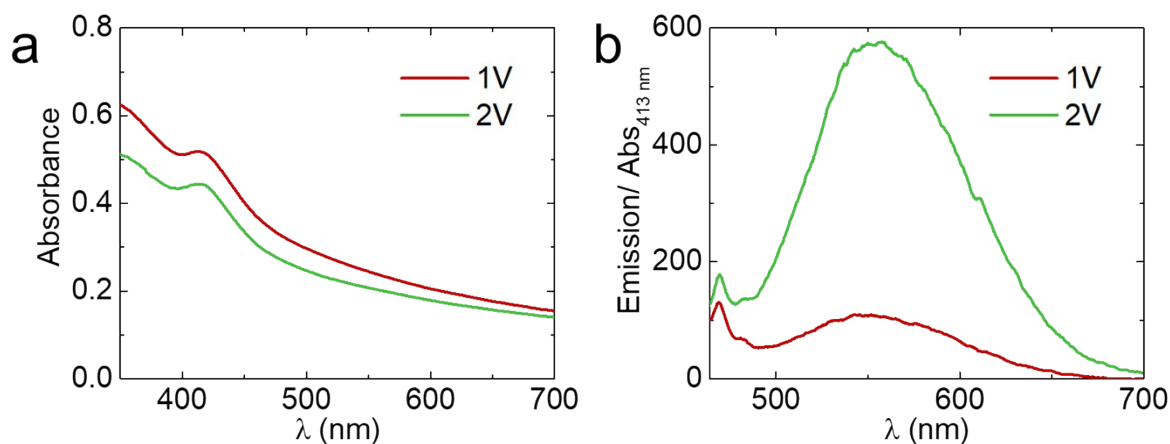
**Figure S5.** Linear sweep voltammograms for (a) MUA-capped CdS QDs and (b) a Ni wire electrode dipped in a 10 mM TBAPF-6 electrolyte solution.



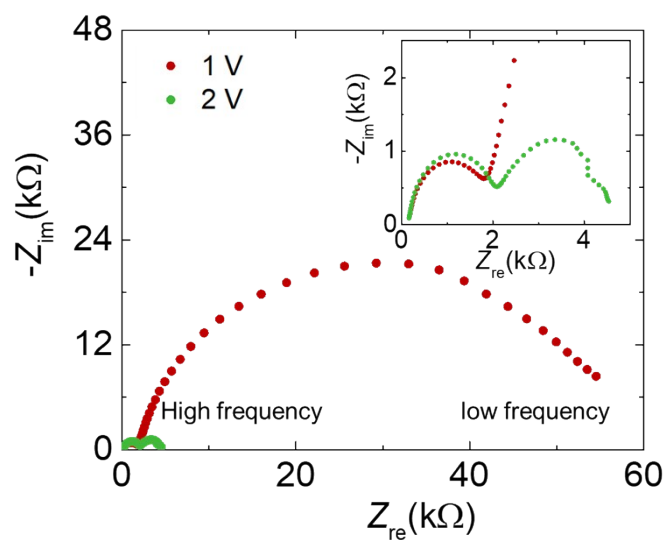
**Figure S6.** STEM-energy-dispersive x-ray spectroscopy (EDS) mapping of (a) 1 V and (b) 2 V gels at two different regions.



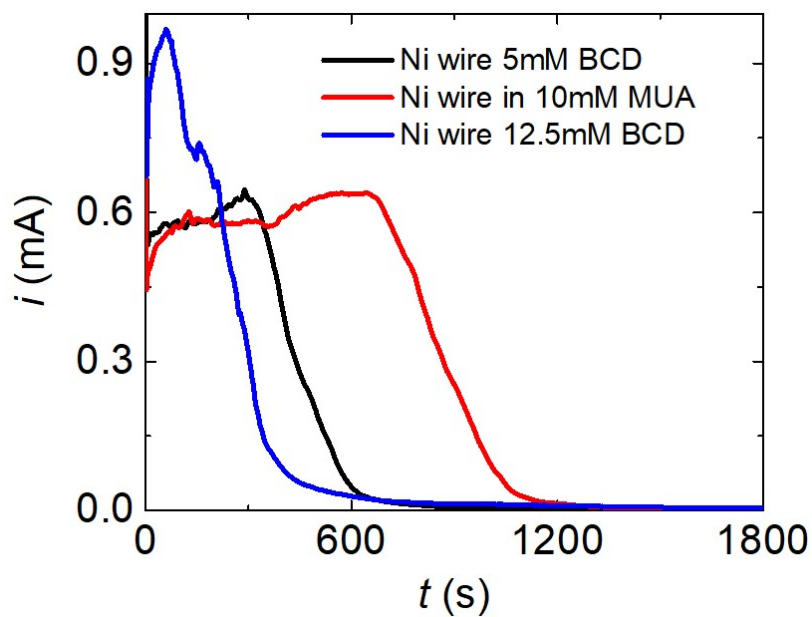
**Figure S7.** Infrared spectra of MUA-capped CdS QD gels prepared at 1 V and 2 V. Asymmetric and symmetric stretching vibrations of carboxylate groups in the gels were observed at  $\sim 1550$  and  $\sim 1410$   $\text{cm}^{-1}$ . The difference between the two carboxylate vibration peaks ( $\Delta\nu$ ) is used to identify the type of bonding between carboxylate and  $\text{Ni}^{2+}$ . A value in the range of 120-250  $\text{cm}^{-1}$  indicates a bridging bidentate interaction.  $\Delta\nu$  for the 1V and 2 V gels are 145 and 144  $\text{cm}^{-1}$ .



**Figure S8.** **a**, UV/Vis absorption and **b**, photoluminescence spectra of CdS QD gels prepared at 1 V and 2V.



**Figure S9.** Nyquist plots collected at 1 V and 2 V in a colloidal MUA-capped CdS QD solution. Inset shows the expanded view.



**Figure S10.** Current-time traces for Ni wire electrooxidation in 5 mM BCD (black), 12.5 mM BCD (blue), and 10 mM MUA (red) at 2 V.

**Table S1.** S 2p XPS peak fitting results. R-S refers to carbon-sulfur bonding.

	QD electrogelation, Ni		Ni electrooxidation, BCD		Ni electrooxidation, MUA	
	BE (eV)	%	BE (eV)	%	BE (eV)	%
S 2p 3/2	161.6	56.6	161.7	20.6	161.8	35.0
S 2p 1/2	162.7		162.8		162.7	
R-S 2p 3/2	163.2	12.7	163.6	77.3	163.6	30.6
R-S 2p 1/2	164.2		164.7		164.8	
S-O 2p 3/2	168.2	30.7	167.7	2.1	167.7	34.4
S-O 2p 1/2	169.3		168.9		168.9	