Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Fast Preparation of Ultrafine Monolayered Transition-Metal Dichalcogenide Quantum Dots using Electrochemical Shock for Explosive Detection

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Experimental Section

Chemicals: Tungsten sulfide (WS_2, 99.9%, Aladdin, USA), molybdenum sulfide (MoS_2, 98%, Aladdin, USA), tungsten selenide (WSe_2, 99.8%, Aladdin, USA), molybdenum selenide ($MoSe_2$, 99.9%, Alfa Aesar, USA), poly(vinylidene fluoride) (PVDF， Sigma, Germany), 1-methyl-2-pyrrolidinone (NMP, 98%, Aladdin USA), oleic acid (OA, aladdin, USA).

Preparation of working electrode and electrochemical shock: In a typical procedure, bulk TMD crystals (i. e. WS_2, MoS_2, WSe_2, $MoSe_2$) were prepared as working electrode by mixing with acetylene black and poly(vinylidene fluoride) (PVDF) dispersed in N-methylpyrrolidone (NMP) solutions. In the mixed slurry, the mass ratio of the bulk TMD material, acetylene black, and PVDF was 80:10:10. The resulting slurry was then uniformly coated on a copper foil and vacuum-dried at 100℃ overnight. Electrochemical nailing of Al^{3+} ions was performed in an open-air type cell with a CHI660 electrochemical workstation using a three-electrode system at room temperature. A platinum disk and an Ag/AgCl electrode were used for the counter and reference electrodes, respectively. 1 M Al^{3+} ion-containing propylene carbonate (PC) solution was used as the electrolyte. The current density during the discharge process after optimization was 0.11 mA/cm^2, 0.056 mA/cm^2, 0.056 mA/cm^2, 0.033mA/cm^2 for WS_2， MoS_2， WSe_2， $MoSe_2$, respectively. After the discharge process, the sample was washed with acetone to remove the residual organic materials, followed by 10 min's ultrasonication in oleic acid/ethanol solution (v:v~0.5:30). After the suspension was centrifuged, TMD QDs were obtained for further characterizations.

Characterization: A drop of a solution containing the produced TMD QDs were placed on a holey carbon-coated copper grid or a mica plate, and then naturally dried in air prior to characterization with transmission electron microscopy (TEM, FEI Technai G20) coupled with a field emission gun and EDS unit, atomic force microscopy (AFM, bruker instrument Dimension Icon), Raman spectrum was recorded on a LabRAM HR Raman spectrometer(HORIBA Jobin Yvon) with excitation laser of 532 nm. FT-IR spectra of QDs in KBr pellets were acquired using a Nicolet 6700 FT-IR spectrometer. UV-Vis absorption measurement was carried out on a UV-Vis spectrophotometer (V660, JASCO), PL were recorded on a fluorolog-3 fluorescence spectrophotometer.

Explosive detection. In typical experiment setup, 50uL of TNP (10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}M, respectively) was added to cuvette containing 3mL of WS_2 QDs under gently shake, the photoluminscence of pure WS_2 QDs upon excitation at 370 nm was measured, then the quenching experiment was set after the incremental addition of freshly prepared quencher, other control experiments were carried out according to the method described above.

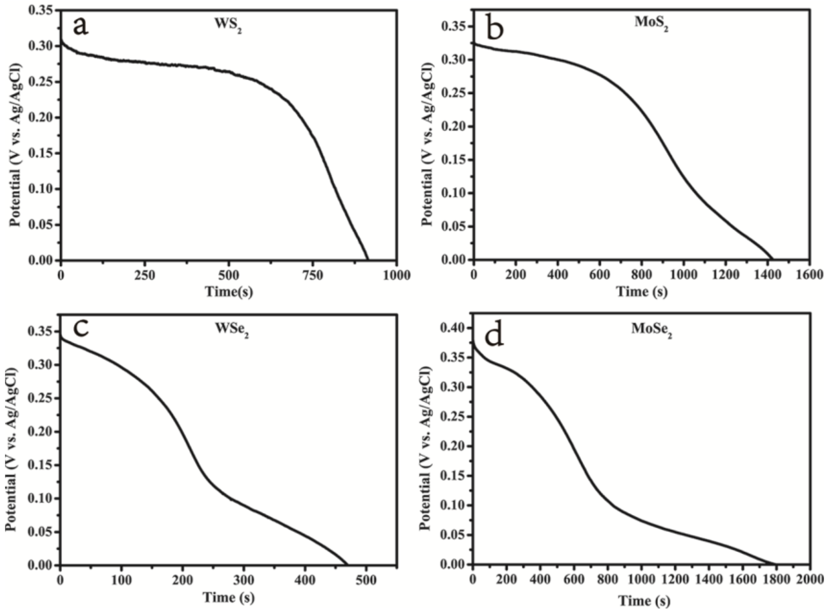


Figure S1. Galvanostaic discharge curves for a) WS_2, b) MoS_2, c) WSe_2, d) $MoSe_2$.

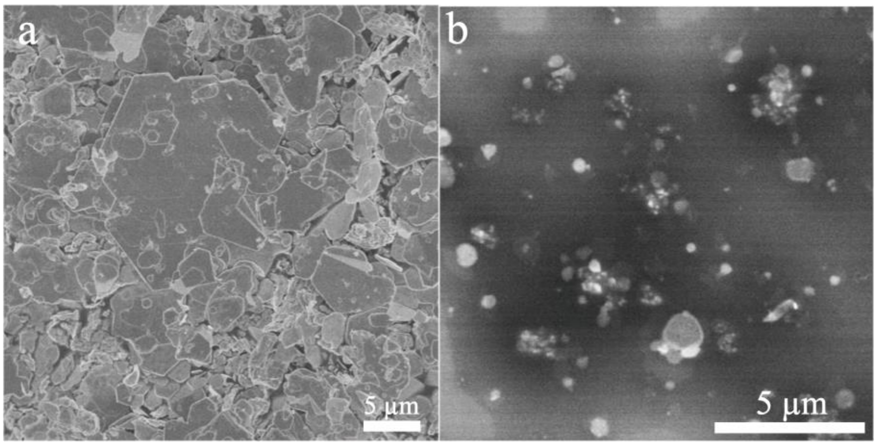


Figure S2. Typical SEM image before (a) and after (b) electrochemical shock

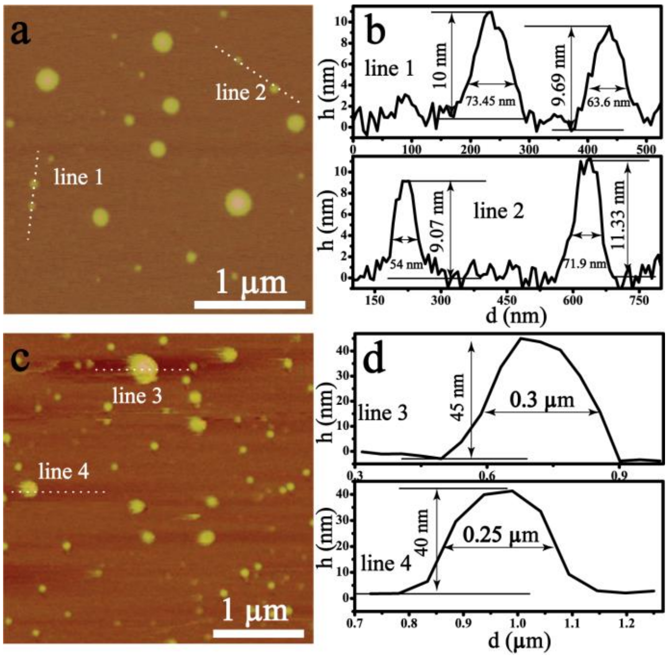


Figure S3. AFM images of WS_2. (a) WS_2 without oleic acid treatment. (b) Size profiles along the white dashed line in (a). (c) WS_2 without Al^{3+} ion treatment. (d) Size profiles along the white dashed line in (c). Without oleic acid treatment, the samples exhibit a large lateral size of dozens nanometers , although their thickness is only several nanometers (Fig. S3b). Without Al^{3+} ion treatment, WS_2 QDs can hardly be obtained, but only see particles larger than several hundred nanometers (Fig. S3d). These results confirm that oleic acid and Al^{3+} ion treatment are crucial to a successful fabrication of ultrafine QDs with high dispersion.

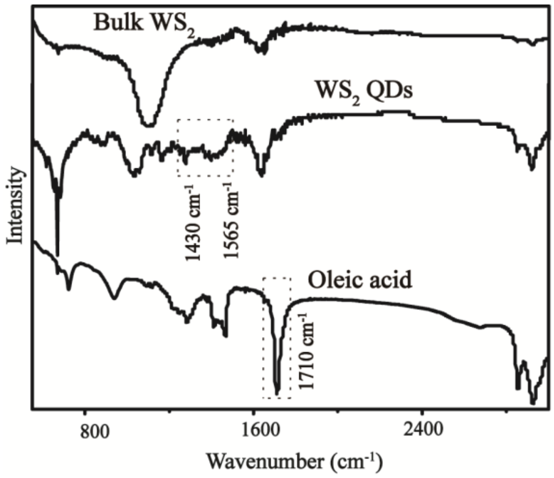


Figure S4. FTIR spectra of bulk WS_2, pristine oleic acid and the as-prepared WS_2 QDs. The sharp band at 1710 cm^{-1} deriving from C=O strech is absent in the FTIR of WS_2 QDs, while there appear two new peaks at 1430 and 1560 cm^{-1}, which can be attributed to the asymmetric $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ stretch between the carboxylate head of oleic acid and W atom.[1]

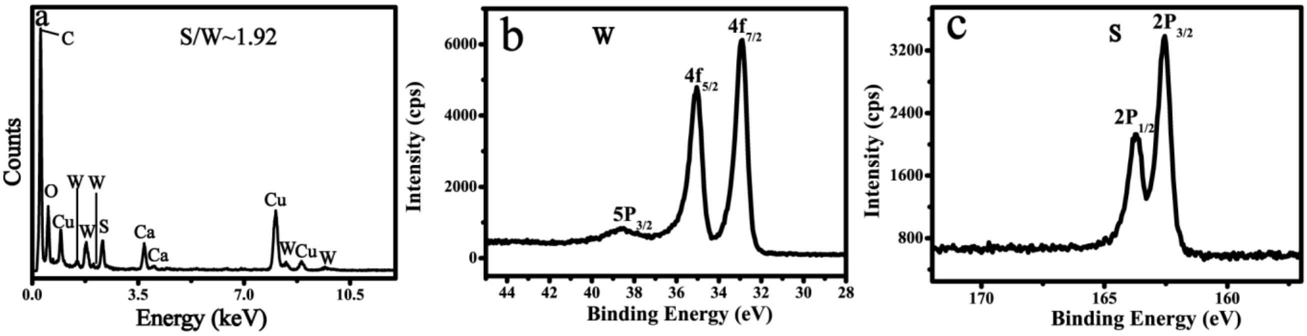


Figure S5. EDS and XPS spectra of the as-prepared WS_2 QDs. The signal of Cu, C, O and Ca elements originates from the copper grid and acetylene black impurity.

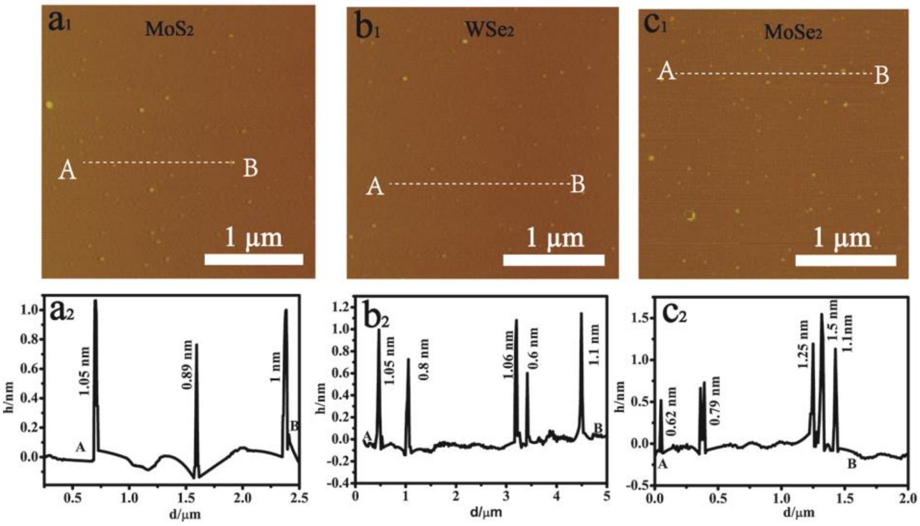


Figure S6. AFM images for a_1) MoS_2, b_1) WSe_2, c_1) $MoSe_2$, which give average thickness of ~0.78 nm, ~0.72 nm, ~1nm for a_2) MoS_2, b_2) WSe_2, c_2) $MoSe_2$ respectively, confirming other monolayer TMD QDs could also be successfully produced by our method.

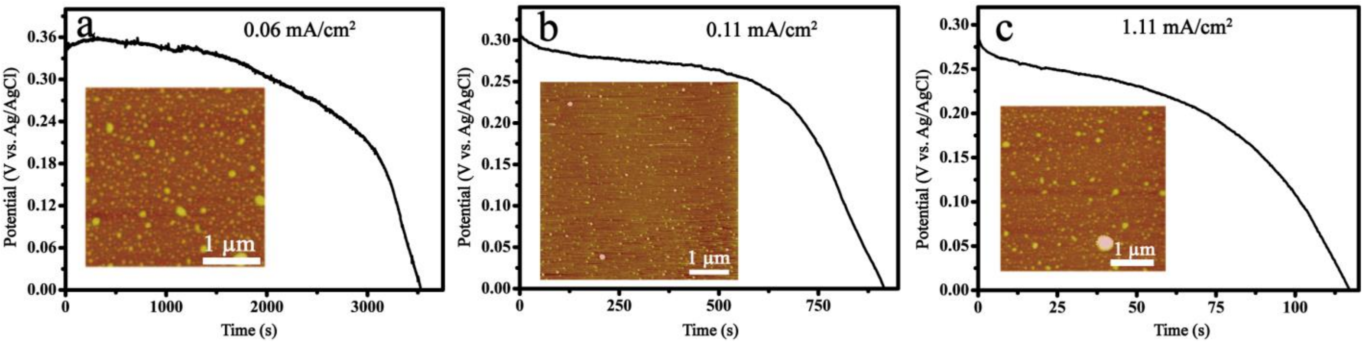


Figure S7. The discharge curves and corresponding AFM images under different current density for a) 0.06 mA/cm^2, b) 0.11 mA/cm^2, c) 1.11 mA/cm^2.

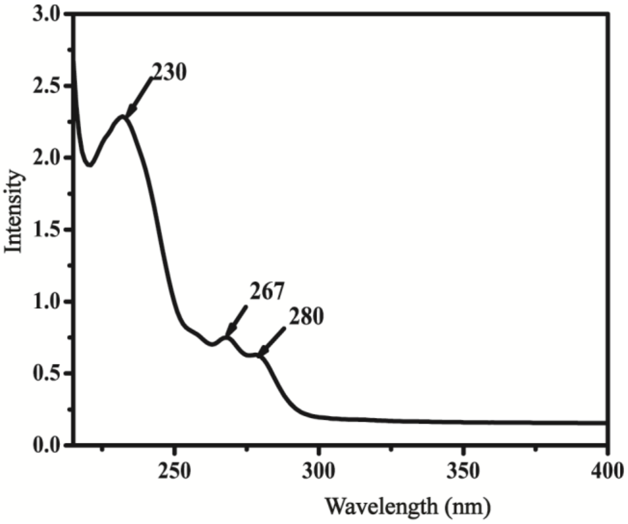


Figure S8. UV spectrum of pristine oleic acid, confirming the blue shift of the WS_2 QDs does not result from the adding of oleic acid in figure 3b.

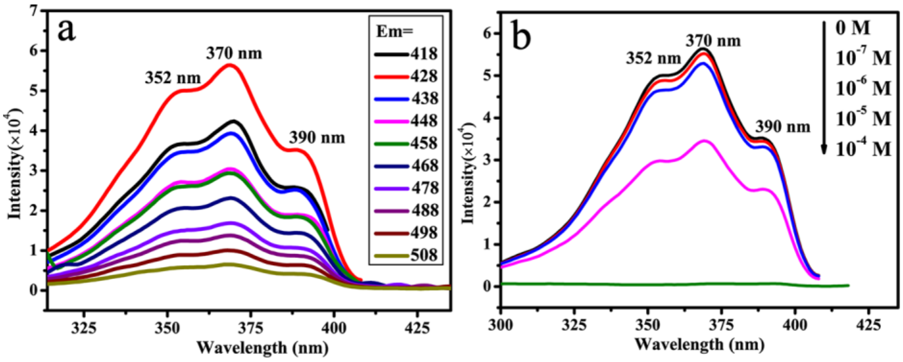


Figure S9. a) Photoluminescence excitation spectra (PLE) of pure WS_2 QDs with various excitation wavelengths. b) PLE spectra of WS_2 QDs in the presence of different TNP with different concentrations under the emssion wavelength at 428 nm.

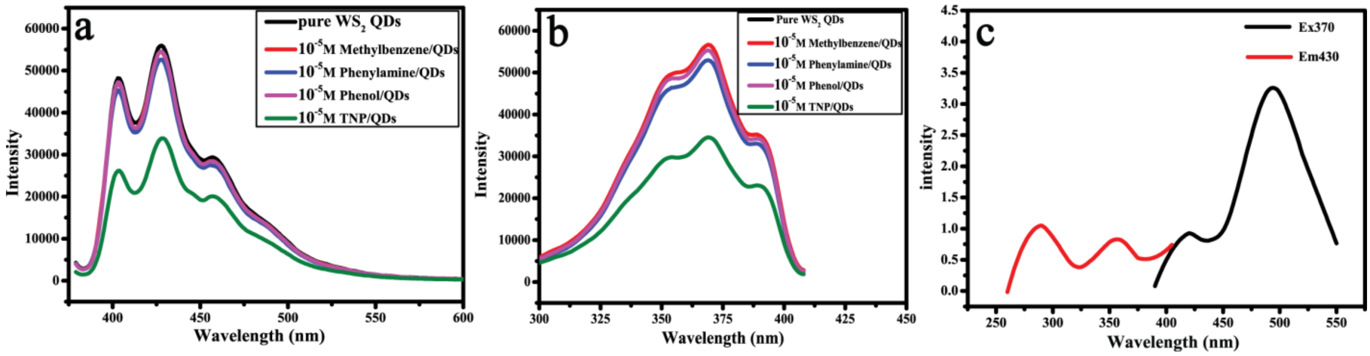
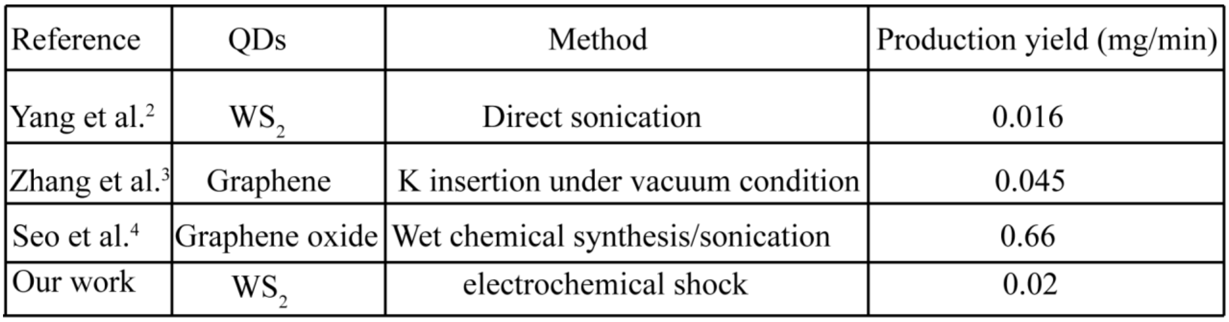


Figure S10. a) PL spectra of WS_2 QDs solution under excitation at 370 nm with different quenchers. b) The corresponding PLE spectra under emission at 430 nm. c) PL and PLE spectra of pure TNP solution.

Table S1 Production yield of quantum dots from literatures[2-4]



Reference	QDs	Method	Production yield (mg/min)
Yang et al.[2]	WS_2	Direct sonication	0.016
Zhang et al.[3]	Graphene	K insertion under vacuum condition	0.045
Seo et al.[4]	Graphene oxide	Wet chemical synthesis/sonication	0.66
Our work	WS_2	electrochemical shock	0.02

Notes and references

1 S. V. P. Vattikuti, C. Byon and Chittun, V, *Superlattice Microstruct*., 2016, **94**, 39-50.

2 X. Zhao, X. Ma, J. Sun, D. H. Li and X. R. Yang, *ACS Nano*, 2016, **10**, 2159-2166.

3 L. X. Lin and S. W. Zhang, *Chem. Commun*., 2012, **48**, 10177-10179.

4 F. Liu, M. H. Jang, H. D. Ha, J. H. Kim, Y. H. Cho and T. S. Seo, *Adv. Mater*., 2013, **25**, 3657-3662.