Electronic Supplementary Information

1% defect enriches MoS_2 quantum dots: catalysis and blue luminescence

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1. Supporting Figures

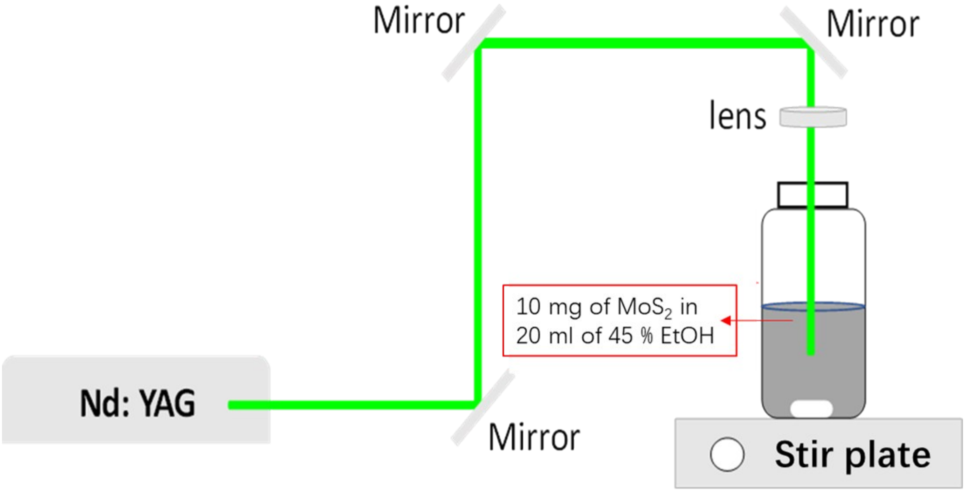

Fig. S1 MoS$_2$ QDs synthesis by PLA in the binary solvent.

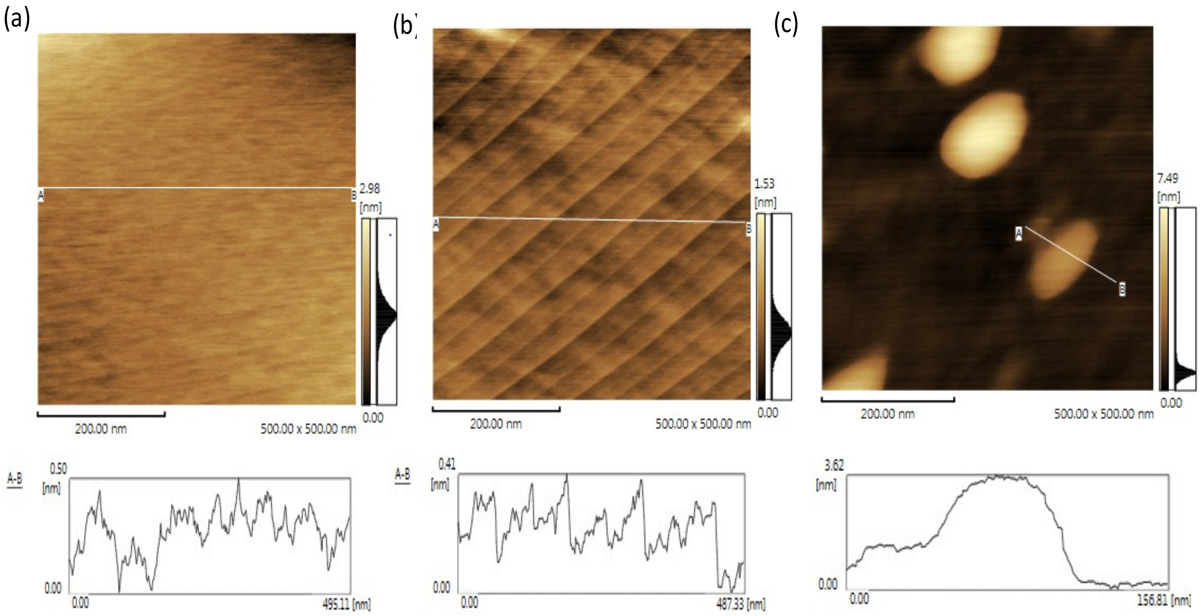

Fig. S2 AFM images of (a) silicon wafer, (b) binary solvent dropped on the silicon wafer and dried, and (c) MoS$_2$ QDs dissolved in the binary solvent dropped on the silicon wafer and dried.

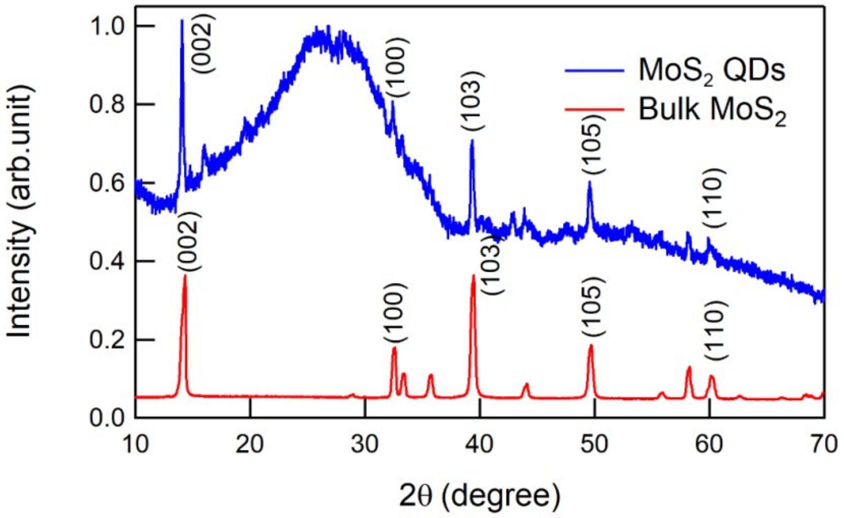

Fig. S3 XRD patterns of the MoS_2 QDs prepared by PLAL (blue) and bulk MoS_2 (red). These Miller indices are attributed to those of ref. 1. The data indicates that MoS_2 is crystalline. The broad diffraction at around 25 degree is due to the sample holder made of low reflection silicon.

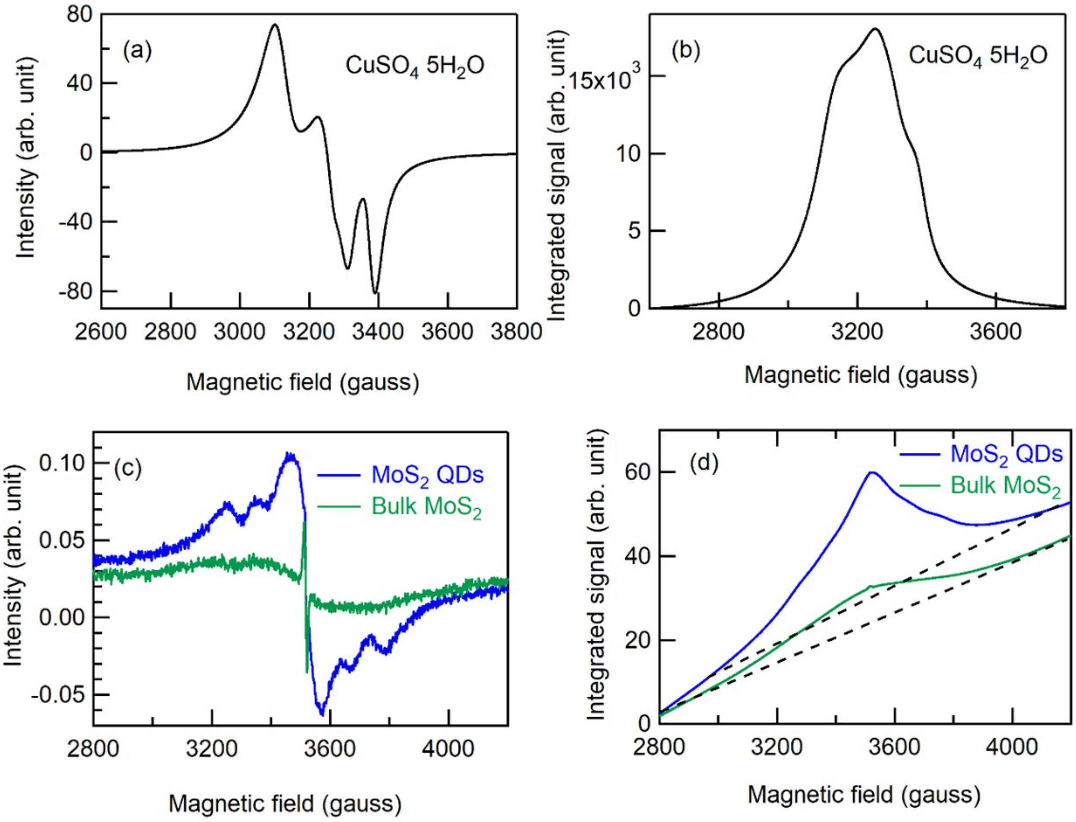

Fig. S4 ESR spectra of (a) $CuSO_4$•$5H_2O$ as a standard sample to estimate spin density and (c) MoS_2 QDs (blue) and bulk MoS_2 (green). Integrated profiles of ESR spectra of (b) $CuSO_4$•$5H_2O$ and (d) MoS_2 QDs (blue) and bulk MoS_2 (green). Spin density, sulfur vacancy density, is estimated from the area of sample (d) divided by that of standard (b). Under the same molar amount between sample and standard, sulfur vacancies of MoS_2 QDs and bulk MoS_2 are obtained as 0.97 % and 0.16 %, respectively, indicating the percentage of vacancies in all of sulfur atoms involved in those MoS_2

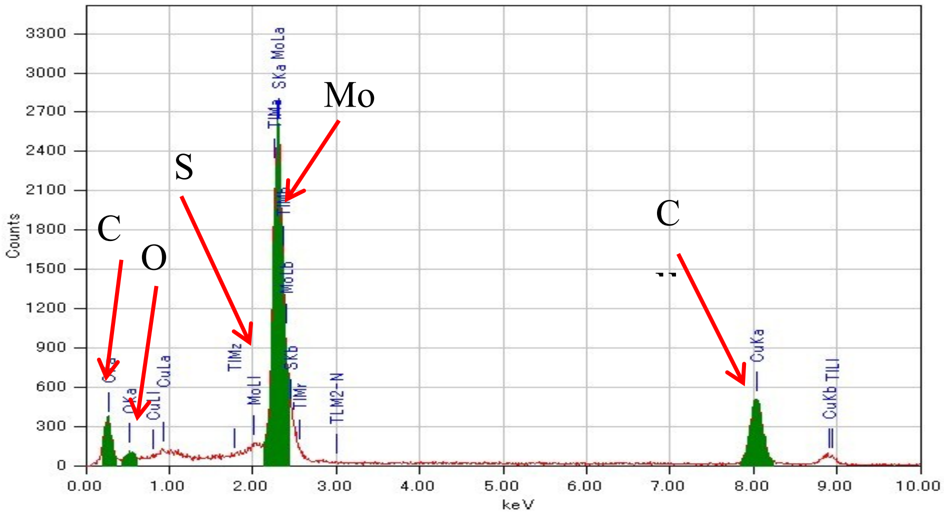

Fig. S5 EDS elemental analysis of MoS_2 QDs. The Cu signal is from the copper grid, and the C and O signals are from a supporting polymer film on the grid. The data shown is MoS_2 QDs on the grid. There are no impurities.

2. Size effect of the absorption of 2D MoS_2

It has been well known that semiconductor materials show the quantum confinement effect, which increases the band gap energy (E_g), as its size, i.e. quantum dot (QD), approaches to the Bohr radius of exciton.[2,3] The experimental data for the size effect of QD prepared from a 3D semiconductor, e.g. CdSe, have been well characterized.[4] As for the quantum confinement effect on the 2D layer materials, it has been described by the confinement along z-axis as eqs. (1) and (2).[5-8]

$$E_g^* = E_g + \Delta E_g \tag{1}$$

$$\Delta E_g = \frac{\hbar^2 \pi^2}{2\mu L_z^2} \tag{2}$$

where E_g^* is the band gap energy of a 2D layer material, E_g the band gap energy of a 2D bulk material, ΔE_g the increased amount due to the quantum confinement effect, $\hbar$ the Dirac constant, μ reduced mass of exciton, L_z the layer thickness along z-direction, based on the effective mass approximation. Figure S6a shows the results of four bands of MoS_2 calculated from eqs. (1) and (2); reduced mass μ was used as a reported value of $\mu = 0.18m_0$,[8] where m_0 is the electron rest mass. However, the calculated data deviate from the experimental ones, as shown in Fig. S6b. Such a deviation has been observed in various systems of 2D nanomaterials.[5-8] One of the reasons for their deviations seems to be due to dimensionality, i.e. how an anisotropic structure of 2D materials is treated in 0 or 1 D materials such as a QD, quantum wire, and cluster. Figure S6b shows the size vs. E_g^* by reproducing well-defined experimental data of MoS_2 clusters as a function of size (diameter)[8] (see Figs. 5 and 8 in ref.8). The data indicates significant size dependence of E_g*. According to eq. (2), the calculated E_g is linearly proportional to the

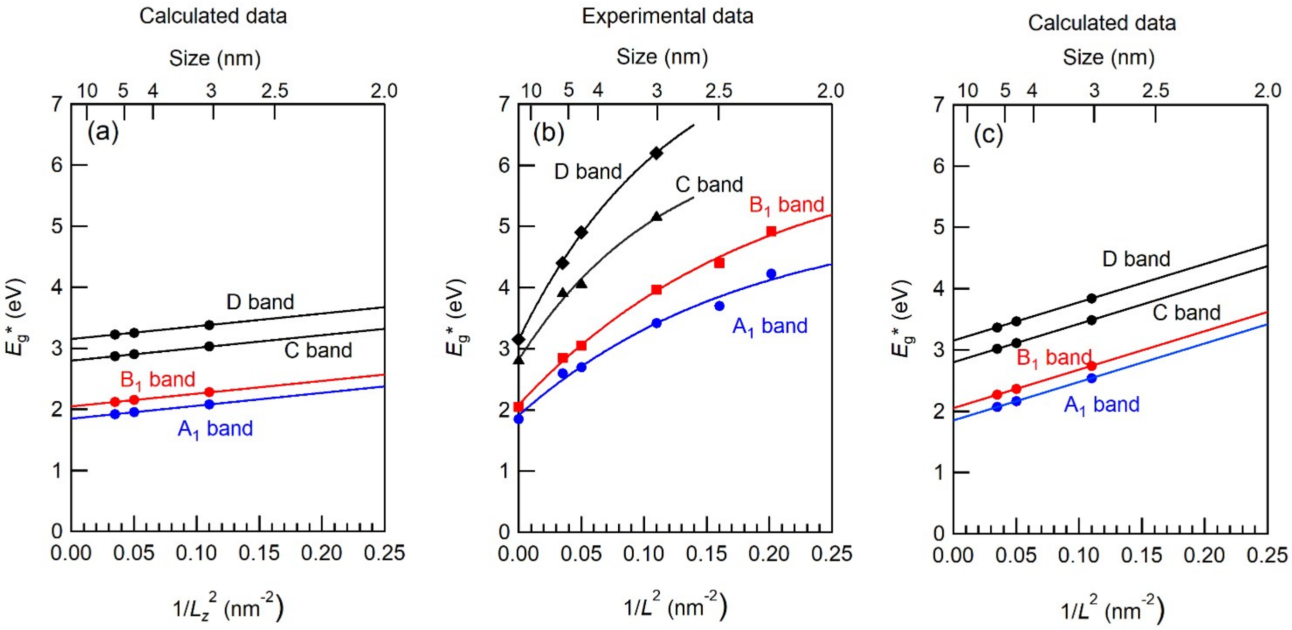

Fig. S6 Changes of band gap energies due to quantum conferment effects of MoS_2 QD of (a) calculated data using eqs. (1) and (2) and (b) experimental data reproduced from Fig. 8 in ref. 8. (c) calculated data using $E_g^*=E_g+3\Delta E_g$. Sizes, *L*, in (a), (b), and (c) denote the thickness of MoS_2 layer, the diameter of MoS_2 cluster, and a side length of MoS_2 nanocubic.

$1/L_z^2$, whereas the experimental data show nonlinear profile. In addition, the amount of ΔE_g is significantly larger in the experimental data. As for another case, we examined $E_g^*=E_g+3\Delta E_g$, if MoS_2 QD would confine the exciton as an isotropic in *x*-, *y*-, *z*- directions, as shown in Fig. S6c. This enhances the change of E_g^*, but the calculated values are smaller than those of experimental data. Therefore, the experimental data become crucial to characterize the quantum confinement effect of 2D QDs. Studies on a theoretical research to characterize 2D QDs will be important to understand the quantum confinement effect of anisotropic QDs.

References

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