Electronic Properties of Triangle Molybdenum Disulfide (MoS₂) Clusters with Different Sizes and Edges

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Abstract: The electronic structures and transition properties of three types of triangle MoS₂ clusters, A (Mo edge passivated with two S atoms), B (Mo edge passivated with one S atom), and C (S edge) have been explored using quantum chemistry methods. The highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap of B and C is larger than that of A, due to the absence of the dangling of edge S atoms. The frontier orbitals (FMOs) of A can be divided into two categories, edge states from S p at the edge and hybrid states of Mo d and S p covering the whole cluster. Due to edge/corner states appearing in the FMOs of triangle MoS₂ clusters, their absorption spectra show unique characteristics along with the edge structure and size.

Keywords: molybdenum disulfide clusters; electronic properties; quantum chemistry; nanomaterials

1. Introduction

Since the successful isolation of graphene [1,2], atomic layer-thick two-dimensional (2D) nanomaterials have attracted a great deal of attention due to their excellent mechanical flexibility and optical transparency, as well as their ultrahigh specific surface, which are related to their strong in-plane covalent bond and atomic thickness [3–7]. Beyond graphene, single-layer transition-metal dichalcogenides (TMDs) have been receiving increasing interest. For example, the structural and physical properties of the MoS₂ monolayer and bulk have been extensively studied both theoretically and experimentally. The monolayer of MoS₂ consists of a layer of Mo atoms sandwiched between two layers of S atoms, forming a trilayer. The absence of inversion symmetry and dominant d-electron interactions of the heavy transition metal atom Mo, endow the monolayer (MoS₂) with intriguing physical properties that are not found in sp-bonded nanomaterials [8–11].

In recent years, an increasing amount of effort has been devoted to 2D materials with ultrasmall sizes, due to increasing demand for miniaturizing photonic and optoelectronic devices. For MoS₂, from the three-dimensional (3D) bulk structure to the 2D monolayer, the band gap transforms from an indirect band gap (∼1.2 eV) to a direct band gap (∼1.8 eV, in the visible frequency range) [12,13]. Compared with their 2D and one dimensional (1D) counterparts, zero dimensional (0D) MoS₂ clusters possess tunable energy levels, more active edges, and larger surface-area-to-volume ratios, which give them fascinating properties. This makes them promising candidates for application in fields such as optoelectronics [14,15], electrochemical technology [16,17], biology [18], catalysis [19] and so forth [20–22]. Jaramillo et al. [23] pointed out that 2D TMDs are hydrogen evolution reaction (HER) active because of their highly active edges, which makes them potential
candidates for electrocatalytic hydrogen evolution. Yin et al. [24] pointed out that a strong second-harmonic generation (SHG) can be observed at the edges and corners of MoS$_2$ clusters, implying the important role that edges and corner states play in determining the properties of the 0D structures. However, the detailed transition natures are ambiguous. In order to shed light on the essence of the various applications and obtain full use of the MoS$_2$ clusters, it is crucial to gain a comprehensive understanding of the electronic structures and their transition properties.

It is well known that when the physical size of the material is comparable to or smaller than the Bohr radius, the excitons are confined in all three dimensions, so there exists a 3D quantum confinement effect. Superimposed on the intrinsic size-dependent electronic structure, one thus has the effect of edges, corners, atomic vacancies and so forth, all these are likely to induce additional local effects. As a result, the electronic properties become increasingly sensitive not only to sizes, but to the shapes, edge atomic structures, and compositions [25–27]. Despite the breakthroughs in preparation of MoS$_2$ clusters over the years, mainly including top-down [28–33] and bottom-up methods [34–36], a cost-effective yet efficient technique for the high yield production of MoS$_2$ clusters with desirable sizes remains a challenge. Consequently, it is still difficult to provide a specific illustration about the properties of MoS$_2$ clusters experimentally. Aiming to obtain the whole picture in relation to MoS$_2$ clusters and to clarify the relationships between structures and properties, the density-of-states (DOS), frontier molecular orbitals (FMOs), electronic absorption spectra, and electron-hole characteristics of a series of triangular MoS$_2$ clusters with different sizes and edges will be explored using quantum chemistry methods in the present paper. This will be of great significance not only in fundamental physics exploration but also in device applications.

2. Models and Computational Details

Based on different edge structures, there are mainly three types of triangle MoS$_2$ clusters, as shown in Figure 1. A and B represent the Mo-terminated (commonly referred as Mo-edge) triangle MoS$_2$ clusters, while C is the S-terminated cluster (commonly referred as S-edge). Considering that a bare Mo-edge is not stable, it is often passivated by one or two S atoms per edge-Mo atom. In A, each edge-Mo atom is passivated with two S atoms forming an S-dimer normal to the basal plane, usually called a Mo edge, with 100% S coverage.

In the case of B, two adjacent edge-Mo atoms share one S atom forming an S-monomer parallel to the basal plane, usually called a Mo edge, with 50% S coverage. Consequently, the S atoms of C dimerize along the direction normal to the basal plane, often called a S edge, with 100% coverage. By changing the number of the edge-Mo atoms n (n = 3, 4, 5, and 6) in A, B, and C, a series of different triangle MoS$_2$ clusters with different sizes and edges could be gained. In the following discussions, A refers to four triangle MoS$_2$ clusters with the same edges but different sizes, including 3A, 4A, 5A, and 6A, as B and C.

The density functional theory (DFT) based on Becke's three-parameter hybrid exchange combined with the Lee–Yang–Parr correlation (B3LYP) [37,38] and the LANL2DZ basis set were adopted to optimize the geometries of the triangular MoS$_2$ clusters. With both the merits of B3LYP and long-range corrected properties, CAM-B3LYP is able to predict molecular charge-transfer spectra properly due to the improved description of the long-range exchange interactions [39–42]. It is employed to evaluate the electron excitations with the LANL2DZ basis set in the present work.

The DFT calculations were performed using the Gaussian 09 program [43]. The data of DOS, electronic absorption spectra, and electron-hole distributions were obtained with the Multiwfn package [44].
3. Results and Discussion

In order to indicate the stability of A, B, and C, the formation energy was calculated according to the formula: 

$$E_{\text{formation}} = E_{\text{cluster}}(\text{Mo}_m\text{S}_n) - mE(\text{Mo}) - nE(\text{S})$$

where $E_{\text{cluster}}(\text{Mo}_m\text{S}_n)$, $E(\text{Mo})$, and $E(\text{S})$ denote the energy of the cluster having $m$ Mo atoms and $n$ S atoms, the energy of a single Mo atom, and the energy of a single S atom, respectively. The calculated $E_{\text{formation}}$ values of A, B, and C are listed in Tables 1–3, respectively. The negative $E_{\text{formation}}$ values imply that the clusters are stable. The $E_{\text{formation}}$ decrease with increasing the sizes of the cluster, suggesting that the larger the cluster, the more energy is released.

Table 1. Formation energy $E_{\text{formation}}$ (eV), energy of the highest occupied molecular orbital (HOMO) $E_H$ (eV), energy of the lowest unoccupied molecular orbital (LUMO) $E_L$ (eV), energy gap between HOMO and LUMO $E_{gap}$ (eV), as well as orbital composition of HOMO $C_H$ and LUMO $C_L$ of 3A, 4A, 5A, and 6A.

|       | 3A   | 4A   | 5A   | 6A   |
|-------|------|------|------|------|
| $E_{\text{formation}}$ | −151.84 | −240.28 | −348.85 | −476.47 |
| $E_H$ | −5.06 | −5.55 | −5.29 | −5.71 |
| $E_L$ | −6.84 | −6.25 | −5.95 | −6.45 |
| $E_{gap}$ | 1.78 | 0.70 | 0.66 | 0.73 |
| $C_H$   | Mo: $d_{xy}$, $d_{x^2y^2}$, $d_{z^2}$ | S: $p_x$, $p_y$ | S: $p_x$, $p_y$ | S: $p_x$, $p_y$ |
| $C_L$   | S: $p_x$, $p_y$ | S: $p_x$, $p_y$ | S: $p_x$, $p_y$ | Mo: $d_{xy}$, $d_{x^2y^2}$, $d_{z^2}$ |

Figure 1. Top view of the triangle MoS$_2$ clusters with different sizes and edges. The Mo and S atoms are represented by green and yellow spheres, respectively.
Table 2. Formation energy $E_{\text{formation}}$ (eV), energy of HOMO $E_{\text{H}}$ (eV), energy of LUMO $E_{\text{L}}$ (eV), energy gap between HOMO and LUMO $E_{\text{gap}}$ (eV), as well as orbital composition of HOMO $C_H$ and LUMO $C_L$ of 3B, 4B, 5B, and 6B.

|        | 3B   | 4B   | 5B   | 6B   |
|--------|------|------|------|------|
| $E_{\text{formation}}$ | -120.27 | -200.28 | -297.42 | -415.25 |
| $E_{\text{H}}$ | -5.80 | -5.23 | -5.72 | -5.96 |
| $E_{\text{L}}$ | -7.00 | -7.33 | -6.74 | -7.07 |
| $E_{\text{gap}}$ | 1.19 | 2.10 | 1.02 | 1.11 |

For the three different classes of clusters, their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and their energy gaps, as well as the orbital compositions of HOMO $C_H$ and LUMO $C_L$ of 3C, 4C, 5C, and 6C.

Table 3. Formation energy $E_{\text{formation}}$ (eV), energy of HOMO $E_{\text{H}}$ (eV), energy of LUMO $E_{\text{L}}$ (eV), energy gap between HOMO and LUMO $E_{\text{gap}}$ (eV), as well as orbital composition of HOMO $C_H$ and LUMO $C_L$ of 3C, 4C, 5C, and 6C.

|        | 3C   | 4C   | 5C   | 6C   |
|--------|------|------|------|------|
| $E_{\text{formation}}$ | -137.42 | -219.60 | -321.09 | -441.37 |
| $E_{\text{H}}$ | -5.59 | -5.74 | -5.57 | -5.71 |
| $E_{\text{L}}$ | -6.54 | -6.67 | -6.74 | -6.79 |
| $E_{\text{gap}}$ | 0.96 | 0.92 | 1.17 | 1.08 |

For the three different classes of clusters, their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies and their energy gaps, as well as the orbital compositions of HOMO $C_H$ and LUMO $C_L$.

For these ultrasmall MoS$_2$ clusters, the band gap does not decrease monotonically with size as is the case for graphite flakes, which might be attributed the deformation of structures due to large the ratio of number of edge atoms to core atoms in ultrasmall clusters. The energy of HOMO ($E_{\text{H}}$) in 3A is $-5.06$ eV, while that of LUMO ($E_{\text{L}}$) is $-6.84$ eV, resulting in a $1.78$ eV energy gap ($E_{\text{gap}}$). The $E_{\text{gap}}$ value of 4A, 5A, and 6A is $0.70$, $0.66$, and $0.73$ eV, respectively, far smaller than that of 3A. For the Mo-terminated triangle MoS$_2$ clusters with 100% S coverage, some FMOs contributed from S$_{3p}$ at the edge exhibit evident edge states, and the other FMOs exhibit hybrid states of Mo$_{4d}$ and S$_{3p}$ whose charge distribution covers the whole cluster. By comparing the electronic structures of three classes of clusters, it can be seen that the energy gap of the ultrasmall MoS$_2$ clusters is dependent on the edge structure, which is similar to graphite flake. For Mo-terminated triangle MoS$_2$ clusters with 50% S coverage (B) and S-terminated triangle MoS$_2$ clusters (C), their S atoms at the edge of the cluster are shared by two adjacent Mo atoms. In contrast to the A system, the absence of dangling edge S atoms in the two class clusters increases their HOMO–LUMO gap and evident edge/corner states can be observed in the FMOs of these clusters. For B, all the FMOs comes from the hybridization between Mo$_{4d}$ and S$_{3p}$. While the occupied FMOs mainly comes from the S$_{3p}$, and the unoccupied FMOs from the hybridization between Mo$_{4d}$ and S$_{3p}$ in the case of C.
Figure 2. The density-of-states (DOS) map, as well as HOMO and LUMO distributions of A, B, and C. The discrete represents the MOs, the black, blue, and red curves represent the total DOS, partial DOS of S3, and partial DOS of Mo4d, respectively.

The electronic absorption spectra of A, B, and C and their corresponding electron-hole distributions where the process of single-electron excitation is described as “an electron goes to the electron from the hole” are given in Figures 3–6, respectively. Moreover, the percentage of Mo4d and S3p in the electron and hole are provided in Tables 4–6, respectively. The maximum absorption shows a red shift along with increasing size of the clusters in the A, B and C systems. For 3A, 4A, 5A, and 6A, the maximum absorption is ~623.61, ~591.50, ~670.54, and 796.87 nm, respectively. From Table 4, the percentage of S3p is larger than that of Mo4d in both the electron and hole in 3A, Mo4d takes the larger proportion in the electron and the hole in 4A and 5A. The S3p and Mo4d make almost the same contribution to the electron and the hole in 6A. Combined with the data in Figure 4, there are two types of electron transitions: one is a d-d transition of the Mo atoms, and the other occurs at the S atoms along the edges, which is associated with the edge states.

Figure 3. Electronic absorption spectra with full width at half maximum (FWHM) 0.26 of A, B, and C.
Figure 4. Electron (green) and hole (blue) distributions with isosurface 0.0006 for 3A, 4A, 5A and 6A.

Figure 5. Electron (green) and hole (blue) distributions with isosurface 0.0006 for 3B, 4B, 5B and 6B.

Figure 6. Electron (green) and hole (blue) distributions with isosurface 0.0006 for 3C, 4C, 5C and 6C.
The maximum absorption is ~422.32, ~609.91, ~656.23, and 678.05 nm for 3B, 4B, 5B, and 6B, respectively. The electrons and holes distribute along the edges/corners. The percentage of Mo_{4d} in the electron is larger than that of S_{3p}, while the percentage of S_{3p} in the hole is larger than that of Mo_{4d}, leaving S atoms with the feature of hole and Mo atoms with the feature of the electron. In other words, the electron prefers to transfer from the S_{3p} to the connected Mo_{4d} along the edges/corners of B. The maximum absorption is ~502.21, ~654.45, ~633.81, and 845.93 nm for 3C, 4C, 5C, and 6C, respectively. The electron and hole distribute at the corners with the S atoms at the top vertex acting as hole and the Mo atoms neighboring acting as the electron (see Table 6 and Figure 6).
Table 6. $S_0 \rightarrow S_1$ transition, $S_0 \rightarrow S_n$ transition, and the percentage of $Mo_{4d}$ and $S_{3p}$ in electron and hole of 3C, 4C, 5C, and 6C.

| Transition | Electron, % | Hole, % |
|------------|-------------|---------|
| $3C$       |             |         |
| $S_0 \rightarrow S_1$ | $Mo_{4d}$: 58.26 | $Mo_{4d}$: 20.09 |
|            | $S_{3p}$: 27.97 | $S_{3p}$: 64.86 |
| $S_0 \rightarrow S_{17}$ | $Mo_{4d}$: 55.81 | $Mo_{4d}$: 34.75 |
|            | $S_{3p}$: 26.89 | $S_{3p}$: 43.73 |
| $S_0 \rightarrow S_1$ | $Mo_{4d}$: 47.55 | $Mo_{4d}$: 2.55 |
|            | $S_{3p}$: 36.23 | $S_{3p}$: 86.51 |
| $S_0 \rightarrow S_31$ | $Mo_{4d}$: 54.91 | $Mo_{4d}$: 21.46 |
|            | $S_{3p}$: 41.67 | $S_{3p}$: 74.25 |
| $4C$       |             |         |
| $S_0 \rightarrow S_1$ | $Mo_{4d}$: 57.86 | $Mo_{4d}$: 2.79 |
|            | $S_{3p}$: 23.43 | $S_{3p}$: 83.63 |
| $S_0 \rightarrow S_{17}$ | $Mo_{4d}$: 49.91 | $Mo_{4d}$: 28.54 |
|            | $S_{3p}$: 31.92 | $S_{3p}$: 49.41 |
| $5C$       |             |         |
| $S_0 \rightarrow S_1$ | $Mo_{4d}$: 55.02 | $Mo_{4d}$: 2.45 |
|            | $S_{3p}$: 17.42 | $S_{3p}$: 76.37 |
| $6C$       |             |         |
| $S_0 \rightarrow S_1$ | $Mo_{4d}$: 42.57 | $Mo_{4d}$: 12.33 |
|            | $S_{3p}$: 21.73 | $S_{3p}$: 53.19 |

Overall, the $S_0 \rightarrow S_n$ transitions corresponding to the maximum absorption of the Mo-terminated triangle MoS$_2$ clusters with 100% S coverage A come from two aspects, the $d$-$d$ transitions of the Mo atom and transitions of $S_{3p}$ along the edge. The $S_0 \rightarrow S_n$ transitions of B and C occur at the edges/corners, with an electron transferring from the S atoms to the neighboring Mo atoms. In other words, the S atoms act as the hole and the adjacent Mo atoms act as the electron in the case of the clusters with no dangling of edge S atoms in them. The $S_0 \rightarrow S_1$ transition directly leads to the lowest excited state and is always the excited state for luminescence. For the $S_0 \rightarrow S_1$ transition of A, the electron and hole mainly distribute throughout the whole triangular clusters; this can be observed faintly at the S atoms along the edges (see Figure 4). Referred to the data in Table 4, the percentage of $Mo_{4d}$ in electron and hole not only takes a larger proportion but also has nearly the same values, which implies obvious $d$-$d$ transitions of the Mo atoms. The $S_0 \rightarrow S_1$ transitions of B also occur at the edges/corners, as shown in Figure 5. By referring to the data in Table 5, both the Mo and S atoms possess the distribution of electrons and holes, which ascribes the $S_0 \rightarrow S_1$ from local transition. For the $S_0 \rightarrow S_1$ transitions of C, the percentage of $Mo_{4d}$ in the electron is larger than that in the hole, while the percentage of $S_{3p}$ in the hole is larger than that in the electron, implying significant electron transfer from the S atoms to the neighboring Mo atoms along the edges (see Figure 6).

4. Conclusions

The electronic properties of three types of triangle MoS$_2$ clusters, A (Mo-edge passivated with two S atoms), B (Mo-edge passivated with one S atom), and C (S-edge) have been explored using quantum chemistry methods in the present paper. The DOS appears to have different features in A, B, and C. For A, the MOs can be divided into two types: the edge state from $S_{3p}$ along the edges, the hybrid state from $Mo_{4d}$ and $S_{3p}$ covering the whole cluster. Evident edge/corner states appear in the FMOs of B and C. The hybridization of $Mo_{4d}$ and $S_{3p}$ in B generate the occupied and unoccupied MOs. The occupied MOs mainly come from $S_{3p}$, and the unoccupied MOs from the hybridization of $Mo_{4d}$ and $S_{3p}$ in C.

For the electron excitation processes of A, B, and C, the absorption peaks show a red shift along with increasing the size of the clusters. Electron–hole analysis indicated that the $S_0 \rightarrow S_1$ transitions appear to have different characteristics compared with the $S_0 \rightarrow S_n$ transitions (associated with the intense absorption in the electronic absorption spectrum) in A, B, and C. In A, the $S_0 \rightarrow S_1$ transitions mainly stem from the $d$-$d$ transitions of the Mo atoms, while the $S_0 \rightarrow S_n$ transitions come from the $d$-$d$ transitions of the Mo atom or transitions of the $S_{3p}$ along the edges. Both the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_n$ transitions of B occur
at the edges/corners, with the local $S_0 \rightarrow S_1$ transitions originating from Mo$_{4d}$ and S$_{3p}$, but charge transfer $S_0 \rightarrow S_n$ transitions caused by the electron transferring from S$_{3p}$ to the connected Mo$_{4d}$. In C, the $S_0 \rightarrow S_1$ transitions mainly occur along the edge with the S atoms acting as hole and the adjacent Mo atoms as electron, while the $S_0 \rightarrow S_n$ transitions mainly occur at the corners, where the two S atoms at the vertex acts as the hole and the adjacent Mo atoms act as the electron.

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References

1. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Electric Field Effect in Atomically Thin Carbon Films. Science 2004, 306, 666–669. [CrossRef] [PubMed]
2. Geim, A.K.; Novoselov, K.S. The rise of graphene. Nat. Mater. 2007, 6, 183–191. [CrossRef]
3. Xu, M.; Liang, T.; Shi, M.; Chen, H. Graphene-Like Two-Dimensional Materials. Chem. Soc. Rev. 2013, 113, 3766–3798. [CrossRef]
4. Tan, C.; Cao, X.; Wu, X.-J.; He, Q.; Yang, J.; Zhang, X.; Chen, J.; Zhao, W.; Han, S.; Nam, G.-H.; et al. Recent Advances in Ultrathin Two-Dimensional Nanomaterials. Chem. Rev. 2017, 117, 6225–6331. [CrossRef]
5. Zhang, X.; Lai, Z.; Ma, Q.; Zhang, H. Novel structured transition metal dichalcogenide nanosheets. Chem. Soc. Rev. 2018, 47, 3301–3338. [CrossRef]
6. Jariwala, D.; Sangwan, V.K.; Lauhon, L.J.; Marks, T.J.; Hersam, M.C. Emerging Device Applications for Semiconducting Two-Dimensional Transition Metal Dichalcogenides. ACS Nano 2014, 8, 1102–1120. [CrossRef] [PubMed]
7. Rao, C.N.R.; Gopalakrishnan, K.; Maitra, U. Comparative Study of Potential Applications of Graphene, MoS$_2$, and Other Two-Dimensional Materials in Energy Devices, Sensors, and Related Areas. ACS Appl. Mater. Interfaces 2015, 7, 7809–7832. [CrossRef]
8. Mak, K.F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T.F. Atomically Thin MoS$_2$: A New Direct-Gap Semiconductor. Phys. Rev. Lett. 2010, 105, 136805. [CrossRef] [PubMed]
9. Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-layer MoS$_2$ transistors. Nat. Nanotechnol. 2011, 6, 147–150. [CrossRef] [PubMed]
10. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS$_2$. Nano Lett. 2010, 10, 1271–1275. [CrossRef]
11. Wang, Q.H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J.N.; Strano, M.S. Electronics and optoelectronics of two-dimensional transition metal dichalcogenides. Nat. Nanotechnol. 2012, 7, 699–712. [CrossRef] [PubMed]
12. Chhowalla, M.; Shin, H.S.; Eda, G.; Li, L.-j.; Loh, K.P.; Zhang, H. The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. Nat. Chem. 2013, 5, 263–275. [CrossRef] [PubMed]
13. Lauritzen, J.V.; Kibsgaard, J.; Helveg, S.; Topsoe, H.; Clausen, B.S.; Laegsgaard, E.; Besenbacher, F. Size-dependent structure of MoS$_2$ nanocrystals. Nat. Nanotechnol. 2007, 2, 53–58. [CrossRef]
14. Yin, W.; Liu, X.; Zhang, X.; Gao, X.; Colvin, V.L.; Zhang, Y.; Yu, W.W. Synthesis of Tungsten Disulfide and Molybdenum Disulfide Quantum Dots and Their Applications. Chem. Mater. 2020, 32, 4409–4424. [CrossRef]
15. Lu, G.-Z.; Wu, M.-J.; Lin, T.-N.; Chang, C.-Y.; Lin, W.-L.; Chen, Y.T.; Hou, C.-F.; Cheng, H.-J.; Lin, T.-Y.; Shen, J.-L.; et al. Electrically Pumped White-Light-Emitting Diodes Based on Histidine-Doped MoS$_2$ Quantum Dots. Small 2019, 15, 1901908. [CrossRef]
16. Liu, A.; Lv, H.; Liu, H.; Li, Q.; Zhao, H. Two dimensional MoS$_2$/CNT hybrid ink for paper-based capacitive energy storage. J. Mater. Sci. Mater. Electron. 2017, 28, 8482–8489. [CrossRef]
17. Hota, P.; Miah, M.; Bose, S.; Dinda, D.; Ghori, U.K.; Su, Y.-K.; Saha, S.K. Ultra-small amorphous MoS$_2$ decorated reduced graphene oxide for supercapacitor application. J. Mater. Sci. Technol. 2020, 40, 196–203. [CrossRef] [PubMed]
18. Guo, Y.; Li, J. MoS$_2$ quantum dots: Synthesis, properties and biological applications. Mater. Sci. Eng. C 2020, 110, 110511. [CrossRef] [PubMed]
19. Tian, X.; Sun, Y.; Fan, S.; Boudreau, M.D.; Chen, C.; Ge, C.; Yin, J.-J. Photogenerated Charge Carriers in Molybdenum Disulfide Quantum Dots with Enhanced Antibacterial Activity. ACS Appl. Mater. Interfaces 2019, 11, 4858–4866. [CrossRef]
20. Guo, X.; Huang, J.; Zeng, Q.; Wei, Y.; Liu, X.; Wang, L. Boronic acid functionalized molybdenum disulfide quantum dots for ultrasensitive analysis of dopamine basing on synergistic quenched effects from IFE and aggregation. J. Mater. Chem. B 2019, 7, 2799–2807. [CrossRef] [PubMed]
21. Yadav, S.; Chaudhury, P.; Uttam, K.N.; Varma, A.; Vashistha, M.; Yadav, B.C. Facile Synthesis of Molybdenum Disulfide (MoS2) Quantum Dots and its Application in Humidity Sensing. Nanotechnology 2019, 30, 295501. [CrossRef]
22. Dong, H.; Tang, S.; Hao, Y.; Yu, H.; Dai, W.; Zhao, G.; Cao, Y.; Lu, H.; Zhang, X.; Ju, H. Fluorescent MoS2 Quantum Dots: Ultrasonication, Up-Conversion and Down-Conversion Bioimaging, and Photodynamic Therapy. ACS Appl. Mater. Interfaces 2016, 8, 3107–3114. [CrossRef] [PubMed]
23. Jaramillo, T.F.; Jørgensen, K.P.; Bonde, J.; Nielsen, J.H.; Horch, S.; Chorkendorff, I. Identification of Active Edge Sites for Electrochemical H2 Evolution from MoS2 Nanocatalysts. Science 2007, 317, 100–102. [CrossRef]
24. Yin, X.; Ye, Z.; Chenet, D.A.; Ye, Y.; O’Brien, K.; Hone, J.C.; Zhang, X. Edge Nonlinear Optics on a MoS2 Atomic Monolayer. Science 2014, 344, 488–490. [CrossRef] [PubMed]
25. El-Sayed, M.A. Small Is Different: Shape-, Size-, and Composition-Dependent Properties of Some Colloidal Semiconductor Nanocrystals. Acc. Chem. Res. 2004, 37, 326–333. [CrossRef] [PubMed]
26. Yoffe, A.D. Low-dimensional systems: Quantum size effects and electronic properties of semiconductor microcrystallites (zero-dimensional systems) and some quasi-two-dimensional systems. Adv. Phys. 2002, 51, 799–890. [CrossRef]
27. Lv, R.; Terrones, H.; Elias, A.L.; Perea-López, N.; Gutiérrez, H.R.; Cruz-Silva, E.; Rajukumar, L.P.; Dresselhaus, M.S.; Mauricio, T. Two-dimensional transition metal dichalcogenides: Clusters, ribbons, sheets and more. Nano Today 2015, 10, 559–592. [CrossRef]
28. Šteglo, V.; Henych, J. Strongly luminescent monolayered MoS2 prepared by effective ultrasound exfoliation. Nanoscale 2013, 5, 3387–3394. [CrossRef] [PubMed]
29. Xu, S.; Li, D.; Wu, P. One-Pot, Facile, and Versatile Synthesis of Monolayer MoS2/WS2 Quantum Dots as Bioimaging Probes and Efficient Electrocatalysts for Hydrogen Evolution Reaction. Adv. Funct. Mater. 2015, 25, 1127–1136. [CrossRef]
30. Zeng, Z.; Yin, Z.; Huang, X.; Li, H.; He, Q.; Lu, G.; Boey, F.; Zhang, H. Single-Layer Semicontacts of Nanosheets: High-Yield Preparation and Device Fabrication. Angew. Chem. Int. Ed. 2011, 50, 11093–11097. [CrossRef] [PubMed]
31. Shaijumon, M.; Damien, D.; Li, B.; Gullapalli, H.; Pillai, V.K.; Ajayan, P.M.; Shaijumon, M.M. Electrochemical synthesis of luminescent MoS2 quantum dots. Chem. Commun. 2015, 51, 6293–6296. [CrossRef] [PubMed]
32. Gu, W.; Yan, Y.; Cao, X.; Zhang, C.; Ding, C.; Xian, Y. A facile and one-step ethanol-thermal syn-thesis of MoS2 quantum dots for two-photon fluorescence imaging. J. Mater. Chem. B 2016, 4, 27–31. [CrossRef] [PubMed]
33. Ali, J.; Siddiqui, G.U.; Choi, K.H.; Jang, Y.; Lee, K. Fabrication of blue luminescent MoS2 quantum dots by wet grinding assisted co-solvent sonication. J. Lumin. 2016, 169, 342–347. [CrossRef]
34. Ren, X.; Pang, L.; Zhang, Y.; Ren, X.; Fan, H.; Liu, S. (Frank) One-step hydrothermal synthesis of monolayer MoS2 quantum dots for highly efficient electrocatalytic hydrogen evolution. J. Mater. Chem. A 2015, 3, 10693–10697. [CrossRef]
35. Zhu, H.; Zhang, H.; Xia, Y. Planar Is Better: Monodisperse Three-Layered MoS2 Quantum Dots as Fluorescent Re-porters for 2,4,6-Trinitrotoluene Sensing in Environmental Water and Luggage Cases. Anal. Chem. 2018, 90, 3942–3949. [CrossRef]
36. Han, G.G.D.; Tu, K.-H.; Niroui, F.; Xu, W.; Zhou, S.; Wang, X.; Bulović, V.; Ross, C.A.; Warner, J.H.; Grossman, J.C. Photoluminescent Arrays of Nanopatterned Monolayer MoS2. Adv. Funct. Mater. 2017, 27, 1703688. [CrossRef]
37. Becke, A.D. Density-functional thermochemistry. III. The role of exact exchange. J. Chem. Phys. 1993, 98, 5648–5652. [CrossRef]
38. Lee, C.; Yang, W.; Parr, R.G. Development of the Colic-Salvetti correlation-energy formula into the functional of the electron density. Phys. Rev. B 1988, 37, 785–798. [CrossRef] [PubMed]
39. Yanai, T.; Tew, D.P.; Handy, N.C. A new hybrid exchange-correlation functional using the Cou-lomb-attenuating method (CAM-B3LYP). Chem. Phys. Lett. 2004, 393, 51–57. [CrossRef]
40. Tawada, Y.; Tsuneda, T.; Yanagisawa, S.; Yanai, T.; Hirao, K. A long-range-corrected time-dependent density functional theory. J. Chem. Phys. 2004, 120, 8425–8433. [CrossRef] [PubMed]
41. Hu, Y.-Y.; Gu, J.; Li, W.; Yang, L.; Feng, J.-K.; Tian, W.Q. From Graphene to Carbon Nanotubes: Variation of the Electronic States and Nonlinear Optical Responses. ChemPhysChem 2015, 16, 2151–2158. [CrossRef] [PubMed]
42. Sheng, X.; Zhu, H.; Yin, K.; Chen, J.; Wang, J.; Wang, C.; Shao, J.; Chen, F. Excited-State Absorption by Linear Response Time-Dependent Density Functional Theory. J. Phys. Chem. C 2020, 124, 4693–4700. [CrossRef]
43. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. Gaussi- an 09, Revision A02; Gaussian, Inc.: Walingford, CT, USA, 2009.
44. Lu, T.; Chen, F.J. Multiwfnn: A Multifunctional Wavefunction Analyzer. Comp. Chem. 2012, 33, 580–592. [CrossRef] [PubMed]