Photochemistry

Significant Enhancement of Hydrogen Production in MoS₂/Cu₂ZnSnS₄ Nanoparticles

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Hydrogen produced from water splitting is a renewable and clean energy source. Great efforts have been paid in searching for inexpensive and highly efficient photocatalysts. Here, significant enhancement of hydrogen production has been achieved by introducing $\approx 1 \mod \%$ of MoS₂ to Cu₂ZnSnS₄ nanoparticles. The MoS₂/Cu₂ZnSnS₄ nanoparticles showed a hydrogen evolution rate of $\approx 0.47 \mod g^{-1} h^{-1}$ in the presence of sacrificial agents, which is 7.8 times that of Cu₂ZnSnS₄ nanoparticles (0.06 mmol $g^{-1} h^{-1}$). In addition, the MoS₂/Cu₂ZnSnS₄ nanoparticles exhibited high stability, and only $\approx 3\%$ of catalytic activity was lost after a long time irradiation (72 h). Microstructure investigation on the MoS₂/Cu₂ZnSnS₄ nanoparticles reveals that the intimate contact between the nanostructured MoS₂ and Cu₂ZnSnS₄ nanoparticles provides an effective oneway expressway for photogenerated electrons transferring from the conduction band of Cu₂ZnSnS₄ to MoS₂, thus boosting the lifetime of charge carriers, as well as reducing the recombination rate of electrons and holes.

1. Introduction

Photocatalytic water splitting is one of the most promising way to produce hydrogen serving as an environmental friendly energy source. Generally, photocatalytic water splitting involves

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three stages.^[1,2] First, photogenerated electron–hole pairs migrate to the surface of semiconductor. Second, the electron transfer to water molecules while the holes transfer either to water or to other holeacceptor sacrificial agents presented in solution. Third, the electrons reduce H⁺ to H₂ in water.^[3,4] Therefore, searching for energetic photocatalysts which first can directly generate electron–hole pairs under visible light–irradiation, second, can efficiently separate and transport photogenerated carriers to water, and last can reduce H⁺ to H₂ in water is a critical mission.

 Cu_2ZnSnS_4 is a direct bandgap p-type semiconductor with a high optical absorption coefficient of about 10^5 cm⁻¹.^[5] It can directly generate electron-hole pairs under visible light irradiation due to its favorable bandgap (1.5 eV). Further-

more, the conduction band (CB) minimum of Cu2ZnSnS4 is about -0.7 eV (vs Normal hydrogen electrode (NHE), pH = 0,^[6] which is more negative than the redox potential of H^+/H_2 (0 eV vs NHE, pH = 0). Therefore, in theory, Cu₂ZnSnS₄ is suitable for water reduction.^[7] Accordingly, Cu2ZnSnS4 has been investigated as a potential visible light driven photocatalyst for hydrogen production and showed inspiring results.^[8,9] However, as the valence band (VB) minimum of Cu_2ZnSnS_4 is ≈ 0.8 eV (vs NHE, pH = 0),^[6] which is less positive than the redox potential of O_2/H_2O (1.23 eV vs NHE, pH = 0), the photogenerated holes can only be absorbed by sacrificial agents, not by water. It results in a high charge carrier recombination rate of photogenerated electron-hole pairs, as well as leading to a low photocatalytic efficiency. Up to now, it is still a challenge to improve the photocatalytic efficiency of Cu₂ZnSnS₄. Some self-assembly of nanoparticle (NP) and diverse single molecule detections are studied.^[10,11] Most recently, employing nanosized noble metals, such as Pt and Au, to decorate Cu2ZnSnS4 to form a new Fermi level equilibrium to inhibit the charge carrier recombination has been proved to be a feasible method.^[12] Besides introducing noble metals, designing optimal core/shell nanostructure between noble metal and Cu₂ZnSnS₄ was further studied and greatly improved the photocatalytic efficiency of Cu₂ZnSnS₄.^[13] However, the scarcity and high cost of noble metals may hinder them from being widespread used. Therefore, developing nonnoble metal, abundant and efficient cocatalysts to promote the effective charge carrier transfers becomes an urgent requirement.



Among the 2D materials, MoS₂ has attracted a lot of considerable attention due to its catalytic properties and anomalous electronic, it has been study for its important applications in potential hydrogen storage, field emission tips, solid lubricants, and solid-state secondary lithium battery cathodes^[14] Also,MoS₂ with a 2D structure has been proved as an encouraging cocatalyst for hydrogen production because nanostructured MoS₂ is rich in active edge sites.^[15,16] Particularly, it has been investigated as an effective cocatalyst for improving the photocatalytic activities of various materials such as graphene, TiO₂ and CdS.^[17-20] In our previous work, we have successful synthesized nanostructured MoS2 and Cu2ZnSnS4.^[21,22] Herein, we developed a one-pot microwave assisted synthesis method to introduce ≈1 mol% of MoS₂ to Cu₂ZnSnS₄ NPs. The photocatalytic activity of the as-synthesized MoS₂/Cu₂ZnSnS₄ NPs toward hydrogen production from water was further studied under visible light irradiation by adopting Na₂SO₃ and Na₂S as sacrificial agents. Photocatalytic efficiency can be improved by the addition of sacrificial reagents such as ascorbic acid Na2S, NaSO4, methanol, ethanol, ethylene diamine tetraacetic acid (EDTA), lactic acid, etc.^[23,24] And also because sulfide (S²⁻) and sulfide (SO_3^2) are usually used as sacrificial agents to avoid the corrosion of the sulfide in the process of photocatalytic decompo-

 a)
 b)

 total
 b)

 total
 total

 b)
 total

 total
 total

 c)
 total

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 total

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Figure 1. a) SEM image of pure Cu_2ZnSnS_4 nanoparticles. b) SEM image, (c) TEM image, and (d) HRTEM image of the as-synthesized MoS_2/Cu_2ZnSnS_4 nanoparticles.

sition of water,^[25] Na₂S and Na₂SO₃ were used as sacrificial here. Notably, the MoS₂/Cu₂ZnSnS₄ NPs exhibited significant improvement of photocatalytic performances compared to Cu₂ZnSnS₄ NPs. In addition, the MoS₂/Cu₂ZnSnS₄ NPs showed high stability after 72 h visible light–irradiation.

2. Results and Discussion

The surface morphology of the MoS₂/Cu₂ZnSnS₄ NPs was investigated by scanning electron microscopy (SEM). For reference, **Figure 1**a presents a typical SEM image of the Cu₂ZnSnS₄ NPs we synthesized for control experiment. The Cu₂ZnSnS₄ NPs possess diameters in the range of about 20–50 nm, and the surface of Cu₂ZnSnS₄ NPs are clearly clean. No contamination was observed. Figure 1b demonstrates an SEM image of the as-synthesized MoS₂/Cu₂ZnSnS₄ NPs. It can be seen that, after introducing MoS₂, the diameters of the NPs obviously decreased. It is believed that the introduced nanostructured MoS₂ increased the change of Gibbs free energy (ΔG) and in the meantime, reduced the surface energy of Cu₂ZnSnS₄ NPs NPs, which made the diameters of MoS₂/Cu₂ZnSnS₄ NPs smaller.^[26,27]

Transmission electron microscopy (TEM) characterization was further conducted on the MoS₂/Cu₂ZnSnS₄ NPs. Figure 1c shows a typical TEM image of the MoS₂/Cu₂ZnSnS₄

NPs. It can be seen that there is a slight contrast in the TEM image caused by the difference in the atomic masses of MoS_2 and $Cu_2ZnSnS_4.^{\left[28\right]}$ The average diameter of the MoS₂/Cu₂ZnSnS₄ NPs shown in Figure 1c is about 20 nm extracted from 50 nanoparticles.^[29] Previously, porous MoS₂ has been obtained by employing hydrothermal method using sodiummolybdate and thioacetamide as source materials.^[21] Here, porous MoS₂ was not observed both in the SEM and TEM measurements. From the TEM measurement results, it can be seen that the nanostructured MoS₂ binds to the surface of Cu₂ZnSnS₄ NPs tightly. The formed intimate contact between nanostructured MoS₂ and Cu₂ZnSnS₄ NPs is partly attributed by Van der Walls interactions.^[30,31] To have a qualitative understanding of the binding energy between the MoS₂ and Cu2ZnSnS4 NPs, we dissolved the MoS2/Cu2ZnSnS4 NPs in ethanol solution in a 50 mL flask, stirred it vigorously for 8 h, and treated it with 30 min ultrasonic vibration. Interestingly, similar SEM and TEM measurement results were observed, the nanostructured MoS₂ was still binding on the surface of Cu2ZnSnS4 NPs (see Figure S1, Supporting information). The applied external mechanical force did not separate the nanostructured MoS₂ from the Cu₂ZnSnS₄ NPs. The intimate contact is beneficial to efficient electron transfer between MoS₂ and Cu₂ZnSnS₄. Particularly, because the CB edge of Cu_2ZnSnS_4 (≈ -0.7 eV at pH = 7)^[6] is higher than that of bulk MoS_2 (≈ 0.25 eV) and monolayer MoS_2





Wavelength (nm)

Figure 2. XRD pattern of the prepared MoS₂/Cu₂ZnSnS₄ nanoparticles.

(~-0.12 eV),^[32-34] the photogenerated electrons in the CB of Cu₂ZnSnS₄ tend to transfer to the CB of MoS₂. The optimized MoS₂/Cu₂ZnSnS₄ photocatalysts just contain 0.35 wt% MoS₂. MoS₂ was tightly attached on the surface of Cu₂ZnSnS₄, as evidenced by the high resolution TEM (HRTEM) images in Figure 1d. The intimate contact between the MoS₂ and Cu₂Z-nSnS₄ provides an effective one-way expressway for electrons to transfer. Figure 1d shows an HRTEM image of the MoS₂/Cu₂ZnSnS₄ NPs. The lattice fringes clearly observed suggest the high degree of crystallinity of MoS₂ and Cu₂ZnSnS₄.^[35,36] The measured interplanar spacings of 0.32 nm and 0.27 nm can be ascribed to the (112) plane of kesterite Cu₂ZnSnS₄ and (100) plane of hexagonal MoS₂, respectively.^[37-40]

Powder X-ray diffraction (XRD) measurement was employed to further confirm the crystal structure of the MoS_2/Cu_2ZnSnS_4 NPs. **Figure 2** shows the XRD pattern. The diffraction peaks appeared at $2\theta = 28.5^{\circ}$, 33.0° , 47.3° , and 56.2° are attributed to the (112), (200), (220), and (312) planes of a hexagonal structure Cu₂ZnSnS₄ and match well with those of kesterite Cu₂ZnSnS₄ (JCPDS 26–0575). The other two peaks observed at $2\theta = 32.6^{\circ}$ and 58.3° are assigned to the (100) and (110) planes of 2H–MoS₂ (JCPDS 37–1492).^[41,42] The XRD result is in good agreement with the TEM result. Furthermore, as revealed by the XRD result, Cu₂ZnSnS₄ and MoS₂ share the same hexagonal crystalline structure, ensuring that a high-quality intimate contact can be obtained.^[43]

The optical properties of the MoS₂/Cu₂ZnSnS₄ NPs were investigated using UV–vis spectroscopy. **Figure 3** shows the absorption spectra of the MoS₂/Cu₂ZnSnS₄ NPs and Cu₂ZnSnS₄ NPs. It can be seen that both of the MoS₂/Cu₂ZnSnS₄ NPs and the Cu₂ZnSnS₄ NPs exhibited broad absorption in the visible region. The bandgaps of the MoS₂/Cu₂ZnSnS₄ NPs and the Cu₂ZnSnS₄ NPs were calculated by extrapolating the linear part of the function $(\alpha hv)^2$ versus energy (hv) (where α = absorbance, h = Planck's constant, and v = frequency) as shown in the inset of Figure 3.^[43] The obtained bandgap of MoS₂/Cu₂ZnSnS₄ NPs is ≈1.59 eV, which is higher than that

Figure 3. UV-vis spectra of the Cu_2ZnSnS_4 and MoS_2/Cu_2ZnSnS_4 nanoparticles. The inset shows the corresponding Tauc plots.

of Cu₂ZnSnS₄ NPs (\approx 1.52 eV). It is believed that the quantum confinement effect and the synergic effect of nanostructured MoS₂ contribute to the bandgap enlargement.^[44,45]

Photocatalytic hydrogen evolution activities of MoS₂/Cu₂ZnSnS4 NPs were evaluated under visible light irradiation $(\lambda > 420 \text{ nm}, \text{ intensity of } 100 \text{ mW cm}^{-2})$ in a mixed aqueous solution containing 0.1 M Na₂S and 0.1 M Na₂SO₃. Figure 4a presents the hydrogen evolution rate result of 20 mg of MoS₂/Cu₂ZnSnS₄ NPs under 1 h illumination of simulated sunlight, together with that of Cu2ZnSnS4 NPs for comparison. Cu₂ZnSnS₄ NPs alone exhibited hydrogen evolution rate of 0.06 mmol g⁻¹ h⁻¹, while MoS₂/Cu₂ZnSnS₄ NPs showed a rate of 0.47 mmol g⁻¹ h⁻¹. Under the same test condition, pure MoS_2 spheres showed a rate of 0.22 mmol g^{-1} h^{-1} .^[46] Even though there is only 0.35 wt% MoS₂, more active sites in MoS₂/ Cu₂ZnSnS₄ as well as a higher charge separation make higher photocatalytic activity of MoS₂/Cu₂ZnSnS₄. The result shows that the introduction of MoS₂ led to a significant enhancement in the photocatalytic hydrogen production. We speculated that the ratio of MoS₂ and Cu₂ZnSnS₄ is very important for the hydrogen generation rate. Few MoS₂ addition is not enough to improve the charge carrier separation and transfer, while the overload MoS₂ may leads to the aggregation of NPs for lower photocatalytic performance.

The recycling performance and durability of photocatalysts are two important factors considering their future practical applications. To evaluate the recycling performance of the MoS_2/Cu_2ZnSnS_4 NPs, we conducted the cycling tests of the photocatalytic hydrogen evolution by repeatedly using the same catalyst three times. The result is shown in Figure 4b, after three consecutive experiments, the MoS_2/Cu_2ZnSnS_4 NPs still showed high photocatalytic activity. Only $\approx 3\%$ of the catalytic activity was lost after it was irradiated with visible light for long time (72 h). The nanostructured MoS_2 tightly attached on the surface of Cu_2ZnSnS_4 NPs is expected to act as an efficient electron transfer medium, making charge separation suppress the electron–hole recombination, as well as





Figure 4. a) Hydrogen evolution rate of the Cu_2ZnSnS_4 and MoS_2/Cu_2ZnSnS_4 nanoparticles. b) Photocatalytic hydrogen evolution in 24 h repeated cycles by the MoS_2/Cu_2ZnSnS_4 nanoparticles.

enhancing the photocatalytic performance. Furthermore, previous report shows the lattices of MoS_2 and Cu_2ZnSnS_4 match well,^[47] which is another advantage for charge carrier transfer between the nanostructured MoS_2 and the host of Cu_2ZnSnS_4 NPs.

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A proposed photocatalytic hydrogen production mechanism is illustrated in **Scheme 1**. Due to quantum confinement effect, the bandgap of MoS₂ increases when its volume decreases to nanodimension.^[48] Specifically, the bandgap of monolayer MoS₂ is $\approx 1.9 \text{ eV}$,^[49,50] larger than that of its bulk counterpart ($\approx 1.2 \text{ eV}$).^[51] Upon the absorption of visible light, the photogenerated electrons in the CB of Cu₂ZnSnS₄ rapidly transfer to the CB of MoS₂. The transferred photoelectrons on the edge of MoS₂ sites are rapidly captured by H⁺, and hydrogen production continuously takes place at the surface of MoS₂/Cu2ZnSnS₄ NPs. In the meantime, the photogenerated holes in the VB of Cu₂ZnSnS₄ are captured by the provided sacrificial agents of S^{2–} and SO₃^{2–}, which makes the hydrogen production process go smoothly.

3. Conclusion

In this study, MoS₂/Cu₂ZnSnS₄ NPs have been synthesized by a facile one-pot microwave assisted solvothermal method. The MoS₂/Cu₂ZnSnS₄ NPs possessed an average diameter of ≈20 nm. The MoS₂/Cu₂ZnSnS₄ NPs exhibited significant enhancement in visible light photocatalytic activity compared to Cu2ZnSnS4 NPs. The enhanced photocatalytic activity is attributed to the effective transfer of photogenerated electrons between the CB of Cu₂ZnSnS4 and MoS₂. The encouraging photocatalytic properties make MoS₂/Cu₂ZnSnS₄ a promising visible light-driven photocatalyst for water splitting. Future work should focus on the optimized photocatalytic efficiency of this system such as usage of other sacrificial reagents, etc., which is a critical factor that may influence the overall performance. Our work provides an alternative effective method to introduce MoS₂ to other nanoparticles which keep loaded MoS₂ and host NPs in an intimate contact.

4. Experimental Section

The MoS₂/Cu₂ZnSnS₄ NPs were synthesized by a one-pot microwave assisted solvothermal method. Cu(CH₃COO)₂·H₂O (0.4 g),



Scheme 1. Schematic illustration and energy diagram of the charge transfer and photocatalytic redox reaction in MoS₂/Cu₂ZnSnS₄ nanoparticles.



Zn(CH₃COO)₂·2H₂O (0.220 g), Sn(CH₃COO)₂ (0.237 g), thiocarbamide (0.305 g), sodiummolybdate (0.002 g), and thioacetamide (0.020 g) were mixed with 20 mL of ethylene glycol. The mixed solution was stirred gently at room temperature, transferred into a microwave reactor (MCR-3, Gongyi City Yuhua Instrument Co., Ltd, Gongyi City, China), and then heated at 180 °C for 10 min. Here, the appropriate reaction time and temperature are important to control the size of NPs. The size of NPs increased on increasing the reaction time or temperature. However, other miscellaneous will be generated when the time is too long or the temperature is too high. Black product was gradually observed during the process of heating. After air-cooled to room temperature, the black products were obtained by vacuum filtration, washing with deionized water, acetone, and ethanol successively for three times, and vacuum drying at 40 °C for 24 h. The Cu₂ZnSnS₄ NPs mentioned in this work was prepared in the same procedure without adding sodiummolybdate and thioacetamide as source materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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- [1] S. S. Mao, S. Shen, L. Guo, Prog. Nat. Sci.: Mater. Int. 2012, 22, 522.
- [2] J. X. Low, J. G. Yu, M. Jaroniec, S. Wageh, Adv. Mater. 2017, 20, 1601694.
- [3] H. Ahmad, S. K. Kamarudin, L. J. Minggu, M. Kassim, Renewable Sustainable Energy Rev. 2015, 43, 599.
- [4] S. Y. Tee, K. Y. Win, W. S. Teo, L.-D. Koh, S. H. Liu, C. P. Teng, M.-Y. Han, Adv. Sci. 2017, 4, 1600227.
- [5] H. Zhou, W.-C. Hsu, H.-S. Duan, B. Bob, W. Yang, T.-B. Song, C.-J. Hsu, Y. Yang, *Energy Environ. Sci.* 2013, 6, 2822.
- [6] H. Sheng, L. Wenjun, Z. Zhigang, J. Phys. D: Appl. Phys. 2013, 46, 235108.
- [7] X. Li, J. Yu, J. Low, Y. Fang, J. Xiao, J. Mater. Chem. A. 2015, 3, 2485.
- [8] B.-J. Li, P.-F. Yin, Y.-Z. Zhou, Z.-M. Gao, T. Ling, X.-W. Du, RSC Adv. 2015, 5, 2543.
- [9] L. Wang, W. Wang, S. Sun, J. Mater. Chem. 2012, 22, 6553.
- [10] R. Gao, Y. L. Ying, Y. X. Hu, Y. J. Li, Y. T. Long, Anal. Chem. 2017, 89, 7382.

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- [11] R. Gao, Y. Lin, Y. L. Ying, X. Y. Liu, X. Shi, Y. X. Hu, Y. T. Long, H. Tian, Small 2017, 13, 1700234.
- [12] X. Yu, A. Shavel, X. An, Z. Luo, M. Ibáñez, A. Cabot, J. Am. Chem. Soc. 2014, 136, 9236.
- [13] E. Ha, L. Y. S. Lee, J. Wang, F. Li, K.-Y. Wong, S. C. E. Tsang, Adv. Mater. 2014, 26, 3496.
- [14] X. H. Li, S. H. Guo, C. X. Kan, J. M. Zhu, T. T. Tong, S. L. Ke, W. C. H. Choy, B. Q. Wei, *Nano Eergy.* 2016, 30, 549.
- [15] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science*. 2007, 317, 100.
- [16] C. Tsai, F. Abild-Pedersen, J. K. Nørskov, Nano Lett. 2014, 14, 1381.
- [17] J. Tao, J. Chai, L. Guan, J. Pan, S. Wang, App. Phy. Lett. 2015, 106, 081602.
- [18] J. Xu, X. J. Cao, Chem. Eng. J. 2015, 260, 642.
- [19] N. Qina, J. Xiong, R. Liang, Y. H. Liu, S. Y. Zhang, Y. H. Li, Z. H. Li, L. Wu, Appl. Catal., B 2017, 202, 374.
- [20] K. Chang, Z. Mei, T. Wang, Q. Kang, S. Ouyang, J. Ye, ACS Nano 2014, 8, 7078.
- [21] Z. Zhou, Y. Lin, P. Zhang, E. Ashalley, M. Shafa, H. Li, J. Wu, Z. Wang, *Mater. Lett.* **2014**, *131*, 122.
- [22] Z. Zhou, P. Zhang, Y. Lin, E. Ashalley, H. Ji, J. Wu, H. Li, Z. Wang, Nanoscale Res. Lett. 2014, 9, 477.
- [23] A. Galinska, J. Walendziewski, Energy Fuels 2015, 19, 1143.
- [24] X. Y. Liu, H. Chen, R. L. Wang, Y. Q. Shang, Q. Zhang, W. Li, G. Z. Zhang, J. Su, C. T. Dinh, F. P. García de Arquer, J. Li, J. Jiang, Q. X. Mi, R. Si, X. P. Li, Y. H. Sun, Y. T. Long, H. Tian, E. H. Sargent, Z. J. Ning, *Adv. Mater.* **2017**, *29*, 1605646.
- [25] V. M. Daskalaki, M. Antoniadou, G. L. Puma, D. I. Kondarides, P. Lianos, *Environ. Sci. Technol.* 2010, 44, 7200.
- [26] F. Vines, J. R. B. Gomes, F. Illas, Chem. Soc. Rev. 2014, 43, 4922.
- [27] A. S. Barnard, P. Zapol, J. Chem. Phys. 2004, 121, 4276.
- [28] B. D. Fahlman, *Materials Chemistry*, 2nd ed., Springer, Dordrecht **2011**.
- [29] Z. Zhou, C. Zhan, Y. Wang, Y. Su, Z. Yang, Y. Zhang, Mater. Lett. 2011, 65, 832.
- [30] J. Zhu, F. Lv, S. Xiao, Z. Bian, G. Buntkowsky, C. Nuckolls, H. Li, *Nanoscale* 2014, 6, 14648.
- [31] H. Li, C. Fan, M. Vosgueritchian, B. C. K. Tee, H. Chen, J. Mater. Chem. C 2014, 2, 3617.
- [32] X. Tong, E. Ashalley, F. Lin, H. Li, Z. M. Wang, Nano-Micro Lett. 2015, 7, 203.
- [33] J. Low, S. Cao, J. Yu, S. Wageh, Chem. Commun. 2014, 50, 10768.
- [34] N. Singh, G. Jabbour, U. Schwingenschlögl, Eur. Phys. J. B 2012, 85, 1.
- [35] X. Wang, H. Feng, Y. Wu, L. Jiao, J. Am. Chem. Soc. 2013, 135, 5304.
- [36] Z. Li, A. L. K. Lui, K. H. Lam, L. Xi, Y. M. Lam, Inorg. Chem. 2014, 53, 10874.
- [37] H. Zhou, T.-B. Song, W.-C. Hsu, S. Luo, S. Ye, H.-S. Duan, C.-J. Hsu, W. Yang, Y. Yang, J. Am. Chem. Soc. 2013, 135, 15998.
- [38] Y. Shi, J.-K. Huang, L. Jin, Y.-T. Hsu, S. F. Yu, L.-J. Li, H. Y. Yang, Sci. Rep. 2013, 3, 1839.
- [39] Y.-H. Lee, X. Q. Zhang, W. J. Zhang, M. T. Chang, C. T. Lin, K. D. Chang, Y. C. Yu, Y. C. Yu, J. T.-W. Wang, C. S. Chang, L.-J. Li, T. W. Lin, *Adv. Mater.* **2012**, *24*, 2320.
- [40] Y. Li, D. C. Jeffrey, D. H. Eve, A. M. Akshay, S. Q. Hao, F. Y. Shi, Q. Q. Li, W. Chris, X. Q. Chen, P. D. Vinayak, *Nano Lett.* **2016**, *16*, 7696.
- [41] K. Zhang, Y. Zhao, S. Zhang, H. Yu, Y. Chen, P. Gao, C. Zhu, J. Mater. Chem. A 2014, 2, 18715.
- [42] M. Chhowalla, G. A. J. Amaratunga, Nature. 2000, 407, 164.
- [43] E. J. Mittemeijer, Fundamentals of Materials Science: The Microstructure-Property Relationship using Metals as Model Systems, Springer, Berlin 2010.

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- [44] T. R. Rana, N. M. Shinde, J. Kim, *Mater. Lett.* 2016, *162*, 40.
- [45] A. Safdar, M. Islam, I. Ahmad, A. Akram, M. Mujahid, Y. Khalid, Y. Zhu, Mater. Sci. Semicond. Process. 2016, 41, 420.
- [46] S. H. Guo, X. H. Li, J. M. Zhu, T. T. Tong, B. Q. Wei, Small 2016, 41, 5692.
- [47] L.-L. Long, J.-J. Chen, X. Zhang, A.-Y. Zhang, Y.-X. Huang, Q. Rong, H.-Q. Yu, NPG Asia Mater. 2016, 8, e263.
- [48] X. Liu, H. Cui, C. Kong, X. Hao, Y. Huang, F. Liu, N. Song, G. Conibeer, M. Green, Appl. Phys. Lett. 2015, 106, 131110.
- [49] D. Lloyd, X. Liu, J. W. Christopher, L. Cantley, A. Wadehra, B. L. Kim, B. B. Goldberg, A. K. Swan, J. S. Bunch, *Nano Lett.* **2016**, *16*, 5836.
- [50] K. F. Mak, C. Lee, J. Hone, J. Shan, T. F. Heinz, Phys. Rev. Lett. 2010, 105, 136805.
- [51] J. Ryou, Y.-S. Kim, S. Kc, K. Cho, Sci. Rep. 2016, 6, 29184.