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CdS nanocrystals photocatalyst

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Highly value-added utilization of H₂S in Na₂SO₃ solution over Ca-

Alkaline-earth metal Ca^{2+} modified CdS nanocrystals are firstly designed for highly efficient H₂ evolution from hydrogen sulfide (H₂S) with Na₂SO₃ as a favourable reaction medium. Advantage of Na₂SO₃ was revealed by electrochemical test and conversion of Na₂SO₃ during the reaction was carefully studied. Particularly, most of Na₂SO₃ was converted into Na₂S₂O₃. Highly value-added utilization of wastes H₂S is therefore achieved by photocatalysis.

With continuous increasing of energy consumption over the past years, high acidic oil and gas reservoirs have been gradually performed to satisfy the growing requirement of global energy.¹ However, the generated wastes hydrogen sulfide (H₂S) during the exploitation process are seriously toxic and corrosive.² At present, H₂S is primarily treated by Claus technology in industry wherein it is partially oxidized to yield water and element sulfur (H₂S + 1/2 O₂ \rightarrow $H_2O + S$).³ But drawbacks like high energy consumption, toxic byproducts (SO_x) and underutilized H₂ in Claus plants are the motivations for new research interests towards other available strategies.⁴ Among them, photocatalysis technology is regarded as an appealing and sustainable technology to remove toxic pollution H₂S gas and obtain H₂.⁵ Thermodynamically, hydrogen is obtained more favourablely from H₂S than H₂O due to the lower splitting energy (0.14 V or 33 kJ mol⁻¹ for H_2S , 1.23 V or 273 kJ mol⁻¹ for H₂O).⁶ Therefore, photocatalytic decomposition of H₂S to obtain H₂ has a large potential for practical applications.

Although direct conversion of H_2S to H_2 and sulfur with photocatalysis has been extensively investigated, this technology for H_2 production still encounters tremendous challenges. On the one hand, the poisoning effect of H_2S for catalysts considerably restrict the development of highly active catalysts.⁷ Furthermore, decomposition of H_2S with photocatalysis meets the problem of

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intractable oxidation products that may prevent the continuously stable H₂ production. For example, S and S_n²⁻ are the main byproducts in hydroxide and ethanolamine system, respectively.⁸ Whereas, the photo-generated S will occupy the active sites and S_n²⁻ will shield the visible light absorption of photocatalyst, which greatly inhibit the H₂ evolution performance.^{5b,9} More importantly, complex oxidation products make it difficult to recover sulfur resources, and few studies have been reported on this. Therefore, it is necessary to select the suitable reaction medium to control the final oxidation products for efficient hydrogen production and recovery of sulfur-containing chemicals.

It is noted that Na_2SO_3 is widely applied in the system of H_2 production.¹⁰ First, Na₂SO₃ aqueous solution can provide a sufficiently alkaline environment to absorb quite a few amount of H₂S. More importantly, it can play a role of scavenger to consume the generated S or S_n^{2-} (SO₃²⁻ + $S_n^{2-} \rightarrow S_2O_3^{2-} + S_{n-1}^{2-}$; S + SO₃²⁻ \rightarrow $S_2O_3^{2-}$).¹¹ The as formed $S_2O_3^{2-}$ is colorless and soluble in water that rarely influences the photocatalyst. Remarkably, S₂O₃²⁻ is also a kind of important chemicals for clinical uses, including treatment cyanide and nitrile and heavy metal poisoning as well as that of skin pruritus, chronic dermatitis, chronic urticaria, drug eruption and scabies.¹² Therefore, simultaneously recovery of both S₂O₃²⁻ and H₂ from H_2S in Na_2SO_3 solution with photocatalytic method could be a viable strategy that is beneficial for environment and energy. However, there are few studies on the mechanism of using Na₂SO₃ solution as the reaction media for photocatalytic decomposition of H₂S to produce hydrogen. Specific influence of Na₂SO₃ on hydrogen evolution and whether by-products $(S_2O_6^{2-}, SO_4^{2-})$ and so on) coexist with $S_2O_3^{2-}$ in the system are unclear.^{2c} Thereby, study on the indepth mechanism of photocatalytic H_2S splitting in Na_2SO_3 solution is essential to ultimately realize highly efficient utilization of wastes H₂S by obtaining H₂ and S-containing species.

Herein, Na₂SO₃ solution was proved to be an excellent reaction medium for H₂ production from H₂S over a novel Ca²⁺ modified CdS colloidal nanocrystals (Ca-CdS NCs), which shows a superior photocatalytic hydrogen production activity (56.0 mmol g⁻¹ h⁻¹) from H₂S. Electrochemical test proves that appropriate onset potential and the weak influence of by-product sulfur on Na₂SO₃ solution are the important factors for effective hydrogen evolution. Moreover, Fourier-transform infrared (FT-IR) test as well as quantitative analysis confirms that Na₂SO₃ has been mostly converted into Na₂S₂O₃ after reaction. This study proves the

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Electronic Supplementary Information (ESI) available: XRD, TEM images, XPS spectra, UV-Vis and PL spectra, TA spectra, EIS, i-t curve and FT-IR spectra. See DOI: 10.1039/x0xx00000x

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possibility of resource utilization of H_2S by obtaining H_2 and $Na_2S_2O_3$ in Na_2SO_3 solution, which also provides a reference for reaction mechanism study of photocatalytic H_2S with electrochemical and FT-IR methods.

Ca-CdS NCs were obtained by direct addition of inorganic Ca²⁺ ions into the aqueous solution of CdS NCs according to the previous report.¹³ The broad diffraction peaks in XRD of Ca-CdS NCs mean a small size of the samples with a cubic zinc blende crystal structure type (JCPDS 75-0581) (Figure S1). No peak shift and new peaks appeared over Ca-CdS NCs compared with CdS NCs, except that the average grain size increased from 10.8 nm to 12.5 nm (obtained by Scherrer equation). ICP-AES elemental analysis proved that the contents of Ca are 7.5 wt% in Ca-CdS NCs and over 99.9% of Cd precursor was successfully maintained in Ca-CdS NCs (Table S1 and S2), which excluded the ion exchange between Ca and Cd. All the NCs show spherical and nanometer scale with highly irregular shapes (Figure S2). Moreover, Zeta potential value of CdS NCs decreased with introduction of Ca²⁺ (Table S3), suggesting that the positive Ca2+ has combined with negative S2- on the surface of CdS NCs. Accordingly, we believe that Ca mostly loaded on the surface of CdS NCs. XPS indicated that the chemical states of Ca, S and Cd were +2, -2, and +2, respectively (see Figure S3 and analysis in supplementary information).14



Figure 1 Photocatalytic H₂ production of different amount of Ca²⁺ precursor (0, 0.125 mmol, 0.25 mmol, 0.5 mmol, 0.75 mmol, respectively) of Ca-CdS NCs with error bar based on three experiments. Photocatalytic reaction condition: 5 mL 0.6 M Na₂SO₃-H₂S solution with 1 mg Ca-CdS NCs illuminated by 460 nm LED light.

Photocatalytic hydrogen production ability from H₂S for Ca-CdS NCs were evaluated in 0.6 M Na₂SO₃ solution with saturated 0.24 M H₂S and a 460 nm LED light source. With a favorable amount of Ca²⁺ (0.25 mmol), Ca-CdS NCs exhibits the highest photocatalytic activity with H_2 formation rate of 56.0 mmol g⁻¹ h⁻¹, which was 2.3 times higher than that of pure CdS NCs (24.4 mmol g^{-1} h^{-1}) (Figure 1). Control experiments indicated H_2S is necessary for efficient H_2 production as it could provide both protons and sulfide simultaneously, which could be hardly achieved by extra addition of other acid solution and Na₂S (Table 1). Long time test suggests Ca-CdS NCs presents a high activity within 10 h, with hydrogen evolution rate decreased by 25.2 mmol g⁻¹ h⁻¹ after reaction for 3 h (Figure S4). It turns out that light absorption ability is possibly not the main factor for the improved photocatalytic activity of Ca-CdS NCs due to the blue-shift of the absorption spectrum of Ca-CdS NCs in contrast to that of CdS NCs (Figure S5a). Instead, surface passivation of CdS NCs by Ca2+ and hence a more efficient collection

of photogenerated electrons and holes may be responsible for the higher activity (Figure S5b). This surface passivation 300 confirmed by the higher band-gap emission intensity of Ca-CdS NCs, as well as a closer Gaussian symmetric distribution of transient absorption decay curve in the time scale of several ps, which is often related to the fast non-radiative process (see Figure S6 and analysis in Supplementary information). Elimination of surface defects is beneficial for the separation of photogenerated carrier in Ca-CdS NCs,^{13,15} which is further verified by the electrochemical impedance spectroscopy (EIS) and transient photocurrent response (i-t curve) (Figure S7) with a much smaller semicircle radii and higher transient photocurrent.¹⁶

Table 1 Photocatalytic H_2 production over Ca-CdS NCs in 0.6 M Na_2SO_3 solution as reaction media with different treatment.

Reaction solution	рН	H ₂ production
		(mmol g ⁻¹ h ⁻¹)
0.6 M Na ₂ SO ₃ -H ₂ S	7.55	56.0
0.6 M Na ₂ SO ₃ -H ₂ O	10.60	4.85
0.6 M Na ₂ SO ₃ -H ₂ O-Na ₂ S/HCl	7.60	10.2
0.6 M Na ₂ SO ₃ -H ₂ O-HCl	7.65	14.3
No light ^a	7.55	trace
No catalysts ^a	7.55	trace

a: Reaction at 0.6 M Na_2SO_3 aqueous solution with 0.24 M H_2S . Reaction condition: 5 mL reaction solution, 1 mg Ca-CdS NCs and 460 nm LED light.



Figure 2 Photocatalytic H₂ production in different reaction media with error bar based on three experiments. *Blank* means only H₂S and no reaction media in aqueous solution. Reaction condition: 5 mL aqueous; 1 mg Ca-CdS NCs; 460 nm LED light.

Figure 2 reveals the influence of different reaction media on the hydrogen evolution efficiency of photocatalytic H₂S splitting. Without addition of Na₂SO₃ in the system, only a trace amount of H₂ was obtained in the H₂S-saturated solution. Besides, other reaction media that have been reported in previous systems for photocatalytic splitting of H₂S, including Na₂S, Na₂S/Na₂SO₃ and KOH solution, were also conducted over Ca-CdS NCs for comparison in the present work.^{8a,17} Reaction system with 0.1 M Na₂S alone exhibited poor photocatalytic activity (15.5 mmol g⁻¹ h⁻¹) owing to the sulfur formed has not been efficiently consumed in the reaction progress. Besides, photocatalytic H₂ evolution rate in 0.6 M Na₂SO₃ solution (56.0 mmol g⁻¹ h⁻¹) is dramatically higher than that in 0.1 M

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Na₂S, 0.1 M Na₂S/0.6 M Na₂SO₃ (35.4 mmol g⁻¹ h⁻¹) or 0.5 M KOH (46.4 mmol g⁻¹ h⁻¹) solution after irradiation of 5 h by 460 nm LED light. We found that the pH value of these solutions were dropped to a similar value with 7.55 for Na₂SO₃ solution, 7.65 for KOH solution and 7.60 for Na₂S/Na₂SO₃ solution after bubbling H₂S, even though the initial pH were much discrepant (Table S4). In addition, the concentration of H₂S was determined to be 0.42 M for Na₂S/Na₂SO₃-H₂S solution, 0.3 M for KOH-H₂S solution and 0.24 M for Na₂SO₃-H₂S solution (Table S4), which was mismatched with the hydrogen evolution trend of the reaction system. This proves that the superior activity of the Na₂SO₃ solution system is not the result of a higher concentration of H₂S in the system.

As described before, the oxidation reaction of H₂S to sulfur may influence reduction of protons to some extent. Accordingly, electrochemical liner sweep voltammetry (LSV) curves were recorded over the $Na_2SO_3-H_2S$ solution with addition of a certain amount of sulfur to study its possible influence for hydrogen evolution.⁵ As shown in Figure 3, the onset potential of hydrogen production in Na₂SO₃-H₂S is -0.86 V vs SCE, calculated through the intercept of the plot tangents on horizontal axis. With addition of sulfur, proton reduction is only slightly influenced in Na₂SO₃-H₂S solution with the onset potential shift from -0.86 V to -0.87 V and well-maintained current. This indicates problems of sulfur accumulation in the Na₂SO₃-H₂S solution during photocatalytic splitting of H₂S could be well solved. In contrast, LSV curves of other reaction system like Na₂S/Na₂SO₃-H₂S solution were also conducted as a reference (Figure S8). First of all, the onset potential of hydrogen production in Na₂S/Na₂SO₃-H₂S solution (-0.91 V vs SCE) is more negative than Na2SO3-H2S (-0.86 V vs. SCE). This indicates protons are easier to be reduced in Na2SO3 solution, which is consistent with the result of photocatalytic test (Figure 2). Moreover, proton reduction in Na₂S/Na₂SO₃-H₂S solution was suppressed with dramatically decreased current accompanied by an obvious negative shift of the onset potential from -0.91 V to -0.99 V in the presence of element sulfur (Figure S8). Consequently, the appropriate onset potential and the weak influence of sulfur on the system altogether contribute to the unique H₂ production performance for Na₂SO₃-H₂S solution.



Figure 3 Linear sweep voltammograms (LSV) of Na₂SO₃-H₂S solution and the solution with adding sulfur. All the tests were performed under a scan rate of 50 mV s⁻¹ at room temperature with platinum as working and counter electrode and SCE as reference electrode.

It is generally accepted that the mechanism for photocatalytic H₂S splitting in Na₂SO₃ solution can be described as following:^{1a,17} H₂S + OH⁻ \rightarrow HS⁻ + H₂O (1)

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HS⁻ was firstly produced in the basic Na₂SO₃ solution after introduction of H₂S (Eq. 1). Photogenerated holes from valence band of Ca-CdS NCs under light irradiation were effectively consumed by HS⁻ to generate hydrogen ions and sulfur, and the reduction of protons took place simultaneously with photogenerated electrons on the conduction band of Ca-CdS NCs (Eqs. 2-4). Then, SO₃²⁻ reacted with sulfur on the catalysts surface to avoid the deposition of S (Eq. 5).

Table 2 Assignment of characteristic peaks about S^2 , SO_3^2 , $S_2O_3^2$, SO_4^2 , $S_2O_8^2$			
Assignment	Wavenumber/cm ⁻¹	Reference	
Assignment	Wavenumber/em		
S ²⁻	1418.7	18a	
SO ₃ ²⁻	627.2, 955.8	18a,18b	
S ₂ O ₃ ²⁻	675.8, 998.7, 1134.3	18a,18c	
SO4 ²⁻	606.6, 1114.9	18c	
S ₂ O ₈ ²⁻	1062.8, 1289.2	-	

The characteristic peaks were obtained by testing FT-IR of pure Na_2S , Na_2SO_3 , Na_2SO_3 , Na_2SO_3 , Na_2SO_4 and $Na_2S_2O_8$ solution, which showed unique peaks in their mixed solutions.



Figure 4 FT-IR of the different photocatalytic reaction progresses in the 0.6 M Na_2SO_3 solution with Ca-CdS NCs as photocatalyst. *Blank* means pure Na_2SO_3 solution without H_2S .

Notably, here we introduced FT-IR spectroscopy as an effective tool to verify the above photocatalytic progresses in the presence of Na₂SO₃ over photocatalytic H₂S splitting. First of all, FT-IR spectra of a series of sulfur-related species were recorded as references (Figure S9). Table 2 shows the characteristic peaks of S²⁻ (1418.7 cm⁻¹), SO₃²⁻ (627.2, 955.8 cm⁻¹ ¹), S₂O₃²⁻ (675.8, 998.7, 1134.3 cm⁻¹), SO₄²⁻ (606.6, 1114.9 cm⁻¹) ¹), $S_2O_8^{2-}$ (1062.8, 1289.2 cm⁻¹) according to Figure S9 and references that have been reported.18 FT-IR results of the real photocatalytic system at different reaction stages are shown in Figure 4. After bubbling H_2S in the system, the S^{2-} (1418.7 cm⁻¹) were detected showing H₂S was efficiently absorbed. It is worth noting that side reaction of $S_2O_3^{2-}$ formation (4 $SO_3^{2-} + 4$ $H_2S \rightarrow 2 HS^- + 3 H_2O + 3 S_2O_3^{2-}$) in darkness occurs with IR peaks at 675.8, 998.7 and 1134.3 cm⁻¹ appeared in the progress of H_2S bubbling, which consumed a considerable part of SO_3^{2-} . With light on, SO_3^{2-} continued to convert to $S_2O_3^{2-}$ with the

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complete disappearance of peaks at 627.2 and 955.8 cm⁻¹ after 3 h. No characteristic peaks of other sulfur related species like SO_4^{2-} (606.6, 1114.9 cm⁻¹), $S_2O_8^{2-}$ (1062.8, 1289.2 cm⁻¹) were detected in the real reaction system, demonstrating that SO₃²⁻ could efficiently convert into $S_2O_3^{2-}$. Similar result was also obtained by other photocatalysts including CdS NCs, commercial CdS and Pt-loaded commercial CdS (Figure S10). Iodometry analysis indicates that a total amount of 67.0 ± 0.4 mg mL⁻¹ $S_2O_3^{2-}$ existed in the system after 3h of photocatalysis, which is close the theoretical value (67.2 mg mL⁻¹). ⁹ XRD test (Figure S11) confirms that only Na₂S₂O₃ could be discerned from the reaction solution. This result indicates that it is possible to collect Na₂S₂O₃ as an important sulfur chemical in the reaction system of Na₂SO₃ solution during photocatalytic splitting of H₂S for H₂ evolution, which is often ignored by previous work. Nevertheless, it should be noted that a small amount of polysulfide could be detected from the system in UV-Vis spectra due to the lack of SO32-, which was all consumed within 3 h (Figure S12).19

In summary, photocatalytic splitting of H_2S in Na_2SO_3 solution was carefully investigated with Ca-CdS NCs as the photocatalyst. An excellent photocatalytic hydrogen evolution rate of 56.0 mmol g⁻¹ h⁻¹ could be achieved with an optimal amount of Ca in the NCs. Na_2SO_3 solution was proved to be a better choice for H_2 evolution over Ca-CdS NCs compared to other previously reported reaction media by direct photocatalytic tests and LSV tests. Moreover, FT-IR spectra indicated that Na_2SO_3 could convert into $Na_2S_2O_3$ effectively. This work simultaneously collects clean energy H_2 and sulfur chemicals ($Na_2S_2O_3$) from H_2S by photocatalysis in the presence of Na_2SO_3 , which achieves the highly value-added utilization of toxic H_2S .

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) M. Dan, S. Q. Wei, D. E. Doronkin, Y. Li, Z. Y. Zhao, S. Yu, J.-D. Grunwaldt, Y. H. Lin and Y. Zhou, *Appl. Catal. B: Environ.*, 2019, 243, 790-800; (b) X. Zhang, Y. Y. Tang, S. Q. Qu, J. W. Da and Z. P. Hao, *ACS Catal.*, 2015, 5, 1053-1067. (c) C. L. Geng, J. Gu, Y. Xu and D. Weng, *Mater. Rev.*, 2011, 25, 119-122.
- (a) M. S. Shah, M. Tsapatsis and J. I. Siepmann, *Chem. Rev.*, 2017, **117**, 9755-9803; (b) A. P. Reverberi, J. J. Klemeš, P. S. Varbanov and B. Fabiano, *J. Clean. Prod.*, 2016, **136**, 72-80; (c) G. J. Ma, H. Y. Yan, J. Y. Shi, X. Zong, Z. B. Lei and C. Li, *J. Catal.*, 2008, **260**, 134-140; (d) G. Liu, J. Ji, P. Hu, S. Lin and H. Huang,

Appl. Surf. Sci., 2018, 433, 329-335.

- 3 (a) O. A. Habeeb, R. Kanthasamy, G. A. Modi, So Setting and R. B. M. Yunus, *Rev. Chem. Eng.*, 2018, 34, 837-854; (b) M. Sassi and A. K. Gupta, *Am. J. Environ. Sci.*, 2008, 4, 502-511; (c) A. Vrachnos, G. Kontogeorgis and E. Voutsas, *Ind. Eng. Chem. Res.*, 2006, 45, 5148-5154.
- 4 S. V. Tambwekar and M. Subrahmanyam, Int. J. Hydrogen Energy, 1997, 22, 959-965.
- 5 (a) K. Maeda, K. Teramura, D. Lu, T. Takata, N. Saito, Y. Inoue and K. Domen, *Nature*, 2006, **440**, 295. (b) U. V. Kawade, R. P. Panmand, Y. A. Sethi, M. V. Kulkarni, S. K. Apte, S. D. Naik and B. B. Kale, *RSC Adv.*, 2014, **4**, 49295-49302.
- 6 (a) Z. H. Xie, S. Yu, X.-B. Fan, S. Q. Wei, L. Yu, Y. Zhong, X.-W. Gao, F. Wu and Y. Zhou, *J. Energy Chem.*, 2021, **52**, 234-242; (b) S. Yu, Z. H. Xie, M. X. Ran, F. Wu, Y. Q. Zhong, M. Dan and Y. Zhou, *J. Colloid Interface Sci.*, 2020, **573**, 71-77; (c) X. Zong, J. F. Han, B. Seger, H. J. Chen, G. M. Lu, C. Li and L. Z. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 4399-4403.
- 7 Y. Li, S. Yu, D. E. Doronkin, S. Q. Wei, M. Dan, F. Wu, L. Q. Ye, J.-D. Grunwaldt and Y. Zhou, J. Catal., 2019, **373**, 48-57.
- (a) B. B. Kale, J. O. Baeg, S. M. Lee, H. Chang, S. J. Moon and C. W. Lee, *Adv. Funct. Mater.*, 2006, **16**, 1349-1354; (b) B. B. Kale, J.-O. Baeg, K.-J. Kong, S.-J. Moon, L. K. Nikam and K. R. Patil, *J. Mater. Chem.*, 2011, **21**, 2624-2631; (c) S. A. Naman and M. Grätzel, *J. Photochem. Photobiol. A: Chem.*, 1994, **77**, 249-253.
- 9 M. Dan, Q. Zhang, S. Yu, A. Prakash, Y. H. Lin and Y. Zhou, Appl. Catal. B: Environ., 2017, 217, 530-539.
- (a) A. Prakash, M. Dan, S. Yu, S. Q. Wei, Y. Li, F. Wang and Y. Zhou, *Sol. Energy Mater. Sol. Cells*, 2018, **180**, 205-212; (b) Q. Wang and K. Domen, *Chem. Rev.*, 2020, **120**, 919-985.
- (a) K. Hara, K. Sayama and H. Arakawa, *Appl. Catal. A: Gen.*, 1999, **189**, 127-137; (b) N. Bühler, K. Meier and J.-F. Reber, *J. Phys. Chem. B*, 1984, **88**, 3261-3268.
- (a) A. H. Hall, R. Dart and G. Bogdan, Ann. Emerg. Med., 2007, 49, 806-813; (b) B. R. Sperber, J. Allee, R. Elenitsas and W. D. James, Contact Dermatitis, 2003, 48, 204-208; (c) L. Strazzula, S. U. Nigwekar, D. Steele, W. Tsiaras, M. Sise, S. Bis, G. P. Smith and D. Kroshinsky, JAMA Dermatol., 2013, 149, 946-949.
- 13 X.-B. Fan, S. Yu, H.-L. Wu, Z.-J. Li, Y.-J. Gao, X.-B. Li, L.-P. Zhang, C.-H. Tung and L.-Z. Wu, J. Mater. Chem. A, 2018, 6, 16328-16332.
- 14 (a) J. J. Ding, S. Sun, W. H. Yan, J. Bao and C. Gao, Int. J. Hydrogen Energy, 2013, 38, 13153-13158; (b) M. Dan, J. L. Xiang, F. Wu, S. Yu, Q. Cai, L.Q. Ye, Y.H. Ye, Y. Zhou, Appl. Catal. B: Environ., 2019, 256, 117870; (c) Z. J. Sun, H. F. Zheng, J. S. Li and P. W. Du, Energy Environ. Sci., 2015, 8, 2668-2676.
- 15 A. Nag, D. S. Chung, D. S. Dolzhnikov, N. M. Dimitrijevic, S. Chattopadhyay, T. Shibata and D. V. Talapin, *J. Am. Chem. Soc.*, 2012, **134**, 13604-13615.
- 16 (a) Y. Xu and M. A. A. Schoonen, Am. Mineral, 2000, 85, 543-556; (b) X. Q. Hao, J. Zhou, Z. W. Cui, Y. C. Wang, Y. Wang and Z. G. Zou, Appl. Catal. B: Environ., 2018, 229, 41-51; (c) Y. B. Chen, J.-F. Li, P.-Y. Liao, Y.-S. Zeng, Z. Wang and Z.-Q. Liu, Chinese Chem. Lett., 2020, 31, 1516-1519.
- (a) J. L. Xiang, M. Dan, Q. Cai, S. Yu and Y. Zhou, *Appl. Surf. Sci.*, 2019, **494**, 700-707; (b) M. Dan, S. Yu, Y. Li, S. Q. Wei, J. L. Xiang and Y. Zhou, *J. Photoch. Photobio. C*, 2020, **42**, 100339.
- (a) J. Yota, V. A. Burrows, *J. Vac. Sci Technol. A*, 1993, **11**, 1083-1088; (b) I. V. Pekov, N. V. Chukanov, S. N. Britvin, Y. K. Kabalov, J. Göttlicher, V. O. Yapaskurt, A. E. Zadov, S. V. Krivovichev, W. Schüller and B. Ternes, *Mineral. Mag.*, 2012, **76**, 1133-1152; (c) S.-M. Chen, S.-W. Chiu, *Electrochim. Acta*, 2000, **45**, 4399-4408.
- M. Zhang, J. Guan, Y. C. Tu, S. M. Chen, Y. Wang, S. H. Wang, L. Yu, C. Ma, D. H. Deng and X. H. Bao, *Energy Environ. Sci.*, 2020, 13, 119-126.

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Highly efficient utilization of wastes H_2S by obtaining H_2 and $Na_2S_2O_3$ species was implemented through photocatalytic technology in Na_2SO_3 solution over novel Ca-CdS nanocrystals.