



Recent Advances in Quantum Dots for Photocatalytic CO₂ Reduction: A Mini-Review

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Solar energy-driven carbon dioxide (CO₂) reduction to valuable solar fuels/chemicals (e.g., methane, ethanol, and carbon monoxide) using particulate photocatalysts is regarded as one of the promising and effective approaches to deal with energy scarcity and global warming. The growth of nanotechnology plays an eminent role in improving CO₂ reduction (CO₂R) efficiencies by means of offering opportunities to tailor the morphology of photocatalysts at a nanoscale regime to achieve enhanced surface reactivity, solar light absorption, and charge separation, which are decisive factors for high CO₂R efficiency. Notably, quantum dots (QDs), tiny pieces of semiconductors with sizes below 20 nm, offering a myriad of advantages including maximum surface atoms, very short charge migration lengths, size-dependent energy band positions, multiple exciton generation effect, and unique optical properties, have recently become a rising star in the CO₂R application. In this review, we briefly summarized the progress so far achieved in QD-assisted CO₂ photoreduction, highlighting the advantages of QDs prepared with diverse chemical compositions such as metal oxides, metal chalcogenides, carbon, metal halide perovskites, and MXenes.

Keywords: CO₂ reduction, perovskite, MXene, quantum dots, carbon quantum dot, transition metal chalcogenide, metal oxide, photocatalyst

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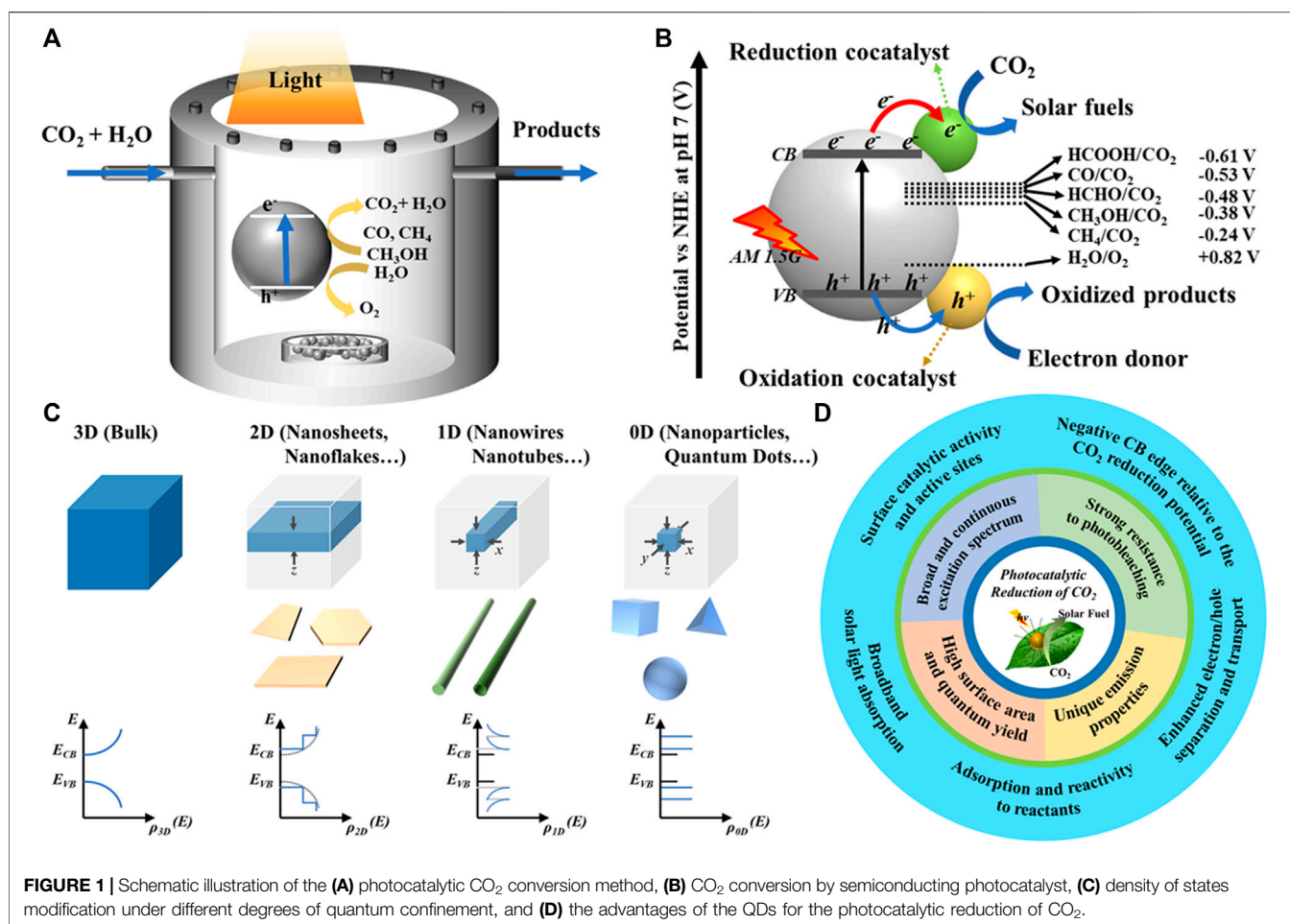
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INTRODUCTION

Carbon dioxide (CO₂) is the major constituent of the global warming gases that are destroying the ozone layer of the Earth. Many researchers have been trying to capture and convert greenhouse gases, especially CO₂, to make it as a pollution-free and recyclable energy source. In the present era, CO₂ has been captured (Ibrahim et al., 2018; Fu et al., 2019; Omodolor et al., 2020; Dhoke et al., 2021; Lau et al., 2021), converted (Fu et al., 2019; Omodolor et al., 2020) and stored (Lau et al., 2021) by using different technologies. There are many methods and techniques that are studied for the conversion of CO₂ into renewable energy sources; among them, photocatalytic CO₂ reduction (CO₂R) (Sorcar et al., 2018; Sorcar et al., 2019; Albero et al., 2020; Li et al., 2021), electrochemical CO₂R (Jia et al., 2019; Liang et al., 2020), photo-biochemical CO₂R (Kim et al., 2018), photo-electrochemical CO₂R (Roy et al., 2016), and thermochemical CO₂R (Maiti et al., 2018; Pullar et al., 2019) are well-known (He and Janáky, 2020). The photocatalysis process promotes the conversion reactions using clean solar energy, which is an eco-friendly CO₂ conversion technology (shown in Figure 1A).



The photocatalytic CO₂R reaction comprises three primary steps: 1) the semiconductor photocatalyst absorbs the solar light energy and generates photocharge carriers, 2) photogenerated charge carriers were separated and transported to the surface of the semiconductor photocatalyst, and 3) oxidation and reduction reactions mediated by holes and electrons take place at the active sites on the photocatalyst surface, that is, electrons for CO₂R and holes for oxidation of sacrificial agent or water, respectively (Xie et al., 2016; Wu et al., 2019) (Figure 1B). However, to exhibit the CO₂ photoreduction, the photocatalyst should have the ability to adsorb CO₂ and must possess its valence band (VB) at more positive potential than the water oxidation potential and conduction band (CB) at more negative potential than the CO₂R potential (Xie et al., 2016). It should be noted that CO₂R into CO₂⁻ radicals through single electrons transfer is unfavorable to occur because of the required high negative potential for the electrons in the CB of photocatalyst (-1.9 V vs NHE) (Shit et al., 2020). However, owing to relatively lower negative potential required for the conversion of CO₂ into hydrocarbons, the proton-assisted multielectron transfer process is more favorable (Shit et al., 2020). Depending on the number of participated electrons, various gas and liquid phase hydrocarbons, such as carbon monoxide (CO), formic acid

(CH₂O₂), oxalic acid (C₂H₂O₄), formaldehyde (CH₂O), acetaldehyde (C₂H₄O), methanol (CH₃OH), methane (CH₄), ethylene (C₂H₄), and ethanol (C₂H₅OH), are produced in the CO₂R reaction (Shit et al., 2020) (Figure 1B). Major concerns existing for the efficient photocatalytic CO₂R are 1) photocatalyst materials' limited light absorption ability, 2) quick recombination of photogenerated charge carriers, and 3) poor adsorption of CO₂ molecules on the photocatalyst surface. It was realized that crystalline phases, size, shape, and exposed facets of photocatalyst are crucially influencing the CO₂R. Maneuvering semiconductors into distinct nanostructures results in significantly altered surfaces and electronic structures, which affect the surface reactivity and positions of energy bands, respectively (Figure 1C). Furthermore, the morphological features are also pivotal for the transfer of photocharge carriers. For instance, 2D nanosheet morphology having one dimension in the atomic thickness level facilitates shorter charge migration lengths, which is beneficial to avoid the quick recombination kinetics. Furthermore, their flat surface allows the facile heterojunction formation with other 2D, 1D, and 0D nanostructures. However, the quantum confinement in three dimension leaves 0D quantum dots (QDs) with very short charge migration lengths and maximum surface-exposed

atoms (Figure 1C). The higher sensitivity of energy band positions to the size of QDs allows the precise tailoring of their VB and CB to the required positions in order to initiate the reduction of CO₂ into selective hydrocarbons. Furthermore, the tiny size allows their easy grafting on other 2D and 1D nanostructures to frame the heterojunctions. Hence, QDs of a variety of semiconductors having several advantages garnered significant attention for the photocatalytic CO₂R applications (Figure 1D).

Metal Oxide Quantum Dots

Metal oxide semiconductor materials such as MgO (Kohno et al., 2001), ZrO₂ (Hengne et al., 2018; Miao et al., 2019), ZnO (Gokon et al., 2003), WO₃ (Jin et al., 2015), and TiO₂ (Kočič et al., 2009; Yu et al., 2014) have been studied as catalysts and co-catalysts for the photocatalytic reduction of CO₂. In order to enhance the photocatalytic reduction of CO₂, 0D metal oxide QDs (MOQDs) have been studied apart from their bulk counterparts due to their advantages like economical, eco-friendly, high surface area, good dispersibility, and well-maintained light absorption ability. For instance, the activity of CuO QDs is in good compatibility with Ti in the metal organic framework (MOF) MIL-125 coupled with g-C₃N₄ toward the efficient photocatalytic CO₂R to form CO, CH₃OH, CH₃CHO, and C₂H₅OH (Li et al., 2020). The good compatibility between CuO QDs and active sites of Ti in MIL-125 the electrons generated by photocatalytic activity will easily transfer to CuO from MIL-125/g-C₃N₄. The combination of g-C₃N₄/CuO on MIL-125 has drastically improved the yield of CO, CH₃OH, CH₃CHO, and C₂H₅OH in the presence of water. However, most of the MOQDs have some unresolved technical issues such as the low yield of available electrons and large intrinsic bandgaps that are restricting the wide range applicability under visible light irradiation (Heng et al., 2021). Introduction of defects, doping, and heterojunction formation are the commonly practicing strategies to improve the CO₂R efficiency of MOQDs.

Transition Metal Chalcogenide Quantum Dots

Transition metal chalcogenide (TMC) materials are formed by the combination of IV–VII transition metal elements (Mo, W, V, Nb, Ta, Ti, Zr, Hf, Tc, or Re) and chalcogens (S, Se, or Te). By the controlled synthesis of the TMCs from bulk to 2D nanosheets or 0D QDs, the bandgaps in TMCs can be tuned with respect to size and shape (Yao et al., 2019; Pandey et al., 2020). There are more than 40 kinds of TMCs available till date, which can be synthesized in large quantities by using synthesis techniques such as the CVD method (Bosi, 2015; Severs Millard et al., 2020), hydrothermal method (Chen and Fan, 2001), and Langmuir–Schaefer deposition method (Kalosi et al., 2019).

The TMCQDs and their composites such as CdS (Kuehnel et al., 2017), CdS/Ni (Wang et al., 2010), CdSe/TiO₂ (Sarkar et al., 2016), PbS (Wang et al., 2011), ZnS/CuInS₂ (Lian et al., 2018), and Mn:CdS/CdSeTe/TiO₂ (Nie et al., 2018) have proven to be effective performing photocatalysts. Wang et al. reported the heterostructured catalyst CdSe/Pt/TiO₂ for the photoreduction of CO₂ under visible light in the presence of water (Wang et al.,

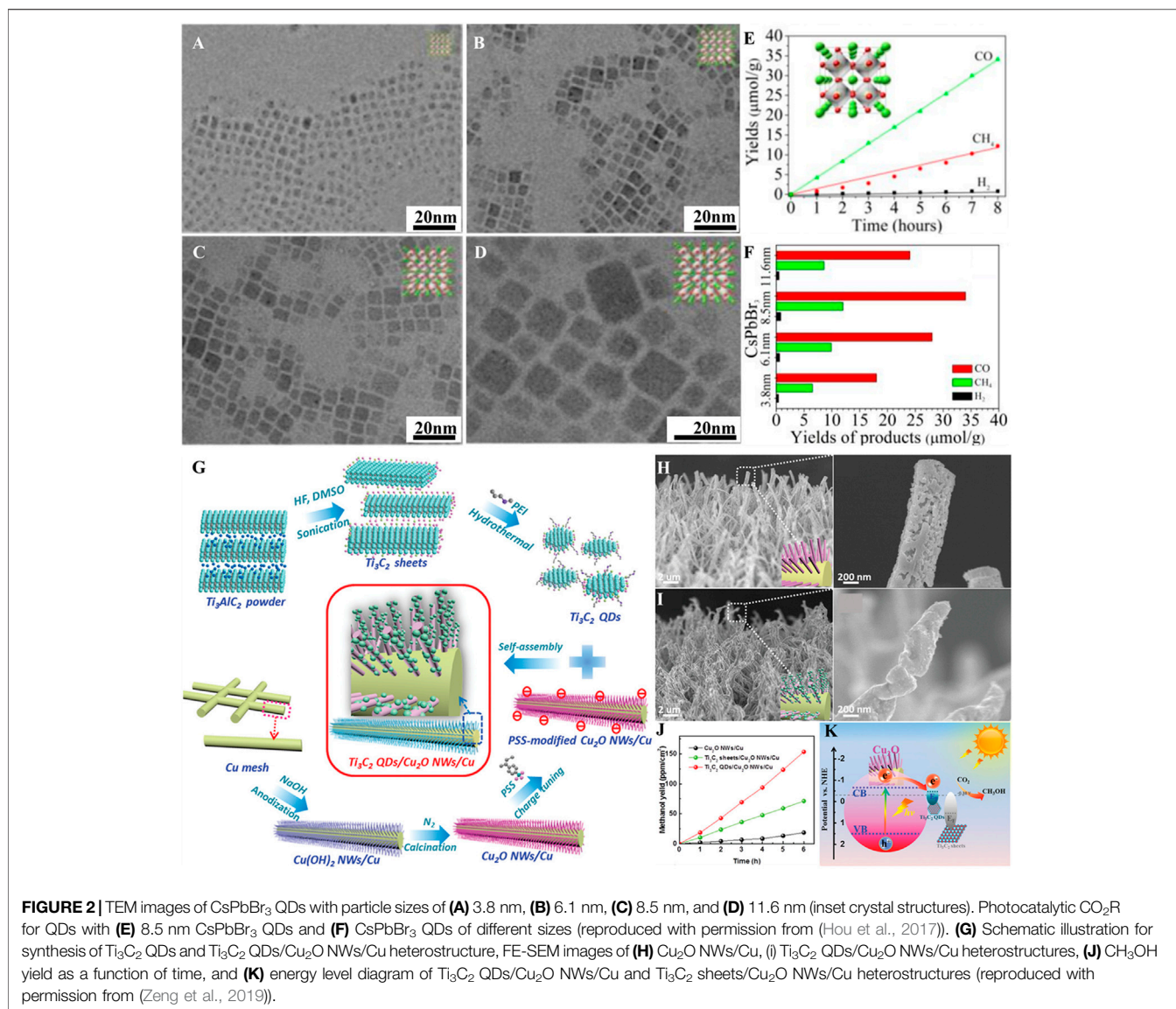
2010). CdSe QD-sensitized TiO₂ heterostructure materials are capable of catalyzing CO₂R under visible light illumination ($\lambda > 420$ nm). The CdSe QD's surface was modified by removing surfactant caps through annealing and using a hydrazine reducing agent, which enhanced the direct contact between CdSe QDs and TiO₂. Although TMCQDs show good performance, they slowly become inactive after continuous exposure to the visible light illumination, which is a commonly observed issue in TMC(QD)s due to gradual oxidation of TMCs. The surface stoichiometry of the TMCQDs influences the exciton kinetics such as in CdSe QDs, the presence of a higher surface ratio of Se increases the possibility of electron–hole recombination at trap sites. The surface stoichiometry manipulation drives effective ways to improve the photocatalytic performance of TMCQDs.

Carbon Quantum Dots

Carbon QDs (CQDs), with their sizes in the range of 20 nm, have attracted much attention for their photoluminescence properties and co-catalyst role in different photocatalytic reactions. They exhibit low toxicity, good chemical stability, and exceptional water solubility compared to widely used semiconductor photocatalysts (CdS, TiO₂, etc) (Murali et al., 2021). Importantly, CQDs possess upconversion photoluminescence property that allows the utilization of NIR light. All the aforementioned features and the high CO₂ adsorption characteristics make CQDs an auspicious candidate for the photocatalytic CO₂R application. Furthermore, surface functionalization with different organic functional groups tailors the semiconducting property and bandgap of CQDs to make them most suitable for CO₂R. The functionalization of CQDs with 1,1'-bi(2-naphthylamine) enables the formation of intramolecular Z-scheme with a narrow bandgap for the efficient CO₂R under visible light (Yan et al., 2018). Combining CQDs with other semiconductors is reported to enhance the CO₂R efficiency by utilizing broad range of solar energy, where CQDs absorb visible light that enables the transfer of photogenerated charge carriers through the interface for efficient charge separation and improved CO₂R. Specifically, heteroatom (N, B, S, Cl, etc.)-doped CQDs are more suitable to form the heterojunction owing to their enhanced light absorption, electron transport, chemical activity, and specific surface area properties. For instance, the N-rich CQDs/TiO₂ composite showed an enhanced performance for the CO₂R with CH₄ and CO yield of 7.79 and 7.61 times higher than that of pristine TiO₂ (Li et al., 2018).

Perovskite Quantum Dots

Metal halide perovskites are a class of semiconductors having ABX₃ chemical stoichiometry, where A represents the alkali (e.g., Cs) or organic (e.g., formamidinium or methylammonium) cation; B denotes the divalent metal cation such as Pb, Bi, or Sn; and X stands for halide anions such as Cl, Br, or I. QDs of these materials are familiar for their excellent optical and electrical properties including strong light absorption, charge carrier's high mobility and long diffusion lengths, and prolonged charge carrier lifetimes. The tuning of the cation/anion composition could facilitate the tailoring of the perovskite



QD (PQD) absorption from UV to the NIR region (Shyamal and Pradhan, 2020). Furthermore, the favorable VB and CB positions of these CQDs enable the utilization of photogenerated charge carriers for CO₂R prior to their recombination. However, selection of appropriate solvent for the photocatalytic CO₂R over PQDs is a difficult task due to their instability upon exposure to polar solvents. Solvents like ethyl acetate have been selected because their mild polarity protects PQDs and CO₂ is highly soluble in them (Xu et al., 2017). The addition of water to this solvent has been demonstrated to increase the selectivity of CO₂R by minimizing H₂ production (Shyamal and Pradhan, 2020). But an excessive amount of water addition will have negative impact on the stability of PQDs (Hou et al., 2017). However, the careful surface protection of cobalt-doped CsPbBr₃/Cs₄PbBr₆ QDs with hexafluorobutyl methacrylate enabled the use of aqueous medium for the CO₂R (Mu et al., 2019). Furthermore, to protect PQDs from contamination and to hinder

their erosion by organic solvents, PQDs were encapsulated with metal oxides and MOFs while applying for CO₂R (Zhang et al., 2016; Xu et al., 2018). The size optimization of PQDs is significant to accomplish the enhanced photocatalytic CO₂R. The large size of PQDs decreases the surface area, while the smaller size leads to the aggregation, which will affect the optical absorption and charge carrier's separation and transport properties. The CO₂R performance of four different size (3.8, 6.1, 8.5, and 11.6 nm) CsPbBr₃ PQDs in ethyl acetate/water medium under the solar illumination for 8 h concluded that PQDs with 8.5 nm size yielded more CH₄, CO, and H₂ products (Hou et al., 2017) (Figures 2A–F). The crystalline phase of PQDs influence the CO₂R performance such as CsPbBr₃ PQDs with the cubic phase are more active than the orthorhombic phase counterparts (Guo et al., 2019). The sluggish catalytic reaction dynamics of PQDs are dealt by employing a conducting material with high electron extraction efficiency (Xu et al., 2017; Pan et al., 2019).

MXene Quantum Dots

MXenes, a set of 2D materials represented by a general formula of $M_{n+1}X_nT_x$ ($n = 1-4$; $X = C, N$, and C/N ; $T_x = -O, -F, -OH$, etc.), have exhibited a great potential in various applications owing to their exceptional electrical conductivity, metal-terminated surfaces, and hydrophilic characteristics (Lim et al., 2020; Tang et al., 2021). DFT calculations predicted that the chemisorption of CO₂ is favorable compared to water on the MXene surface and higher electrical conductivity of MXene could cause the photocatalytic CO₂R (Tahir et al., 2021). MXenes can be synthesized by the selective chemical etching of “A” layers from their sandwich-like parent MAX phase precursors, consisting of a stacked MXene nanosheets separated by the layers of A group elements. Recently, it has been demonstrated that appropriate experimental conditions could fragment the 2D MXenes into tiny pieces (≤ 10 nm), known as MXene QDs (MQDs). MQDs inherit all characteristics of their 2D counterparts and exhibit additional unique properties emanating from their high surface area and quantum size effects. MQDs absorb light in the range of UV to NIR and capable of effectively transforming the absorbed light energy into other forms, including chemical energy. Furthermore, the smaller size and hydrophilic/reactive surface functional groups permit easy grafting on other semiconductor nanostructures to make heterostructures. Recently, a facile incorporation of Ti₃C₂ MQDs onto Cu₂O nanowires (NWs)/Cu mesh (Ti₃C₂ MQDs/Cu₂O/Cu heterostructure) through a self-assembly approach was demonstrated to improve the CO₂R (Zeng et al., 2019) (Figures 2G–K). The grafting of MQDs has improved the stability Cu₂O NWs and led to significant enhancement in CO₂R performance by improving light absorption and inhibiting the charge recombination. Furthermore, the CH₃OH yield obtained with the Ti₃C₂ MQDs/Cu₂O NWs/Cu photocatalyst is 8.25 and 2.15 times higher than Cu₂O NWs/Cu and Ti₃C₂ sheets/Cu₂O NWs/Cu photocatalysts, respectively. As the Fermi level (E_F) of Ti₃C₂ MQDs is less negative than the CB of Cu₂O, photogenerated charge carriers migrate from Cu₂O to Ti₃C₂ MQDs and accumulate. The E_F of MQDs is sufficiently negative to perform the reduction of CO₂ to CH₃OH, with accumulated electrons accelerating the CO₂R. On the other hand, the E_F of MXene nanosheets is positive, which is not suitable for accelerating the CO₂R.

CONCLUSIONS AND PERSPECTIVES

Photochemical CO₂R is one of the efficient methods for the conversion of solar to fuel without releasing any toxic wastes into the environment. An ideal photocatalyst should have the qualities like a high surface area, more active sites, long-term stability, low cost, and easy to produce in industrial scale to commercialize. Several kinds of QDs such as MOQDs, TMCQDs, CQDs, PQDs, and MQDs have been studied so far for the photocatalytic CO₂R. Overall, the research on QDs for CO₂R is still in its infancy, and following aspects need to be addressed to reach further growth for the ease in applicability. The size control of most QDs involves complicated synthesis procedures. Developing a simple, cost-effective, size-controlled, and highly

efficient synthesis approaches will lead to wide utilization of QDs for CO₂R. Most of the TMCQDs and PQDs for CO₂R are based on Cd- and Pb-containing compositions, respectively, which are not ideal in the perspective of safety and eco-friendliness. Hence, more research is needed for improving the stability and CO₂R efficiency of Cd- and Pb-free QDs (such as InP, ZnSe, and ZnS) (Wang et al., 2019). The poor oxidation stability of the TMCQDs, PQDs, and MQDs in the presence of water and light are the major challenging aspects to be addressed immediately. The QD-based hybrids are mostly achieved by simple blending of QDs with other semiconductors, which does not generate a strong chemical interaction at the interfaces for efficient charge transfer process. Hence, *in situ* growth methodologies and/or external functionalization with different functional groups/molecules should be adopted to fully exploit the advantages of QDs. The full spectrum of solar light utilization by QDs for CO₂R is not yet accomplished. More innovative technologies like making QDs comprising upconversion material as core should be investigated. At present, formic acid and CO are the main products of CO₂R via two electron reduction. Hence, CO₂R via four-, six-, and eight-electron reduction needs significant attention. Especially, methane production by eight-electron reduction can make a vital change in the application of QDs for CO₂R. The H₂ production via proton reduction that reduces the CO₂R efficiency is another critical concern for the QD-based systems. Although the efficient properties of CQDs depends on the size, shape, surface defects, and heteroatom doping concentrations, a well-established method(s) for precise tuning is needed. Furthermore, the functional groups of CQDs are known to be reduced with the prolonged exposure of light during the photocatalytic reactions, which may influence their CO₂R activity. Hence, improving the stability is a bottleneck concern in CQD-based CO₂R research. The advancement in QDs stability under light, highly interactive interface with other materials, morphological control, and quick adoptability to the reaction environment will make them as futuristic materials for not only in CO₂R but also in other interdisciplinary fields.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the manuscript writing, editing, and reviewing work, and approved it for publication.

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REFERENCES

- Albero, J., Peng, Y., and García, H. (2020). Photocatalytic CO₂ Reduction to C²⁺ Products. *ACS Catal.* 10, 5734–5749. doi:10.1021/acscatal.0c00478
- Bosi, M. (2015). Growth and Synthesis of Mono and Few-Layers Transition Metal Dichalcogenides by Vapour Techniques: A Review. *RSC Adv.* 5, 75500–75518. doi:10.1039/c5ra09356b
- Chen, X., and Fan, R. (2001). Low-Temperature Hydrothermal Synthesis of Transition Metal Dichalcogenides. *Chem. Mater.* 13, 802–805. doi:10.1021/cm000517+
- Dhoke, C., Zaabout, A., Cloete, S., and Amini, S. (2021). Review on Reactor Configurations for Adsorption-Based CO₂ Capture. *Ind. Eng. Chem. Res.* 60, 3779–3798. doi:10.1021/acs.iecr.0c04547
- Fu, H.-C., You, F., Li, H.-R., and He, L.-N. (2019). CO₂ Capture and *In Situ* Catalytic Transformation. *Front. Chem.* 7, 525. doi:10.3389/fchem.2019.00525
- Gokon, N., Hasegawa, N., Kaneko, H., Aoki, H., Tamaura, Y., and Kitamura, M. (2003). Photocatalytic Effect of ZnO on Carbon Gasification with CO₂ for High Temperature Solar Thermochemistry. *Solar Energ. Mater. Solar Cell* 80, 335–341. doi:10.1016/j.solmat.2003.08.016
- Guo, S.-H., Zhou, J., Zhao, X., Sun, C.-Y., You, S.-Q., Wang, X.-L., et al. (2019). Enhanced CO₂ Photoreduction via Tuning Halides in Perovskites. *J. Catal.* 369, 201–208. doi:10.1016/j.jcat.2018.11.004
- He, J., and Janáky, C. (2020). Recent Advances in Solar-Driven Carbon Dioxide Conversion: Expectations Versus Reality. *ACS Energ. Lett.* 5, 1996–2014. doi:10.1021/acscenergylett.0c00645
- Heng, Z. W., Chong, W. C., Pang, Y. L., and Koo, C. H. (2021). An Overview of the Recent Advances of Carbon Quantum Dots/metal Oxides in the Application of Heterogeneous Photocatalysis in Photodegradation of Pollutants towards Visible-Light and Solar Energy Exploitation. *J. Environ. Chem. Eng.* 9, 105199. doi:10.1016/j.jece.2021.105199
- Hengne, A. M., Samal, A. K., Enakonda, L. R., Harb, M., Gevers, L. E., Anjum, D. H., et al. (2018). Ni-Sn-Supported ZrO₂ Catalysts Modified by Indium for Selective CO₂ Hydrogenation to Methanol. *ACS Omega* 3, 3688–3701. doi:10.1021/acsomega.8b00211
- Hou, J., Cao, S., Wu, Y., Gao, Z., Liang, F., Sun, Y., et al. (2017). Inorganic Colloidal Perovskite Quantum Dots for Robust Solar CO₂ Reduction. *Chem. Eur. J.* 23, 9481–9485. doi:10.1002/chem.201702237
- Ibrahim, M. H., El-Naas, M. H., Zhang, Z., and Van Der Bruggen, B. (2018). CO₂ Capture Using Hollow Fiber Membranes: A Review of Membrane Wetting. *Energy Fuels* 32, 963–978. doi:10.1021/acs.energyfuels.7b03493
- Jia, C., Dastafkan, K., Ren, W., Yang, W., and Zhao, C. (2019). Carbon-Based Catalysts for Electrochemical CO₂ Reduction. *Sustain. Energy Fuels* 3, 2890–2906. doi:10.1039/c9se00527g
- Jin, J., Yu, J., Guo, D., Cui, C., and Ho, W. (2015). A Hierarchical Z-Scheme CdS-WO₃ Photocatalyst with Enhanced CO₂ Reduction Activity. *Small* 11, 5262–5271. doi:10.1002/sml.201500926
- Kalosi, A., Demydenko, M., Bodik, M., Hagara, J., Kotlar, M., Kostiuk, D., et al. (2019). Tailored Langmuir-Schaefer Deposition of Few-Layer MoS₂ Nanosheet Films for Electronic Applications. *Langmuir* 35, 9802–9808. doi:10.1021/acs.langmuir.9b01000
- Kim, H.-W., Lee, K.-S., Razzaq, A., Lee, S. H., Grimes, C. A., and In, S.-I. (2018). Photocoupled Bioanode: A New Approach for Improved Microbial Fuel Cell Performance. *Energy Technol.* 6, 257–262. doi:10.1002/ente.201700177
- Kočí, K., Obalová, L., Matějová, L., Plachá, D., Lacný, Z., Jirkovský, J., et al. (2009). Effect of TiO₂ Particle Size on the Photocatalytic Reduction of CO₂. *Appl. Catal. B: Environ.* 89, 494–502. doi:10.1016/j.apcatb.2009.01.010
- Kohno, Y., Ishikawa, H., Tanaka, T., Funabiki, T., and Yoshida, S. (2001). Photoreduction of Carbon Dioxide by Hydrogen over Magnesium Oxide. *Phys. Chem. Chem. Phys.* 3, 1108–1113. doi:10.1039/b008887k
- Kuehnle, M. F., Orchard, K. L., Dalle, K. E., and Reiser, E. (2017). Selective Photocatalytic CO₂ Reduction in Water through Anchoring of a Molecular Ni Catalyst on CdS Nanocrystals. *J. Am. Chem. Soc.* 139, 7217–7223. doi:10.1021/jacs.7b00369
- Lau, H. C., Ramakrishna, S., Zhang, K., and Radhamani, A. V. (2021). The Role of Carbon Capture and Storage in the Energy Transition. *Energy Fuels* 35, 7364–7386. doi:10.1021/acs.energyfuels.1c00032
- Li, K., Teng, C., Wang, S., and Min, Q. (2021). Recent Advances in TiO₂-Based Heterojunctions for Photocatalytic CO₂ Reduction with Water Oxidation: A Review. *Front. Chem.* 9, 88. doi:10.3389/fchem.2021.637501
- Li, M., Wang, M., Zhu, L., Li, Y., Yan, Z., Shen, Z., et al. (2018). Facile Microwave Assisted Synthesis of N-Rich Carbon Quantum Dots/Dual-Phase TiO₂ Heterostructured Nanocomposites with High Activity in CO₂ Photoreduction. *Appl. Catal. B: Environ.* 231, 269–276. doi:10.1016/j.apcatb.2018.03.027
- Li, N., Liu, X., Zhou, J., Chen, W., and Liu, M. (2020). Encapsulating CuO Quantum Dots in MIL-125(Ti) Coupled with g-C₃N₄ for Efficient Photocatalytic CO₂ Reduction. *Chem. Eng. J.* 399, 125782. doi:10.1016/j.cej.2020.125782
- Lian, S., Kodaimati, M. S., and Weiss, E. A. (2018). Photocatalytically Active Superstructures of Quantum Dots and Iron Porphyrins for Reduction of CO₂ to CO in Water. *ACS Nano* 12, 568–575. doi:10.1021/acsnano.7b07377
- Liang, S., Altaf, N., Huang, L., Gao, Y., and Wang, Q. (2020). Electrolytic Cell Design for Electrochemical CO₂ Reduction. *J. CO₂ Utilization* 35, 90–105. doi:10.1016/j.jcou.2019.09.007
- Lim, K. R. G., Handoko, A. D., Nemani, S. K., Wyatt, B., Jiang, H.-Y., Tang, J., et al. (2020). Rational Design of Two-Dimensional Transition Metal Carbide/Nitride (MXene) Hybrids and Nanocomposites for Catalytic Energy Storage and Conversion. *ACS Nano* 14, 10834–10864. doi:10.1021/acsnano.0c05482
- Maiti, D., Hare, B. J., Daza, Y. A., Ramos, A. E., Kuhn, J. N., and Bhethanabotla, V. R. (2018). Earth Abundant Perovskite Oxides for Low Temperature CO₂ Conversion. *Energy Environ. Sci.* 11, 648–659. doi:10.1039/c7ee03383d
- Miao, Z., Hu, P., Nie, C., Xie, H., Fu, W., and Li, Q. (2019). ZrO₂ Nanoparticles Anchored on Nitrogen-Doped Carbon Nanosheets as Efficient Catalyst for Electrochemical CO₂ Reduction. *J. Energ. Chem.* 38, 114–118. doi:10.1016/j.jechem.2019.01.010
- Mu, Y. F., Zhang, W., Guo, X. X., Dong, G. X., Zhang, M., and Lu, T. B. (2019). Water-Tolerant Lead Halide Perovskite Nanocrystals as Efficient Photocatalysts for Visible-Light-Driven CO₂ Reduction in Pure Water. *ChemSusChem* 12, 4769–4774. doi:10.1002/cssc.201902192
- Murali, G., Modigunta, J. K. R., Park, S., Lee, S., Lee, H., Yeon, J., et al. (2021). Enhancing Light Absorption and Prolonging Charge Separation in Carbon Quantum Dots via Cl-Doping for Visible-Light-Driven Photocharge-Transfer Reactions. *ACS Appl. Mater. Inter.* 13, 34648–34657. doi:10.1021/acscami.1c01879
- Nie, R., Ma, W., Dong, Y., Xu, Y., Wang, J., Wang, J., et al. (2018). Artificial Photosynthesis of Methanol by Mn:CdS and CdSeTe Quantum Dot Cosensitized Titania Photocathode in Imine-Based Ionic Liquid Aqueous Solution. *ChemCatChem* 10, 3342–3350. doi:10.1002/cctc.201800190
- Omodolor, I. S., Otor, H. O., Andonegui, J. A., Allen, B. J., and Alba-Rubio, A. C. (2020). Dual-Function Materials for CO₂ Capture and Conversion: A Review. *Ind. Eng. Chem. Res.* 59, 17612–17631. doi:10.1021/acs.iecr.0c02218
- Pan, A., Ma, X., Huang, S., Wu, Y., Jia, M., Shi, Y., et al. (2019). CsPbBr₃ Perovskite Nanocrystal Grown on MXene Nanosheets for Enhanced Photoelectric Detection and Photocatalytic CO₂ Reduction. *J. Phys. Chem. Lett.* 10, 6590–6597. doi:10.1021/acs.jpcl.9b02605
- Pandey, S. K., Das, R., and Mahadevan, P. (2020). Layer-Dependent Electronic Structure Changes in Transition Metal Dichalcogenides: The Microscopic Origin. *ACS Omega* 5, 15169–15176. doi:10.1021/acscomega.0c01138
- Pullar, R. C., Novais, R. M., Caetano, A. P. F., Barreiros, M. A., Abanades, S., and Oliveira, F. A. C. (2019). A Review of Solar Thermochemical CO₂ Splitting Using Ceria-Based Ceramics with Designed Morphologies and Microstructures. *Front. Chem.* 7, 601. doi:10.3389/fchem.2019.00601
- Roy, N., Hirano, Y., Kuriyama, H., Sudhagar, P., Suzuki, N., Katsumata, K.-I., et al. (2016). Boron-Doped diamond Semiconductor Electrodes: Efficient Photoelectrochemical CO₂ Reduction through Surface Modification. *Sci. Rep.* 6, 38010. doi:10.1038/srep38010
- Sarkar, A., Gracia-Espino, E., Wägberg, T., Shchukarev, A., Mohl, M., Rautio, A.-R., et al. (2016). Photocatalytic Reduction of CO₂ with H₂O over Modified TiO₂ Nanofibers: Understanding the Reduction Pathway. *Nano Res.* 9, 1956–1968. doi:10.1007/s12274-016-1087-9
- Severs Millard, T., Genco, A., Alexeev, E. M., Randerson, S., Ahn, S., Jang, A.-R., et al. (2020). Large Area Chemical Vapour Deposition Grown Transition Metal Dichalcogenide Monolayers Automatically Characterized through Photoluminescence Imaging. *npj 2D Mater. Appl.* 4, 12. doi:10.1038/s41699-020-0146-y

- Shit, S. C., Shown, I., Paul, R., Chen, K.-H., Mondal, J., and Chen, L.-C. (2020). Integrated Nano-Architected Photocatalysts for Photochemical CO₂ Reduction. *Nanoscale* 12, 23301–23332. doi:10.1039/d0nr05884j
- Shyamal, S., and Pradhan, N. (2020). Halide Perovskite Nanocrystal Photocatalysts for CO₂ Reduction: Successes and Challenges. *J. Phys. Chem. Lett.* 11, 6921–6934. doi:10.1021/acs.jpcllett.0c00191
- Sorcar, S., Hwang, Y., Lee, J., Kim, H., Grimes, K. M., Grimes, C. A., et al. (2019). CO₂, Water, and Sunlight to Hydrocarbon Fuels: a Sustained Sunlight to Fuel (Joule-To-Joule) Photoconversion Efficiency of 1%. *Energ. Environ. Sci.* 12, 2685–2696. doi:10.1039/C9EE00734B
- Sorcar, S., Thompson, J., Hwang, Y., Park, Y. H., Majima, T., Grimes, C. A., et al. (2018). High-rate Solar-Light Photoconversion of CO₂ to Fuel: Controllable Transformation from C₁ to C₂ Products. *Energ. Environ. Sci.* 11, 3183–3193. doi:10.1039/c8ee00983j
- Tahir, M., Ali Khan, A., Tasleem, S., Mansoor, R., and Fan, W. K. (2021). Titanium Carbide (Ti₃C₂) MXene as a Promising Co-Catalyst for Photocatalytic CO₂ Conversion to Energy-Efficient Fuels: A Review. *Energy & Fuels* 35 (13), 10374–10404. doi:10.1021/acs.energyfuels.1c00958
- Tang, X., Murali, G., Lee, H., Park, S., Lee, S., Oh, S. M., et al. (2021). Engineering Aggregation-Resistant MXene Nanosheets as Highly Conductive and Stable Inks for All-Printed Electronics. *Adv. Funct. Mater.* 31, 2010897. doi:10.1002/adfm.202010897
- Wang, C., Thompson, R. L., Baltrus, J., and Matranga, C. (2010). Visible Light Photoreduction of CO₂ Using CdSe/Pt/TiO₂ Heterostructured Catalysts. *J. Phys. Chem. Lett.* 1, 48–53. doi:10.1021/jz9000032
- Wang, C., Thompson, R. L., Ohodnicki, P., Baltrus, J., and Matranga, C. (2011). Size-Dependent Photocatalytic Reduction of CO₂ with PbS Quantum Dot Sensitized TiO₂ Heterostructured Photocatalysts. *J. Mater. Chem.* 21, 13452–13457. doi:10.1039/c1jm12367j
- Wang, J., Xia, T., Wang, L., Zheng, X., Qi, Z., Gao, C., et al. (2018). Enabling Visible-Light-Driven Selective CO₂ Reduction by Doping Quantum Dots: Trapping Electrons and Suppressing H₂ Evolution. *Angew. Chem. Int. Ed.* 57, 16447–16451. doi:10.1002/anie.201810550
- Wang, X.-D., Huang, Y.-H., Liao, J.-F., Jiang, Y., Zhou, L., Zhang, X.-Y., et al. (2019). *In Situ* Construction of a Cs₂SnI₆ Perovskite Nanocrystal/SnS₂ Nanosheet Heterojunction with Boosted Interfacial Charge Transfer. *J. Am. Chem. Soc.* 141, 13434–13441. doi:10.1021/jacs.9b04482
- Wu, H. L., Li, X. B., Tung, C. H., and Wu, L. Z. (2019). Semiconductor Quantum Dots: An Emerging Candidate for CO₂ Photoreduction. *Adv. Mater.* 31, 1900709. doi:10.1002/adma.201900709
- Xie, S., Zhang, Q., Liu, G., and Wang, Y. (2016). Photocatalytic and Photoelectrocatalytic Reduction of CO₂ Using Heterogeneous Catalysts with Controlled Nanostructures. *Chem. Commun.* 52, 35–59. doi:10.1039/c5cc07613g
- Xu, Y.-F., Yang, M.-Z., Chen, B.-X., Wang, X.-D., Chen, H.-Y., Kuang, D.-B., et al. (2017). A CsPbBr₃ Perovskite Quantum Dot/Graphene Oxide Composite for Photocatalytic CO₂ Reduction. *J. Am. Chem. Soc.* 139, 5660–5663. doi:10.1021/jacs.7b00489
- Xu, Y. F., Wang, X. D., Liao, J. F., Chen, B. X., Chen, H. Y., and Kuang, D. B. (2018). Amorphous-TiO₂-Encapsulated CsPbBr₃ Nanocrystal Composite Photocatalyst with Enhanced Charge Separation and CO₂ Fixation. *Adv. Mater. Inter.* 5, 1801015. doi:10.1002/admi.201801015
- Yan, Y., Chen, J., Li, N., Tian, J., Li, K., Jiang, J., et al. (2018). Systematic Bandgap Engineering of Graphene Quantum Dots and Applications for Photocatalytic Water Splitting and CO₂ Reduction. *ACS Nano* 12, 3523–3532. doi:10.1021/acsnano.8b00498
- Yao, X., Wang, Y., Lang, X., Zhu, Y., and Jiang, Q. (2019). Thickness-Dependent Bandgap of Transition Metal Dichalcogenides Dominated by Interlayer van der Waals Interaction. *Phys. E: Low-Dimens. Syst. Nanostructures* 109, 11–16. doi:10.1016/j.physe.2018.12.037
- Yu, J., Low, J., Xiao, W., Zhou, P., and Jaroniec, M. (2014). Enhanced Photocatalytic CO₂-Reduction Activity of Anatase TiO₂ by Coexposed {001} and {101} Facets. *J. Am. Chem. Soc.* 136, 8839–8842. doi:10.1021/ja5044787
- Zeng, Z., Yan, Y., Chen, J., Zan, P., Tian, Q., and Chen, P. (2019). Boosting the Photocatalytic Ability of Cu₂O Nanowires for CO₂ Conversion by MXene Quantum Dots. *Adv. Funct. Mater.* 29, 1806500. doi:10.1002/adfm.201806500
- Zhang, H., Wei, J., Dong, J., Liu, G., Shi, L., An, P., et al. (2016). Efficient Visible-Light-Driven Carbon Dioxide Reduction by a Single-Atom Implanted Metal-Organic Framework. *Angew. Chem. Int. Ed.* 55, 14310–14314. doi:10.1002/anie.201608597

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