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Design of heterojunction with components in different dimensions for electrocatalysis applications

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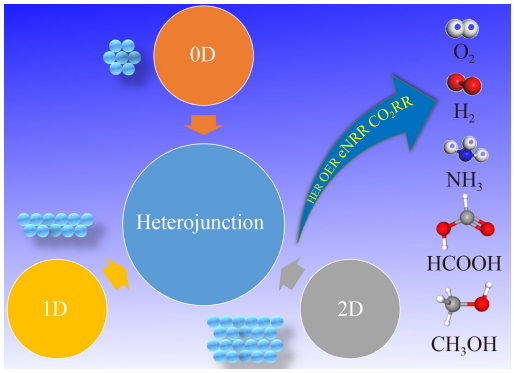
ABSTRACT

Searching for high-performance and cost-effective catalysts is of particular importance for the practical electrocatalysis applications. The heterojunctions with components in different dimensions show unique physical and chemical properties, which can offer large space for rational design of electrocatalysts. In this paper, we firstly reviewed recently related works, and then proposed a few perspectives on exploring heterojunction for electrocatalysis applications.

Keywords heterojunction, electrocatalysis, multiple dimension



Nowadays, the cost of renewable energy generated by wind, water and solar continues to decrease, thus, renewable energy-powered chemical reactions such as oxygen and hydrogen evolution reactions (OER/HER), electrocatalytic nitrogen reduction reaction (eNRR) and the CO_2 electroreduction reaction (CO_2RR) are considered as a totally green and sustainable approach for synthesis of valuable chemical products, as well as achieve the goal of decarbonization [1–3]. The feasibility of electrocatalytic synthesis reactions depends on the performance of electrocatalysts [4, 5]. Therefore, searching for high-performance and cost-effective electrocatalysts is of particular importance for the practical application.

Low-dimensional materials possess intriguing electrical, mechanical, and electrochemical properties, and they serve as potentially inexpensive catalysts in electrocatalysis fields [6]. Two-dimensional (2D) materials can offer large surface areas, however, the active sites often origin from the edges and defects, rather than the basal planes [7]. Optimization strategies such as chemical doping [8, 9] and vacancy engineering [10] were performed to improve the intrinsic activity of these catalysts. One-dimensional (1D) materials have been demonstrated as excellent electrocatalyst candidates due to high specific surface areas, fast charge transport pathways, fast mass transport and chemical accessibility [11]. Electrocatalysts with zero-dimensional (0D), also known as quantum dots (QDs), have better aqueous solvent solubility and more abundant active edge sites than that with 2D and 1D, which have been utilized in CO_2 conversion [12], H_2 production [13], electrochemical oxygen evolution [14, 15], and oxygen reduction reaction [16], etc. Jin *et al.* [17] reported that MXene catalysts can be mediated through the optimization of both QDs

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sizes and functional groups. Both DFT calculations and experiment results demonstrated that the Ti-edge and the –OH surface groups in $Ti_3C_2T_x$ MXene QDs are more conducive to N_2 adsorption and activation, which is beneficially for efficient ammonia production at room temperature. Tian *et al.* [18] have published a detail review on carbon quantum dots (CQDs), which emerge as promising functional materials for the applications in energy-conversion sectors through electrocatalysis due to their outstanding features of low cost, nontoxicity, large surface area, high electrical conductivity, and rich surface functional groups.

The electronic and optical properties, as well as catalysis performance can be adjusted and optimized by the introduction of catalyst-support to construct heterostructures owing to the synergistic effect between the different components [19–21]. Internal electric field will be established in the heterostructure, leading to greatly enhance electrical and ionic conductivities [22]. Heterostructure architectures engineering also can control both of the geometry and electronic structure of the active sites at the interface, which is beneficial to develop heterostructure catalysts with extraordinary properties such as preferable electrochemical stability and superior intrinsic catalytic activities [23]. Wang *et al.* [24] indicated that K_3Sb/graphene performs excellent electrochemical nitrogen reduction reaction (eNRR) activity and graphene substrate can promote electronic conductivity between K_3Sb and dinitrogen. The synergistic effect of TiO_2 and $BiVO_4$ can shorten the proton transport path, and the heterojunction interface and oxygen vacancy can be the active site of N_2 activation, which is conducive to reduce the over potential of eNRR [25]. Electron transfer from $CoTa_2O_6$ to graphene substrate also can be utilized to boost the OER reactivity of Co-site [26]. For MoSSe/GaN heterostructures, the magnitude of the carrier mobility can be tuned by Janus structure and stacking modes, which exhibits a superior high carrier mobility of 281.28 $cm^2 \cdot V^{-1} \cdot s^{-1}$ for electron carrier and 3951.2 $cm^2 \cdot V^{-1} \cdot s^{-1}$ for hole carrier [27]. Liu *et al.* [28] found that the decoration of the MoS_2 by Mo_2C particles has a critical influence on the interaction between catalyst and mass at interfaces such as correct wettability and fast water dissociation kinetics, achieving highly active for hydrogen evolution independent of pH, with low overpotentials of 227 mV and 220 mV in acidic medium and alkaline medium at a high current density of 1 $A \cdot cm^{-2}$, respectively.

Specially, the integration of nanomaterials in different dimensions via non-covalent or covalent strategies to form heterostructures will lead to unique physical and chemical properties. Moreover, materials in 0D, 1D, and 2D show quite different unique properties, which are remarkably different from their bulk counterparts [29–32]. Therefore, a fundamental question would be what will happen when two components with different dimensions are mixed to form a heterojunction, as well as their influence on the electrocatalysis properties (Fig. 1).

Zhang *et al.* [33] reported that ultrafine nickel nitride (Ni_3N) QDs decorated porous vanadium nitride (VN) nanosheets, which can enhance the alkaline oxygen evolution efficiency. The successful construction of Ni_3N QDs chemically coupled with porous VN nanosheets cause structural distortion due to the strong interatomic interaction at the interface, leading to rapid charge transfer and mass transport. Recently, we have presented a concept material by using $Ti_3C_2O_2$ MXene QDs and graphene to construct 0D/1D hybrid structure by DFT calculations [34]. It is demonstrated that slight distortion can be observed in graphene after being decorated with QDs, which can be utilized to tune the electronic structure of QDs and graphene. Due to the zero-dimension feature and interfacial interaction, excellent HER performance can be achieved. As a result, it is expected that 0D/2D heterojunctions, or more general multiple dimension designs, offer large space for rational design of catalysts for HER, OER, eNRR, and CO_2RR, etc.

Inspired by the above-mentioned studies, electrocatalysis performance can be further improved by optimizing QDs with proper composition or/and computationally screening a variety of catalyst supports such as g-C_3N_4, borophene and phosphine. Further works remain to be under progress: (i) High throughput screening of heterojunction with components in different dimensions for high performance electrocatalysis should be systematically carried out by theoretically calculations; (ii) Self-assembly [35] and chemical vapor deposition (CVD) [36], solvent phase engineering methods [37] have been developed to synthesis heterostructures (Fig. 2), however, they suffer many drawbacks. The synthetic method needs further improvement and perfection; (iii) Advanced characterization techniques such as in-situ experiments need to be performed to characterize the actual electronic results and real active sites.

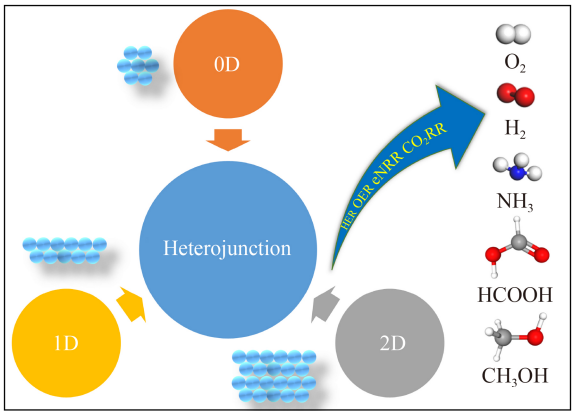

Fig. 1 Schematic illustration of heterojunction with components in different dimensions.

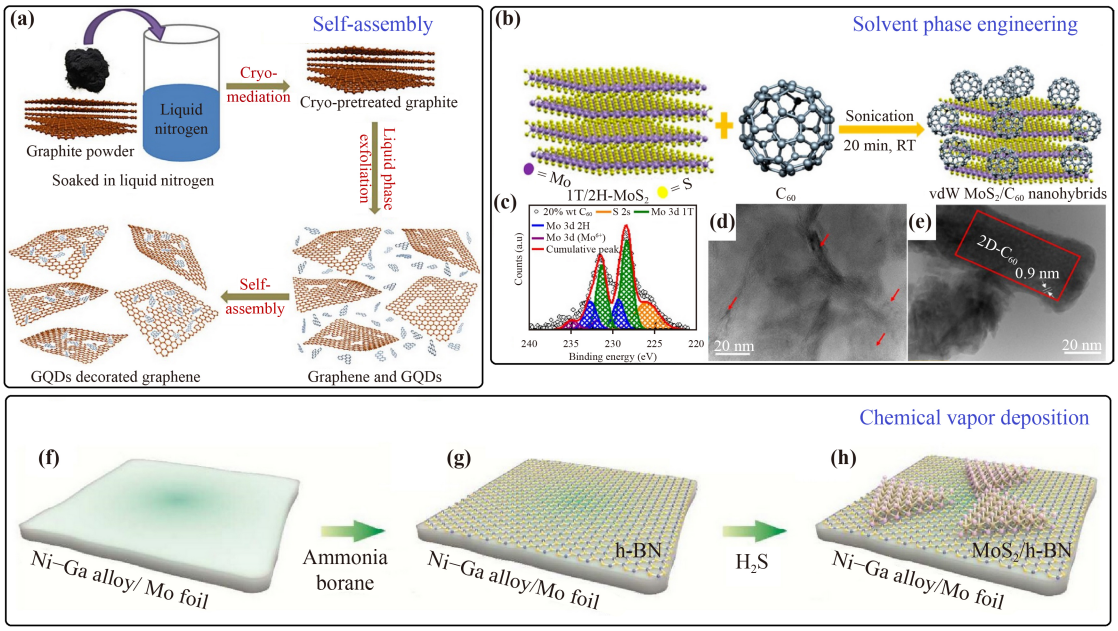

Fig. 2 Typical synthesis methods for heterojunction with components in different dimensions, **(a)** Self-assembly [35], **(b—e)** chemical vapor deposition (CVD) [36], and **(f—h)** solvent phase engineering methods [37].

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