



Computational screening of two-dimensional coordination polymers as efficient catalysts for oxygen evolution and reduction reaction



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ABSTRACT

Oxygen evolution and reduction reactions (OER and ORR) are essential to the development of renewable energy conversion and storage technologies. For the first time, we investigate newly experimentally realized two-dimensional hexaaminobenzene-based coordination polymers (2D HAB-CPs) as OER and ORR catalysts through computational screening approach. We find that the interaction strength between intermediates and the transition metal complex (TM-N₄) govern the catalytic activity of 2D HAB-CPs for OER and ORR. The interaction strength is strongly contingent on *d*-band centers, which can be modulated by changing TM atoms with different *d*-electron occupations. This modification of the interaction strength allows us to screen out the catalyst with the best catalytic performance. The best catalyst for OER is 2D Rh-HAB-CP with an over-potential (η) of 0.32 V, followed by Co-HAB-CP (0.41 V), while for ORR, Fe-HAB-CP has a smallest maximum free energy change ($\Delta G_{max}^{1,23}$) of 0.52 eV under equilibrium potential. Furthermore, these results inspire us to design a bifunctional OER/ORR catalyst by mixing Fe/Co precursors in 2D HAB-CP with the ORR/OER theoretical overpotentials even lower than that of the best ORR/OER catalysts (Pt/RuO₂). In addition, all the 2D HAB-CPs are metallic due to the effects of *d*-*p*- π conjugation, which ensures fast electron transfer during the electrochemical reactions. Our findings highlight a new family of 2D materials as efficient non-precious-metal metal-air battery catalyst and offer a novel strategy in catalyst design.

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1. Introduction

The conversion of sunlight into fuels through renewable energy conversion and storage technologies is considered a promising solution for the energy and environment challenges facing us now [1–3]. Promising technologies include water splitting [4,5], fuel cell [6] and metal-air batteries [7]. The performance of these technologies is limited by two bottleneck reactions with slow kinetics: the evolution and reduction of molecular oxygen (OER/ORR) [2,8,9]. A telling example is the rechargeable metal-air battery, where OER and ORR take place during both the charging and discharge processes, respectively [10]. To boost the kinetics of OER and ORR, noble metals including Pt [11], Pd [12], Ru [13] and Ir [14], have been assessed to be efficient electrocatalysts. However, the price and scarcity of these catalyst materials hamper the commercialization of the energy technologies based on these electrocatalysts. Intensive research efforts have recently focused on catalysts with less-loading noble metal for OER/ORR, or replacing them with earth-abundant catalysts [10,15]. Any technical

breakthrough in these aspects would be advantageous for solving future energy and environment problems [16].

Hybrid metallic/organic materials are potential OER/ORR catalysts to replace noble metal [17–20]. One example is the transition metal macrocycles (TM-N₄) [21–23]. This basic structure has been widely synthesized in metal-organic frameworks such as phthalocyanine and porphyrin metal complexes [24–26]. They are considered as promising, non-precious electrocatalysts with OER and ORR activity approaching the performance of the platinum-based catalysts [27,28], due to their fast electron transfer. Recently, the TM-N₄ complexes have also been integrated into graphitized carbon. The experimentally observed excellent OER performance [27–29] is attributed to the high level of individually nitrogen-coordinated TM atom, which minimizes the overall usage of the metal material while also display extraordinary catalytic selectivity [30].

2D coordination polymers represent an emerging set of organometallic framework materials that have the potential for useful application as topological insulators and electrocatalysts [31–34]. Recently, Louies et al. have successfully prepared a family of hexaaminobenzene-based 2D coordination polymers (2D HAB-CP) by using hexaaminobenzene (HAB) as the coordinating

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ligand and TM ions such as Co^{2+} , Ni^{2+} and Cu^{2+} as the TM linkers [35]. As the catalytic properties of organometallic frameworks depend on the TM atoms, the extension of these TM linkers to a wide range of TMs, in particular Mn, Fe and Rh, can allow us to change the *d*-electron occupation and modulate the adsorption strength of reaction intermediates on TM atom sites of the 2D HAB-CP. Too strong and too weak adsorptions show inverse effects to the reaction according to the Sabatier's principle [36]. By modifying the *d*-electron occupation, the ORR/OER reaction rate can be tuned and the optimal TM-based 2D HAB-CP for the OER/ORR can be screened out.

In this work, for the first time, we explore newly experimentally realized 2D hexaaminobenzene-based coordination polymers as OER and ORR catalysts. We find that the catalytic activity of 2D HAB-CPs is determined by the transition metal complex (TM- N_4) whose *d*-band centers can be modulated by changing TM atoms with different *d*-electron occupations. This will allow tuning of the interaction strength between TM and reaction intermediates, upon which, catalytic performance depends. The overpotentials for OER and ORR are 0.32 V and 0.52 V for 2D Rh-HAB-CP and Fe-HAB-CP, respectively. We also propose that a bifunctional OER/ORR catalyst can be designed by mixing Fe/Co precursors in 2D HAB-CP. In addition, the metallic properties of the 2D HAB-CPs ensure fast electron transfer during the electrochemical reactions. Our results highlight a new catalyst based on 2D coordination polymers for efficient OER/ORR.

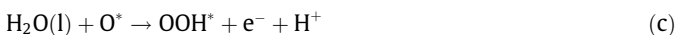
2. Computational methods

Geometry optimization and electronic structure calculations were performed by using Density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) code [37,38]. The exchange-correlation interactions were described by the generalized gradient approximation (GGA) [39] in the form of the Perdew-Burke-Ernzerhof functional (PBE) [40]. The van der Waals interaction was described by using the empirical correction in Grimme's scheme, i.e. DFT + D3 [41]. Spin-polarized calculations are applied in all the cases. The electron wave-functions were expanded by plane waves with cut-off energies of 500 eV, and the convergence tolerance for residual force and energy on each atom during structure relaxation were set to 0.005 eV/Å and 10^{-5} eV, respectively. The vacuum space was more than 20 Å, which was enough to avoid the interaction between periodical images. Oxidation states of the transition metals in the active sites obtained with the spin analysis using in the Calle-Vallejo et al.'s works [22,42].

The overall OER in the acid environment can be written in Eq. (1), which happens on the anode of a water splitting cell and a metal air battery during charge [8]:



In our model, we assume that the OER proceeds in the four electrons pathway as shown in Eqs. (a)–(d) and Fig. 4a–e as previous works did [43–46].



where the * denotes an activity site on the catalyst. (l) and (g) refer to liquid and gas phases. For each step, the reaction Gibbs free energy ΔG is defined by the following equation [47]:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S + \Delta G_U + \Delta G_{\text{pH}} \quad (2)$$

The ΔE , ΔZPE and ΔS is the energy difference, the zero-point energy and entropy of the reaction, respectively. The total energy and vibrational frequencies of the intermediates on Co-HAB (listed in Table S3, Supporting information) obtained by DFT calculation are used to calculate the ΔE and the ΔZPE , respectively. The ΔS are calculated with the values of Ref. [48]. These zero point energy corrections and entropic contributions (listed in Table S4, Supporting information) are applied to other catalysts. To calculate the Gibbs free energy of O_2 , we assume that the Gibbs free energy change of the total reaction $\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2$ is fixed at the experimentally found value of 2.46 eV per water molecule [44]. Therefore, $1/2G_{\text{O}_2} = 2.46 - G_{\text{H}_2\text{O}} + G_{\text{H}_2}$. $\Delta G_U = -eU$, in which U is the potential related to the standard hydrogen electrode. ΔG_{pH} is the corrected Gibbs free energy of H^+ ions depending on the concentration. $\Delta G_{\text{pH}} = -kT \ln 10 \cdot \text{pH}$. The overpotential (η) for OER is obtained by:

$$\eta = \frac{\max\{\Delta G_a, \Delta G_b, \Delta G_c, \Delta G_d\}}{e} - 1.23 \quad (3)$$

where $\Delta G_a, \Delta G_b, \Delta G_c$, and ΔG_d are the reaction Gibbs free energy of reactions (a)–(d), when $U = 0$ V, $\text{pH} = 0$.

The ORR is the reverse reaction of OER [49], which occurs on the cathode of the fuel cell and the air battery in discharge [50]:



In acidic solution, the ORR proceeds via the four-electron-transfer pathway as shown in Eqs. (a')–(d') and Fig. 5a–e [51],



The computational Gibbs free energy change ($\Delta G_{a'}, \Delta G_{b'}, \Delta G_{c'}, \Delta G_{d}'$) of each step is used to determine the barrier at any given pH and applied potential U . The theoretical maximum free energy change ($\Delta G_{\text{max}}^{1.23}$) for ORR at the equilibrium potential (1.23 V) is obtained by

$$\Delta G_{\text{max}}^{1.23} = \max\{\Delta G_{a'}, \Delta G_{b'}, \Delta G_{c'}, \Delta G_{d}'\} + 1.23 \text{ eV} \quad (5)$$

As step a', b', c' and d' is the reverse reaction of d, c, b, and a, respectively, $\Delta G_{a'} = -\Delta G_d$, $\Delta G_{b'} = -\Delta G_c$, $\Delta G_{c'} = -\Delta G_b$, and $\Delta G_{d}' = -\Delta G_a$. Therefore, Eq. (5) can be rewritten into Eq. (6):

$$\Delta G_{\text{max}}^{1.23} = \max\{-\Delta G_d, -\Delta G_c, -\Delta G_b, -\Delta G_a\} + 1.23 \text{ eV} \quad (6)$$

3. Results and discussions

Fig. 1a and b present the top and side view of the 2D HAB-CP, respectively. The unit cell of 2D HAB-CP is connected by three equivalent TM atoms (linkers) in a hexagonal honeycomb lattice. Each TM atom is surrounded by four N atoms forming a square planar arrangement of nitrogen-coordinated metal macrocycles (TM- N_4). The TM- N_4 complex is structurally similar to that in phthalocyanine metal complexes [52] and TM- N_4 embedded graphene [53,54], which have attracted intensive research interest for use as OER/ORR catalysts. To systematically explore the influence of *d*-electron occupation on the catalytic activity, we vary the TM atom linkers (highlighted in green in Fig. 1c) in 2D HAB-CP from V to Cu, in which Co, Ni and Cu were realized in the

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