Rare-Earth Elements Modified 1T Phase MoS2 Synergy with Defects for Enhanced Hydrogen Evolution

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Abstract. Earth-abundant MoS2 has drawn continuous attentions in many fields, especially hydrogen evolution reaction (HER), which has been regarded as an effective technology for renewable energy. However, its activity is limited by edge sites, to the disadvantage of atomic economy. Herein, combination with theoretical calculation, we propose that rare-earth element (Ce, La, and Tb) synergy with defect can optimize bulk site of MoS2 for HER. Furthermore, self-supporting electrode was designed for integrating the optimized activity site, leading to an excellent HER performance. Compared to La, Tb, and pristine MoS2, the Ce-based MoS2 synergy with defect has a better activity with an overpotential of 165 mV to achieve 100 mA cm⁻², close to the state-of-the-art noble metal Pt.

1. Introduction
As one of typical materials in two-dimensional transition-metal dichalcogenides (TMDCs), MoS2, has drawn continuous attentions due to their fascinating properties, such as exceptional electronic, optical, mechanical, and chemical properties [1]. The recent proliferation of research into TMDCs includes electronic and optical nanodevices and hydrogen evolution reaction (HER) catalysis especially, which has been regarded as an effective technology for H₂ economy.

Generally, MoS2 appears in two main types of polymorphs (semiconducting 2H phase and metallic 1T phase), depending on the different coordination modes between Mo and S atoms (The coordination environment are shown in Figure 1). Theoretical and experimental evidences reveal the unsaturated Mo atom at edge of 2H MoS₂, rather than the basal plane, is active for HER, because of a H atom absorption free energy (ΔG_H⁺) close to the state-of-the-art noble metal Pt [2]. In contrast, the in-plane of 1T MoS₂ is active for HER, leading to a higher atomic effectively [3]. Therefore, 1T MoS2 has been regarded as a promising candidate for HER, as well as to the advantage of superior conductivity. However, their HER performance still away off from the Pt-based materials, limiting the larger scale application.

Rare earth elemental, possessing unique properties of 4 f electrons, and lattice defects modification have been widely used to regulate the materials in many catalytic systems to achieve an optimized site [4, 5]. However, its effects on layered TMDs and electro catalytic HER properties have not been previously investigated to date.
Herein, to enhance the capability of 1T MoS$_2$ for HER, rare earth elements (Ce, La, and Tb) were doped into the lattice of MoS$_2$ synergy with defects to modify the active site. Meanwhile, a self-supporting electrode was applied to integrate the modified active site for further improving the performance.

![Figure 1](image1.png)

**Figure 1.** The coordination environment of 2H MoS$_2$ and 1T MoS$_2$.

### 2. Experimental details

#### 2.1. Synthesis

In a typical synthesis, sodium molydate dihydrate (60 mg), l-cysteine (65 mg), cerous nitrate (or lanthanum nitrate or terbium nitrate), polyethylene glycol (14 g) and urea (0.4 g) were dissolved in aqueous citric acid solution (pH=3.5 ± 0.2, 16 g) with magnetic stirring for 10 min. Then, the well-dispersed solution was transferred into a 50 mL Teflon-lined stainless steel autoclave with a piece of carbon cloth (CC, 1 × 4 cm). The autoclave was heated at 200 °C for 20 h. After naturally cooled at room temperature, the as-prepared sample washed subsequently with water and absolute ethanol several times and vacuum drying at 60 °C for 12 h. To study the effect between rare-earth element and activity, the same content of rare-earth element was applied (0.01 mol).

#### 2.2. Theoretical calculations

Theoretical calculations were performed using Vienna ab initio simulation packages (VASP) based on density functional theory (DFT) [6]. The atomic structures for all models were fully relaxed and the convergence of energy and forces were set to $1 \times 10^{-4}$ eV and $0.02$ eV Å$^{-1}$ respectively. The Brillouin zone was sampled by the Monkhorst-Pack method with a $6 \times 6 \times 1$ k-point grid [7]. The free energy of hydrogen adsorption ($\Delta G_{H^+}$) can be calculated as follows: $\Delta G_{H^+} = \Delta E + 0.24$ eV [8].

### 3. Results and discussions

Firstly, the $\Delta G_{H^+}$ was investigated based on first-principle calculation. Figure 2a show the adsorption site of H atom on different mode. The ideal $\Delta G_{H^+}$ value should be close to 0 eV, meaning the H$_2$ evolution not controlled by proton adsorption and H$_2$ desorption. The mode of Ce doping synergy with defect possess a $\Delta G_{H^+}$ of 0.48 eV, lower than that of La (0.51 eV), Tb (0.50 eV), and pristine MoS$_2$ (0.83 eV) (shown in Figure 2b). This indicates that the Ce doping synergy with defect is the optimized site for HER.

To validate the above theoretical analysis, different samples were synthesized. For clarity, the as-synthesized samples of Ce, La, and Tb doped MoS$_2$ with defects were labelled as DCD, DLD, and DTD, respectively. The microstructure of the sample was investigated by high-resolution transmission electron microscopy (HRTEM). Figure 3a presents the selected area electron diffraction (SAED) pattern of the samples, where the diffuse diffraction ring can be observed. Meanwhile, as shown in Figure 3b, some defects can be observed on the basal plane of MoS$_2$, confirming the abundant defects. Furthermore, the atomic arrangements belong to 1T MoS$_2$, indicating that the crystal structure still maintain after Ce doping. Scanning electron microscopy (SEM) images suggest the MoS$_2$ nanosheets can uniformly disperse on the whole CC as a self-supporting electrode, benefitting for mass transfer (Figure 3c and 3d). Based on above characterization, the rare-earth elements modified 1T MoS$_2$ with defects can be synthesized by a simple hydrothermal reaction.
Electrochemical performance was tested at room temperature by a Chenhua CHI 660D electrochemical workstation with a typical three-electrode setup, using a piece of freshly-made DCD (or DLD, DTD, and pristine MoS2) as the working electrode, a graphite rod as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Linear sweep voltammetry measurements were performed with a scan rate of 5 mV s\(^{-1}\) in N\(_2\)-saturated 0.5 M H\(_2\)SO\(_4\) electrolyte, as shown in Figure 4. The applied overpotential of DCD is 165 mV at catalytic current density of 100 mA cm\(^{-2}\), while the overpotential gradually increase to 170, 184, 200 mV for DTD, DLD, and pristine MoS\(_2\), respectively. Therefore, DCD with defects exhibits excellent HER activity, agreeing well with experiment result.
4. Conclusion
HER by rare-earth element (Ce, La, and Tb) doped 1T phase MoS$_2$ synergy with defects was investigated. Theoretical and experimental results indicate that Ce doped 1T phase MoS$_2$ synergy with defects exhibit highest HER activity. Furthermore, when integration the optimized activity site in a self-supporting electrode by CC supporting, an excellent HER activity was achieved.

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