Emerging trends in electrochemistry and electrocatalysis of platinum dichalcogenides: Towards activation for charge transfer and hydrogen evolution

Xinyi Chia,[a] **Adriano Ambrosi,**[a] **Petr Lazar,**[b] **Zdeněk Sofer,**[c] **Jan Luxa,**[c] **Martin Pumera**[a]*****

[a] *Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore*

[b] *Regional Centre of Advanced Technologies and Materials, Palacký University Olomouc, 771 46 Olomouc, Czech Republic*

[c] *Department of Inorganic Chemistry, University of Chemistry and Technology Prague,166 28 Prague, Czech Republic*

**Corresponding author: (+65) 6316 8796, pumera.research@gmail.com*

Abstract: This work annotates the electrochemistry and electrocatalysis of the Group 10 TMDs; specifically, the platinum (Pt) dichalcogenides consisting of PtS_2, $PtSe_2$ and $PtTe_2$. The variation in electronic property of the Pt dichalcogenide from semiconducting in PtS_2; semimetallic, in $PtSe_2$ and then to metallic in $PtTe_2$, stirs up interest in their charge transfer and catalytic attributes. We draw parallels between the chalcogen type (S, Se and Te) and the electrochemical and electrocatalytic performances of Pt dichalcogenides. Towards the goal of electrochemical activation, we evaluate the effectiveness of an oxidative and reductive treatment in promoting their charge transfer and HER electrocatalytic properties.

Keywords: Platinum dichalcogenides, electrochemistry, hydrogen evolution.

1. Introduction

Presently, transition metal dichalcogenides (TMDs) have gradually gained traction as a prominent class of layered nanostructures. A TMD is represented by a general formula MX_2 where M denotes a transition metal belonging to groups 4-10 and X is a chalcogen (S, Se or Te). Each layer of TMD contains repeating units of MX_2 that are held by strong covalent bonds. These layers are stacked together by weak van der Waal's forces. Due to the weak interlayer interactions, TMDs are readily exfoliated into thin sheets[1] and renders them highly anisotropic in their physical properties. Layered TMDs have hitherto attained success in applications ranging from electronics, energy storage to photoluminescence.[2-4] However, current research in layered TMDs favors Group 6 TMDs like MoS_2 and WS_2 whereas other groups in the TMD family linger in their shadows. Akin to structures of 1T-MoS_2, Group 10 TMD crystals adopt an octahedral geometry such that the transition metal center is coordinated to 6 chalcogen atoms. Electronic structures of Group 10 TMDs have intrigued the scientific community due to the close proximity in binding energies of valence d-orbitals of the Group 10 transition metals and valence p-orbitals of the chalcogen atoms. This phenomenon results in hybridization between d- and p-orbitals.[5] Hence, Group 10 TMDs exhibit unique electronic structures and properties which differentiate them from TMDs in the earlier groups. Platinum (Pt) dichalcogenides, including PtS_2, $PtSe_2$, and $PtTe_2$, are at the helm of studies into electronic structures of Group 10 TMDs. As we advance down the chalcogen group, the paradigm shift in the electronic property of the Pt dichalcogenide from semiconducting in PtS_2; semimetallic, in $PtSe_2$ and to metallic in $PtTe_2$, sparks curiosity into their charge transfer and catalytic attributes.[6] Herein, we present a cardinal study on the electrochemistry of layered Pt dichalcogenides, namely, PtS_2, $PtSe_2$ and $PtTe_2$. This work emphasizes the correlation between varying the chalcogen type (S, Se and Te) to the electrochemical and catalytic performances of Pt dichalcogenides. Toward the goal of electrochemical activation, we also evaluate the effectiveness of an oxidative and reductive treatment in stimulating their charge transfer and electrocatalytic properties for hydrogen evolution reaction (HER).

2. Experimental (or Theoretical)

Voltammetric measurements were recorded on a μAutolab III electrochemical analyser (Eco Chemie B.V., Utrecht, The Netherlands) with the software NOVA version 1.8 (Eco Chemie). Electrochemical measurements of the Pt dichalcogenides were performed in a 3 mL electrochemical cell at 25 °C in a default three electrode configuration. A platinum electrode and an Ag/AgCl electrode functioned as auxiliary and reference electrodes, respectively and a glassy carbon (GC, 3 mm diameter) electrode was adopted as the working electrode.

Density functional theory (DFT) calculations were performed using the projector-augmented wave method in the Vienna Ab Initio Simulation Package (VASP).

3. Results and discussion

Using density functional theory (DFT) calculations, we show that the density of states concurs with previous investigations. It can be explained that the electrochemical and catalytic behaviors of Pt dichalcogenides are rationalized to depend on their electronic structures.

After subjecting the Pt dichalcogenides to their respective characteristic reductive or oxidative potentials, we note the feasibility of electro-treatment towards tailoring their charge transfer and catalytic properties. In terms of charge transfer, all Pt dichalcogenides are successfully activated when subject to an electrochemical reductive treatment. Accelerated heterogeneous electron transfer (HET) rates are evident in electrochemically reduced Pt dichalcogenides.

The electrocatalytic attributes of the Pt dichalcogenides for HER unveil an interesting trend of $PtTe_2$ > $PtSe_2$> PtS_2 whereby the HER catalytic property enhances upon proceeding down the chalcogen group. Moreover, Pt dichalcogenides are effectively activated for HER such that reduced PtS_2 and oxidized $PtTe_2$ exhibit improved HER performance compared to before treatment. $PtSe_2$ manifests enhanced HER properties when electrochemically oxidized or reduced. Such distinct electrochemical responses of Pt dichalcogenides to activation largely originate from their intrinsic electronic structures.

Among all electrochemically activated Pt dichalcogenides, PtS_2 demonstrates most accentuated improvement as an HER electrocatalyst (Figure 1) with an exceptional 50 % decline in HER overpotential at -10 mA cm^{-2}.

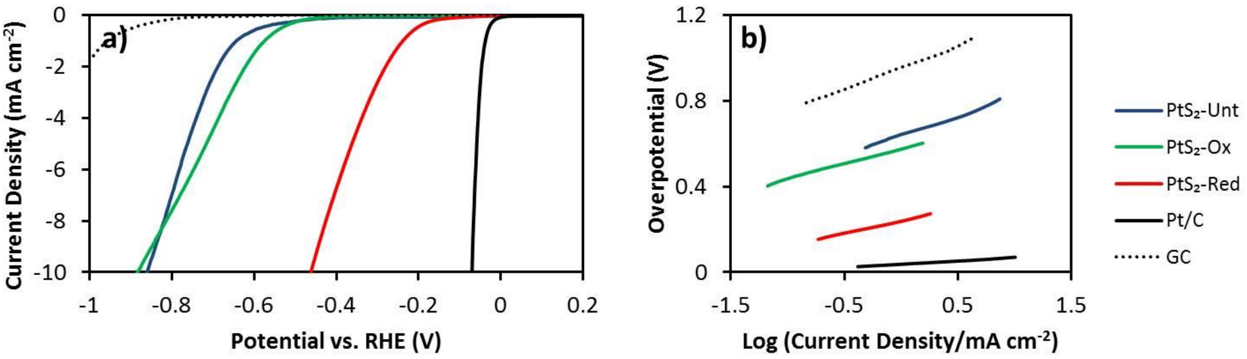

Figure 1. a) Linear sweep voltammograms for hydrogen evolution reaction (HER) on PtS_2 and their respective electrochemically oxidized and reduced counterparts. b) Tafel plots of PtS_2 and their respective electrochemically oxidized and reduced counterparts.

4. Conclusions

While these electrochemically activated Pt dichalcogenides will be promising electrode materials for HER electrocatalysts, knowledge on Pt dichalcogenides would provide valuable insights in the field of TMD electrochemistry; in particular, for the currently inadequately represented Group 10 TMDs.

References

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