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Self-gating in semiconductor electrocatalysis

The semiconductor-electrolyte interface dominates the behaviors of semiconductor electrocatalysis, which has been modeled as a Schottky-analog junction according to the classic electron transfer theories (1-4). However, this model cannot be used to explain the extremely high carrier accumulations in ultrathin semiconductor catalysis observed in our work. Inspired by the recently developed ion-controlled electronics (5-8), we revisited the semiconductor-electrolyte interface and unraveled a universal self-gating phenomenon through micro-cell based in-situ electronic/electrochemical measurements to clarify the electronic-conduction modulation of semiconductors during electrocatalytic reaction. We further unveiled a surface conductance mechanism under self-gating that dominates the charge transport in semiconductor electrocatalysts, and demonstrate the strong correlation between Then we demonstrate that the type of semiconductor catalysts strongly correlates and their electrocatalysis, i.e., n-type semiconductor catalysts favor cathodic reactions such as hydrogen evolution reaction (HER), p-type ones prefer anodic reactions such as oxygen evolution reaction (OER), and bipolar ones tend to perform both anodic and cathodic reactions. Furthermore, we also propose a model of leakage metal-insulator-semiconductor (LMIS) junction to describe the aforementioned self-gating phenomenon, i.e., leakage ionic gating. It is distinct from the conductance modulation based on Schottky-analog junction in electrochemical classic electron transfer theories. Our study provides a new insight into the electronic origin of semiconductor-electrolyte interface during electrocatalysis, paving the way for designing high-performance semiconductor catalysts.

References

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Figures

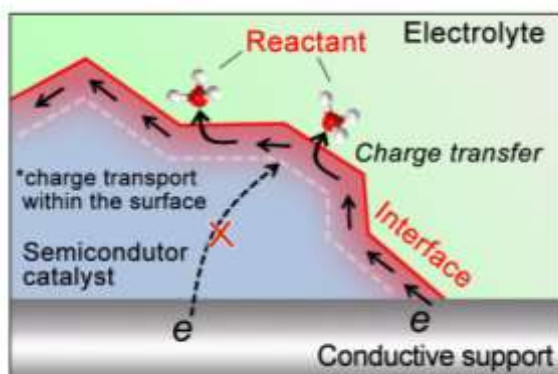


Figure 1: Schematic illustration of the surface conductance of semiconductor electrocatalyst. A surface conductive pathway is formed when the surface of the semiconductor electrocatalyst is turned on by the electrochemical potential under self-gating, allowing the charges transfer via the semiconductor-electrolyte interface, i.e., the electrocatalytic reaction happens.