Ultra-thin Defective TiO_2 Films as Photocathodes for Selective CO_2 Reduction to Formate

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In this study, titanium dioxide (TiO_2) is utilized as a photoelectrocatalyst in the carbon dioxide reduction reaction (CO_2RR). TiO_2 is cheap, stable, and exhibits substantial absorption in the near-visible ultraviolet spectrum. Despite these advantages, TiO_2 has low efficiency in electrochemical processes due to its low electrical conductivity. We address this issue by developing ultra-thin and highly defective TiO_2 films (TiO_2-DTF) with a thickness of less than 15 nanometers to enhance the electrical conductivity and selectivity towards formate production during photoelectrochemical CO_2RR. These TiO_2-DTF were synthesized through a simple, replicable sol-gel technique, resulting in smooth, ultra-thin layers with a high density of surface defects.

The catalytic performance of TiO_2-DTF was investigated under photochemical and photoelectrochemical conditions for CO_2RR. It was observed that applying an electrical potential improved both the product yield and selectivity for formate. To understand the underlying mechanism of photoelectrochemical CO_2RR on TiO_2-DTF, *in-situ* attenuated total reflection Fourier-transform infrared spectroscopy (*in-situ* ATR-FTIR) was utilized. This analysis provided insights into the CO_2 photoelectroreduction process. Additionally, the experimental findings were supported by density functional theory (DFT) studies.

This research demonstrates that the selectivity and efficiency of TiO_2 films in CO_2 reduction can be significantly enhanced by modulating film thickness and defect density. In addition, this work opens new pathways for using a cost-effective and environmentally friendly sol-gel process for fabricating ultra-thin, defective TiO_2 films and their promising application in photoelectrocatalysis of CO_2RR.

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