

DISSERTATION INFORMATION

Title: *The Multifunctional $Ti_xW_{1-x}O_2$ ($x = 0.5; 0.6; 0.7; 0.8$) Support For Platinum To Enhance The Activity And CO-Tolerance Of Direct Alcohol Fuel Cells*

Major: **Chemical Engineering**

Major code: **62520301**

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Major Contributions of This Dissertation:

The purpose of this dissertation is to fabricate and develop an effective electrocatalyst towards alcohol electro-oxidation reaction through a combination of utilization of non-carbon support and control of morphology and structure of Pt-based catalysts to promote commercialization of direct alcohol fuel cells. This approach is based on multifunctional $Ti_xW_{1-x}O_2$ supports with an electronic transfer from support to Pt-based catalysts, resulting in a downshift of Pt d-band center and weakening CO-like adsorption on Pt's active sites. While 1D Pt structures facilitate electron transfer by path-directing effects in catalyst electrodes, enhancing reaction kinetics and catalytic activity. The contributions and novelty of this dissertation are listed as follows:

- Various $Ti_xW_{1-x}O_2$ ($x = 0.5; 0.6; 0.7; 0.8$) supports were synthesized by a facile solvothermal route using inorganic precursors without utilizing any surfactants or further calcination process, resulting in small particle size and less agglomeration. The effect of doping tungsten concentrations on the properties of W-doped TiO_2 supports and Pt/W-doped TiO_2 catalysts were explored by many analysis methods. The incorporation of suitable tungsten concentrations into TiO_2 lattices led to the formation of synergistic effects, increasing both surface area and electrical conductivity; however, a reverse trend was observed when the doped tungsten content is too large. Among as-made catalysts, 20 wt% Pt/ $Ti_{0.7}W_{0.3}O_2$ catalyst exhibited the highest performance towards electro-oxidation of ethanol molecules

in an acidic electrolyte, which was attributable to electronic and synergistic effects between support and Pt NPs.

- For the first time, 1D Pt NWs were successfully grown onto $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ surface by a simple chemical reduction route at room temperature without using surface-directing agents, which can avoid strong absorption and coverage of organic macromolecules on the catalyst surface by using surfactants, thereby enhancement in the catalytic performance. The formed Pt nanocatalyst on the $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ surface exhibited a wire-like shape with a length of about 40 nm and 5 nm in diameter. The development of 1D nanostructures is attributable to a very low reduction rate of formic acid in long-term time, which is a favorable environment for anisotropic growth of Pt nuclei along (111) facets by the lowest surface energy. Apart from the unique properties of 1D Pt nanostructure, electronic transfer from $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ support to 1D Pt NWs was evidenced by XPS, leading to improvement in the catalytic performance towards electro-oxidation for both methanol and ethanol molecules. Furthermore, the 1D Pt NWs/ $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ catalyst showed impressive catalytic stability with activity decay of 12.65%, against a large decrease of 45.36% for Pt NPs/C catalyst.
- Apart from, 1D-bimetallic Pt_3Co NWs were grown on $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ support by the surface- and template-free chemical reduction process at room temperature to reduce Pt utilization. Alloying Pt with Co caused a compressive strain in Pt lattice and electronic charge transfer from Co to Pt by a difference of electronegativity of Co and Pt, reducing adsorption of intermediate species and thus increasing active sites of Pt. The 1D Pt_3Co NWs/ $\text{Ti}_{0.7}\text{W}_{0.3}\text{O}_2$ catalyst exhibited superior CO poisoning resistance ability compared to conventional Pt NPs/C catalyst with low onset potential for CO_{ads} species on the catalyst surface, which was proven by the CO-stripping test. This facile but efficient strategy can open a reliable path to design robust catalysts that can replace traditional catalysts and motivate further research in the different fields.

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