

Facile synthesis MXene ($Ti_3C_2T_x$) decorated with Palladium Nanoparticles for electrochemically CO oxidation

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Abstract

Titanium Carbide ($Ti_3C_2T_x$) MXene owns various unique physicochemical and catalytic properties. The electrochemical CO oxidation performance is not yet reported experimentally. Herein, $Ti_3C_2T_x$ MXene decorated with palladium nanoparticles is rationally designed via the selective chemical etching under sonication to form $Ti_3C_2T_x$, which acts as a substrate for Pd nanoparticles via impregnation with Pd salt without a reducing agent. The electrochemical CO oxidation activity was tested in an acidic medium.

Background

Fuel cells are the future of sustainability with a promising different green energy source. Though, CO poisoning reduces its catalytic performance [1]. Consequently, CO oxidation reaction is so important in fuel cells and environmental applications. Different catalysts were used, like transition metals, noble metals, and carbon nitride, for CO oxidation. The engineering of a low-cost catalyst with a favorable property and large-scale production is a critical issue [2]. So the combination of the Pd, which is the most effective catalyst for CO oxidation, and the unique physicochemical properties $Ti_3C_2T_x$ MXene (2D-structure, high surface area, high electron density, abundant active sites, and great defects) can be utilized for the electrochemical CO oxidation. Moreover, the abundant surface functionalities can provide a large number of active sites, so it accelerates charge mobility and enhance the chemisorption of reactants [3]. To address their electrochemical CO oxidation performance is not yet addressed experimentally. Herein, we propose a one-step method for synthesis of Pd NPs decorated $Ti_3C_2T_x$ where $Ti_3C_2T_x$ was etched by HF followed by the delamination under sonication after intercalation with DMSO to form $Ti_3C_2T_x$. Finally, Pd salt was impregnated with $Ti_3C_2T_x$ without a reducing agent to form uniform semi-spherical Pd NPs over exfoliated 2-D $Ti_3C_2T_x$. The electrochemical CO oxidation activity of Pd/ $Ti_3C_2T_x$ was investigated in comparison with $Ti_3C_2T_x$ in acid at RT under CO-gas flow.

Methodology

Synthesis of Pd/ $Ti_3C_2T_x$ nanosheets

- 2D- $Ti_3C_2T_x$ prepared by HF etching method.
- Stabilized and exfoliated in DMSO.
- 2D- $Ti_3C_2T_x$ impregnated with Pd salt at RT to form Pd/ $Ti_3C_2T_x$.
- Washed and stored for analysis and application

Characterization: -

- The shape analyzed by scanning electron microscope (SEM) and transmission electron microscope (TEM)

- Composition by The X-ray photoelectron spectroscopy (XPS) and X-ray diffraction patterns (XRD)

Electrochemical investigations

Cyclic voltammograms (CVs), linear sweep voltammograms (LSVs), EIS, and chrono (IT) experiments were recorded by CHI 832C electrochemical analyzer (Chenhua Co., Shanghai, China).

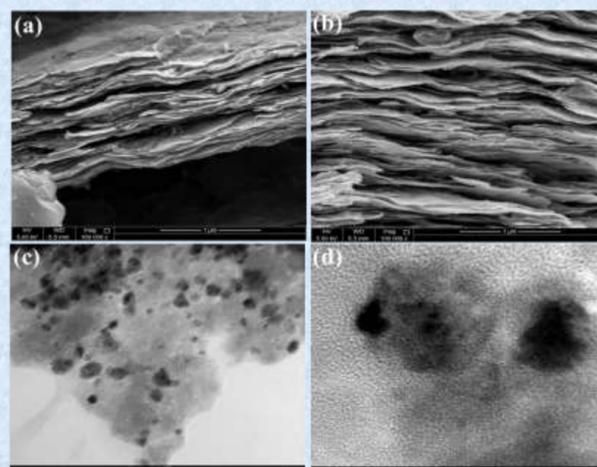


Figure 1 SEM image of (a) $Ti_3C_2T_x$ (b) Pd/ $Ti_3C_2T_x$. TEM image (c) of Pd/ $Ti_3C_2T_x$, HRTEM (d) of Pd/ $Ti_3C_2T_x$.

Fig 1a shows the formed multilayered 2D- $Ti_3C_2T_x$ nanosheets, and Fig 1b the exfoliated Pd/ $Ti_3C_2T_x$ with an interlayer space ~ 50 nm. $Ti_3C_2T_x$ is used as a substrate and reducing agent for Pd salt with highly dispersed NPs. Pd NPs enhanced the exfoliation, which increased the interlayer spacing by Pd nanoparticles. Fig 1(c,d) shows the TEM image for 2D-Pd/ $Ti_3C_2T_x$ nanosheets decorated with Pd NPs with an average size of 30 nm, and the HRTEM image shows the uniform lattice fringes with one direction where no defects or lattice distortion was observed.

Fig 2a displayed the XRD diffraction patterns with assigned facets for $Ti_3C_2T_x$ and no peaks for TiO_2 . Pd/ $Ti_3C_2T_x$ displayed the diffraction peaks for $Ti_3C_2T_x$ besides the fcc Pd-metal without any peaks for Pd oxide. Fig 2(b-d) XPS investigated the electronic structure and valence of Pd/ $Ti_3C_2T_x$ relative to $Ti_3C_2T_x$. The XPS surveys for Pd/ $Ti_3C_2T_x$ and $Ti_3C_2T_x$ showed the elements and the high-resolution spectra of

Results

Ti 2p and Pd 3d spectra confirms Pd⁰ metallic state is the major phase indicate the great reduction power of $Ti_3C_2T_x$.

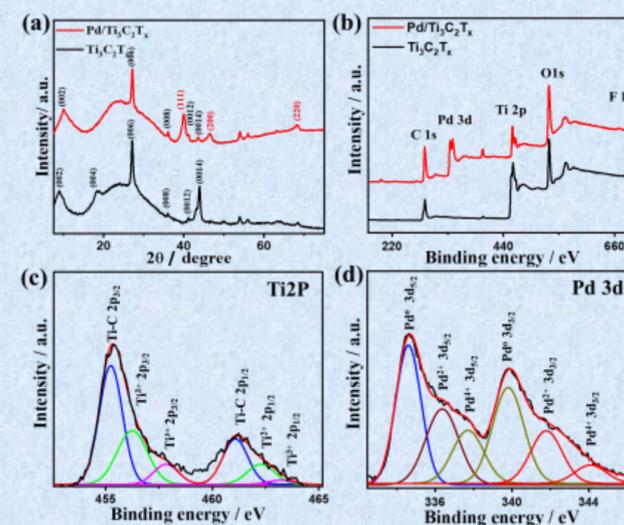


Figure 2 (a)XRD, and (b) XPS survey. High-resolution XPS spectra of (c) Ti, and (d) Pd

In Fig 5, the electrochemical CO oxidation activity of Pd/ $Ti_3C_2T_x$ was compared with $Ti_3C_2T_x$. It shows the CVs without CO. The CVs curves under CO flow, where Pd-free $Ti_3C_2T_x$ displays no activity for CO oxidation, but Pd/ $Ti_3C_2T_x$ displays a CO oxidation with a sharp anodic oxidation peak in the positive direction (0.82-1.01 V) and a small cathodic peak in the negative direction (0.37-0.51V) and a maximum current density of 0.318 mA cm^{-2} , oxidation potential of 0.9 V and onset potential around 0.8 V. The CVs curves of Pd/ $Ti_3C_2T_x$ give a maximum current density 0.544 mA cm^{-2} at 200 mV s^{-1} and the lowest current 0.2

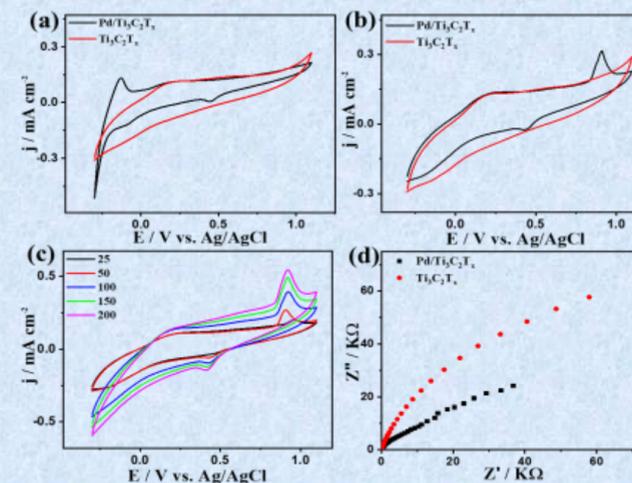


Figure 3 (a) CVs measured in N₂ saturated 0.1 M HClO₄, (b) CVs, and (c) CVs measured at different scan rates in CO-saturated of 0.1 M HClO₄ at 50 mV s^{-1} . (f) EIS.

mA cm^{-2} observed at 25 mV s^{-1} . EIS measurements display a lower resistance of Pd/ $Ti_3C_2T_x$ than $Ti_3C_2T_x$ which give a better electrolyte-electrode interaction and quick charge mobility.

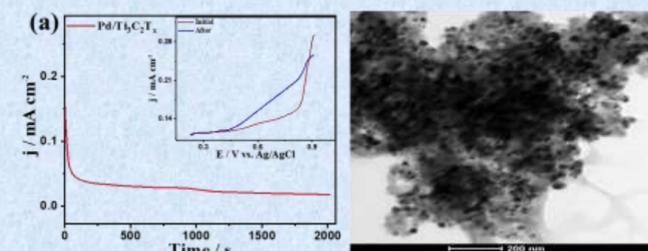


Figure 6 (a) The I-T stability teste measured in CO-saturated , LSV before and after stability testes. (C) TEM image of Pd/ $Ti_3C_2T_x$ after stability teste.

Interestingly, The stability of Pd/ $Ti_3C_2T_x$ gave around 85% of the initial current Fig 4a. where, The TEM after stability tests for Pd/ $Ti_3C_2T_x$ has a good structural stability Fig 4b.

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References

- (1) Wang, H.; Yin, S.; Eid, K.; Li, Y.; Xu, Y.; Li, X.; Xue, H.; Wang, L., Fabrication of mesoporous cage-bell Pt nanoarchitectonics as efficient catalyst for oxygen reduction reaction. ACS Sustainable Chemistry & Engineering 2018, 6 (9), 11768-11774.
- (2) Xie, S.; Wang, Z.; Tan, W.; Zhu, Y.; Collier, S.; Ma, L.; Ehrlich, S. N.; Xu, P.; Yan, Y.; Xu, T., Highly Active and Stable Palladium Catalysts on Novel Ceria-Alumina Supports for Efficient Oxidation of Carbon Monoxide and Hydrocarbons. Environmental Science & Technology 2021.
- (4) Tahimi, H. A.; Tan, X.; Smith, S. C., Facile CO Oxidation on Oxygen-functionalized MXenes via the Mars-van Krevelen Mechanism. ChemCatChem 2020, 12 (4), 1007-1012.
- (4) Alhabeib, M.; Maleski, K.; Anasori, B.; Lelyukh, P.; Clark, L.; Sin, S.; Gogotsi, Y., Guidelines for synthesis and processing of two-dimensional titanium carbide ($Ti_3C_2T_x$ MXene). Chemistry of Materials 2017, 29 (18), 7633-7644.