

Supporting Information

Three-dimensional TiO₂/CeO₂ Nanowire composite for Efficient Formaldehyde Oxidation at Low Temperature

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Experimental Section :

Preparation of TiO₂/CeO₂ nanowires and Pt/TiO₂/CeO₂ nanowires: TiO₂ nanowires were grown on a carbon cloth substrate by a seed-assisted hydrothermal method reported elsewhere.¹ The TiO₂ nanowires were annealed in air at 550 °C for 1 h. TiO₂/CeO₂ nanowires were obtained by depositing a CeO₂ nanowires onto the surface of TiO₂ nanowires by anodic electrodeposition. The electrodeposition was conducted in a solution (15 mL) containing cerous nitrate (0.01 M), ammonium chloride (0.1 M) and potassium chloride (0.03 M) at -2 mA for 60 min at 70 °C. CeO₂ nanowires were deposited on carbon cloth under the same conditions for comparison. The TiO₂/CeO₂ nanowires and CeO₂ nanowires were annealed in air at 550 °C for 1 h. 0.35 g of TiO₂/CeO₂ was added into an H₂PtCl₆ solution under magnetic stirring. After impregnation for 1 h, 2.5 mL of the mixed solution of NaBH₄ solution (0.1 mol·L⁻¹) and NaOH solution (0.5 mol·L⁻¹) were quickly added into the suspension under vigorous stirring for 30 min. After reduction, the suspension was evaporated at 100 °C under stirring. Finally, the samples were dried at 80 °C for 6 h.

Characterization: The morphologies, chemical compositions, and the microstructures of the

products were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, JEM2010-HR), and X-ray photoelectron spectroscopy (XPS, ESCALab250). The crystal phase of the NWs were characterized by XRD (Bruker, D8 ADVANCE) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The electrochemical properties of the products was investigated with cyclic voltammetry (CV) in a conventional three-electron cell employing a CHI 660D electrochemical workstation (Chenhua, Shanghai). The NWs on the carbon cloth substrates with a surface area of 1.0 cm^2 were used as working electrodes. A Ag/AgCl electrode and a Pt wire were used as the reference and counter-electrode, respectively. Nitrogen adsorption/desorption isotherms at 77 K were conducted on an ASAP 2020 V3.03 H instrument. All samples (powders) were out gassed at $100 \text{ }^\circ\text{C}$ for 5 h under flowing nitrogen before measurements.

Temperature-programmed reduction (TPR) analysis was conducted on a T-5080 Autochem analyzer. In a typical TPR experiment, about 0.1 g of the sample was loaded in a tube-shaped quartz cell above a small amount of quartz wool. The TPR profile of sample was recorded between $35 \text{ }^\circ\text{C}$ and $900 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in 10% hydrogen in N_2 with a flow rate of $50 \text{ mL}\cdot\text{min}^{-1}$. Hydrogen uptake was monitored by TCD detector.

Catalytic activity measurement: Catalytic activities of as-prepared catalysts for HCHO oxidation were performed in a fixed-bed reactor under atmospheric pressure. The catalyst (200 mg) was loaded in a quartz tube reactor. Gaseous HCHO was generated by passing a purified air flow ($\text{N}_2/\text{O}_2 = 4,100 \text{ mL}\cdot\text{min}^{-1}$) over HCHO solution in an incubator kept at $0 \text{ }^\circ\text{C}$, leading to a feed gas with 50 ppm of HCHO. The gas hourly space velocity (GHSV) is $30,000 \text{ mL}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. HCHO concentration in the reactant or product gas stream was analyzed by phenol spectrophotometric method. The gas stream containing trace HCHO was bubbled through 5 mL phenol reagent ($\text{C}_6\text{H}_4\text{SN}(\text{CH}_3)\text{C}:\text{NNH}_2\cdot\text{HCl}$) solution (1×10^{-4} (wt.) %) for 30 seconds to collect HCHO by absorption. Then, 0.4 mL (1 wt.%) ammonium ferric sulfate ($\text{NH}_4\text{Fe}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$) solution was added as the coloring reagent. After shaking for 5 seconds and staying for 15 min in the dark, HCHO concentration in the gas stream was then determined by measuring light absorbance at 630 nm with a spectrophotometer (UV-240, Shimadzu Co. Ltd., Japan). The conversion of HCHO was calculated based on its concentration change.

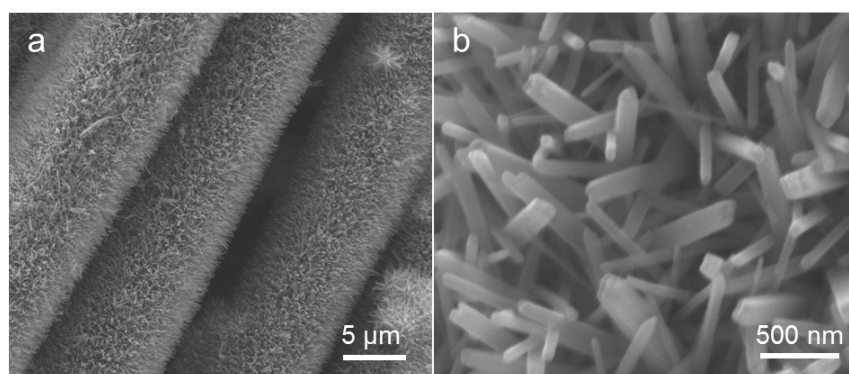


Figure S1. SEM images of the as-prepared TiO₂ nanowires on carbon cloth.

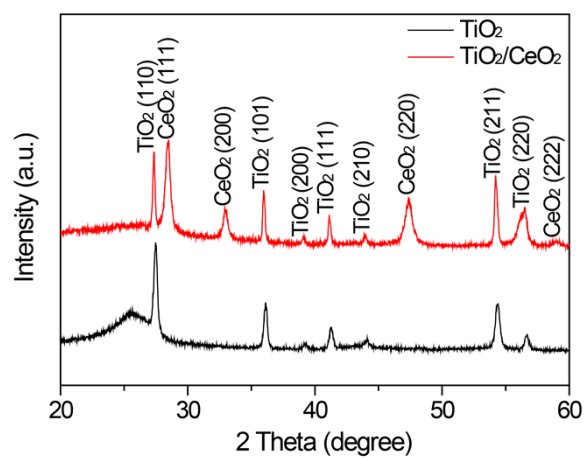


Figure S2. XRD pattern of TiO₂ nanowires and TiO₂/CeO₂ nanowires.

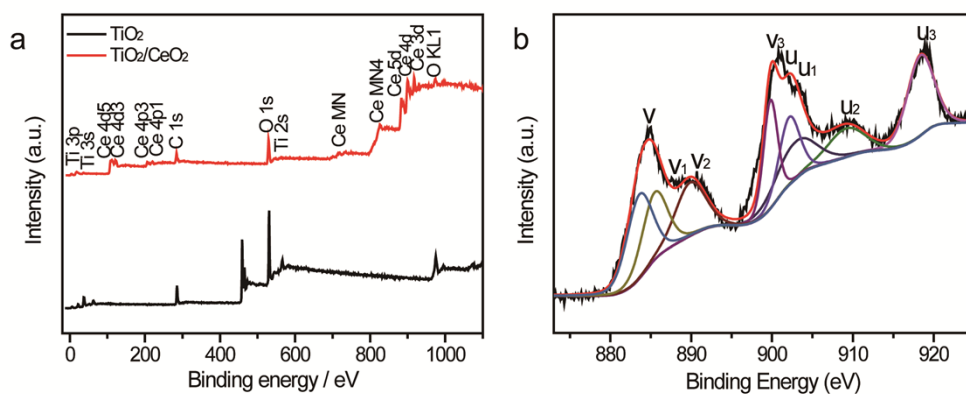


Figure S3. (a) XPS survey spectra of pure TiO₂ nanowires and TiO₂/CeO₂ nanowires. (b) Ce 3d core-level XPS spectrum of TiO₂/CeO₂ nanowires.

According to the XPS result, there are four elements (Ti, Ce, O, C) present on the surface of the final product (Figure S3a). The C signal is attributed to carbon fabric and adventitious carbon. Spectra of TiO₂/CeO₂ nanowires confirm the presence of Ce, while no Ce signal is found for the TiO₂ nanowires. Eight peaks can be found in the Ce 3d spectrum of CeO₂ as shown in Figure S3b. The peaks labeled as u, u₂ and u₃ refer to Ce⁴⁺ 3d_{3/2}, and the peaks labeled as v, v₂ and v₃ refer to Ce⁴⁺ 3d_{5/2}. The characteristic peaks of Ce³⁺ 3d_{3/2} and 3d_{5/2} states are labeled as u₁ and v₁, respectively.²⁻³ All these results reveal the successful fabrication of TiO₂/CeO₂ nanowires composites.

- (1) Lu, X.; Yu, M.; Wang, G.; Zhai, T.; Xie, S.; Ling, Y.; Tong, Y.; Li, Y. *Adv. Mater.*, **2013**, 25, 267.
- (2) P. Burroughs, A. Hamnett, A.F. Orchard, G. Thornton, *J. Chem. Soc., Dalton Trans.* **1976**, 17, 1686.
- (3) A. Q. Wang, P. Panchaipetch, R. M. Wallace and T. D. Golden, *J. Vac. Sci. Technol., B* **2003**, 213, 1169.

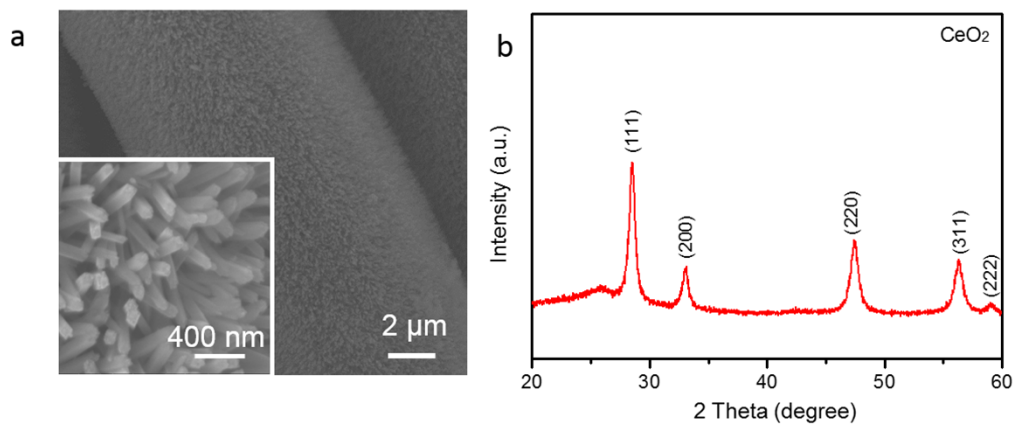


Figure S4. SEM images and XRD pattern of CeO₂ nanowires.

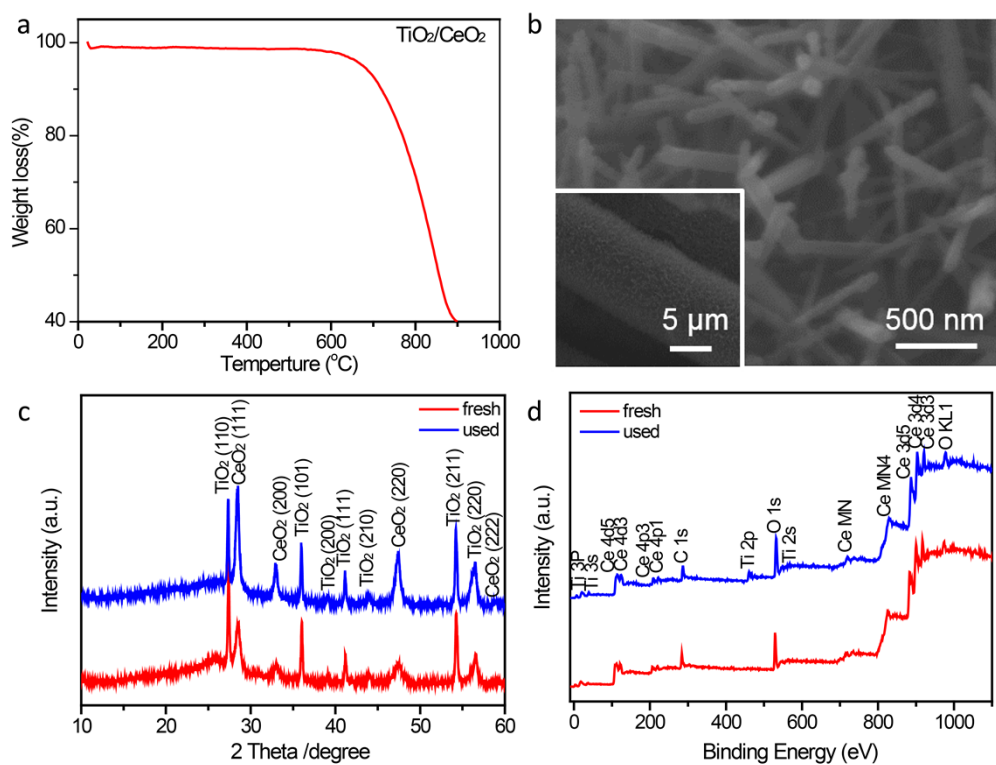


Figure S5. (a) TG pattern of TiO₂/CeO₂ nanowires. (b) SEM images of TiO₂/CeO₂ nanowires on a carbon cloth after the reaction. (c) XRD pattern of TiO₂/CeO₂ nanowires before and after the reaction. (d) XPS patterns of TiO₂/CeO₂ nanowires before and after the reaction.

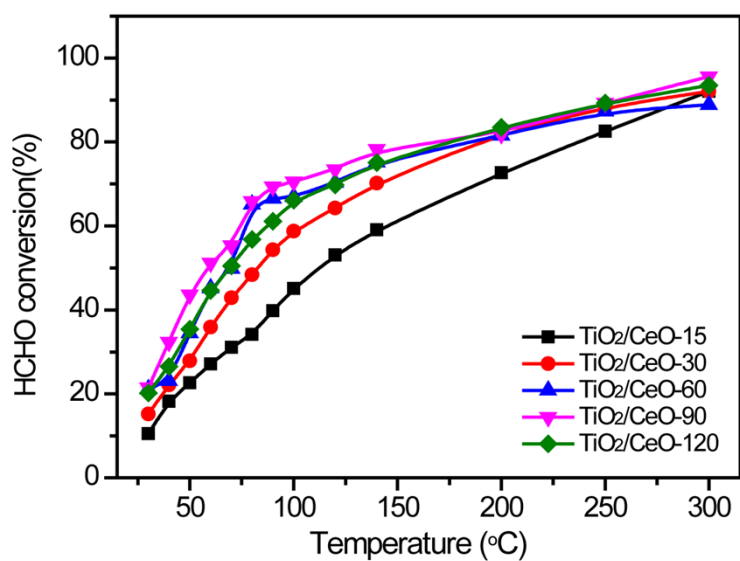


Figure S6. Catalytic performance of HCHO of the TiO₂/CeO₂ at different CeO₂ electrodeposition time variation.

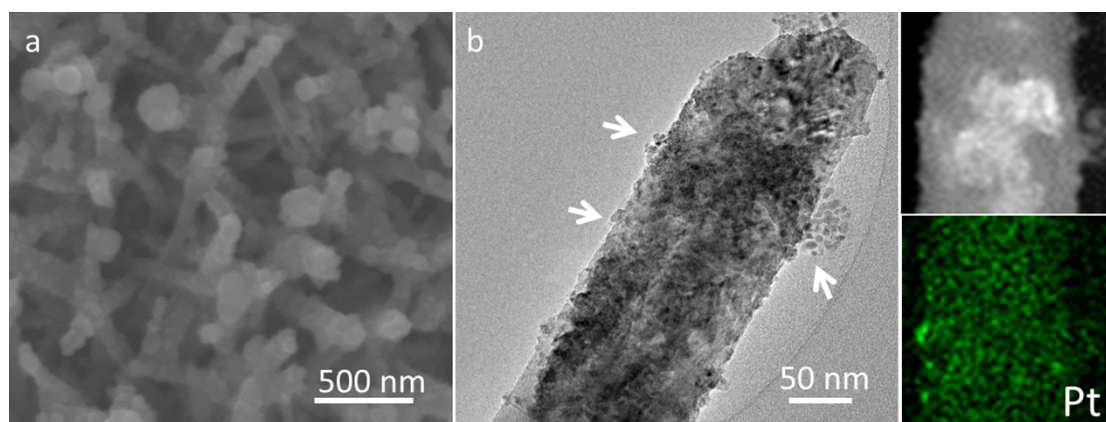


Figure S7. (a) SEM images of Pt/TiO₂/CeO₂ nanowires on a carbon cloth. (b) TEM image of Pt/TiO₂/CeO₂ nanowires and elemental mapping of the Pt element present in Pt/TiO₂/CeO₂ nanowires.