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## 1. Introduction

Direct methanol fuel cells (DMFCs) are small, lightweight, and long-lasting portable power sources that show great promise for competing with current battery technology. However, the development of DMFCs and their practical applications are significantly hindered by the lack of effective electrocatalysts for the methanol oxidation reaction (MOR) that occurs at the anode.<sup>1-4</sup> Therefore, developing robust electrocatalysts for the anodic MOR is essential for the fabrication of commercially viable DMFCs. Regarding anodic electrocatalytic reactions, Pt and Pd have been extensively considered as promising electrocatalysts owing to their inherently high intrinsic activity; however, their high cost and vulnerability to CO poisoning greatly diminish their wide practical application.<sup>5-7</sup> Besides, another main factor that limits the commercial application of DMFCs is their unsatisfactory life span, originating from the corrosion of carbon materials in harsh environments, which would inevitably lead to the agglomeration and sintering of the Pt or Pd catalyst nanoparticles.<sup>8–10</sup> To overcome this drawback, numerous endeavors have been made, aiming to improve the electrochemical durability of electrode materials. With the intensive efforts that have been devoted to this area, a series



## One-step fabrication of CuO-doped TiO<sub>2</sub> nanotubes enhanced the catalytic activity of Pt nanoparticles towards the methanol oxidation reaction in acid media<sup>+</sup>

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To meet the requirements for the potential applications of fuel cells, it is of vital importance to search for advanced electrocatalysts toward the methanol oxidation reaction (MOR) that have both high electrocatalytic activity and great CO resistance. In this work, we herein report the fabrication of a novel class of Pt-CuO-TiO<sub>2</sub>/C catalyst and discover that the as-obtained nanocatalyst exhibited excellent electrocatalytic properties for the MOR. Remarkably, the mass activity is as high as 1537.3 mA mg<sub>Pt</sub> $^{-1}$ , showing 6.0- and 2.75-fold enhancements compared with the reference Pt-C-H and Pt-TiO<sub>2</sub>/C catalysts, respectively. Except the superb electrocatalytic activity, it is also demonstrated that such Pt-CuO-TiO<sub>2</sub>/C has outstanding electrochemical stability and great tolerance to CO poisoning, representing an advanced electrocatalyst for use in fuel cells.

> promote the electrocatalytic performance.<sup>17,18</sup> In consideration of these favorable terms, many materials, including carbon materials,<sup>19,20</sup> transition metal compounds,<sup>21,22</sup> MXene,<sup>23-25</sup> and conductive polymers,<sup>26</sup> have been employed as promising supports to greatly boost the electrochemical reactions. To date, carbon materials have been the typical supports for electrochemical reactions owing to their high specific surface area, rich anchoring sites for stabilizing catalyst nanoparticles, and high electrical conductivity.<sup>27-29</sup> Despite these beneficial factors, carbon supports still undergo the corrosion phenomenon in harsh environments, which may greatly decrease the electrocatalytic performance of the catalyst nanoparticles.

> Recently, metal oxides have been utilized as promoters of Pt catalysts toward fuel cell-related electrochemical reactions by using them as the ideal supports. For one thing, metal oxides can also uniformly disperse the catalyst nanoparticles to expose more surface active sites.<sup>30,31</sup> For another, metal oxides can provide rich hydroxyl groups and oxygen-species release for electrochemical reactions, consequently alleviating the influence

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#### Paper

of CO-like poisoning. Among various metal oxides, titanium dioxide (TiO<sub>2</sub>) has been widely regarded as a promising support for Pt electrocatalysts for fuel cells because of its excellent stability in both acidic and basic solution.<sup>32,33</sup> More importantly, the TiO<sub>2</sub> with hypo-d-electron character can also induce a strong metal-support interaction, which is beneficial for improving the electrochemical stability of the catalysts.34,35 Nevertheless, the lower electrical conductivity compared to conventional carbon supports limits their commercial applications in fuel cells. Therefore, exploring effective routes to ameliorate these weaknesses is highly imperative and meaningful for the future development of DMFCs.36,37 Generally, doping TiO2 with metal elements or introducing another metal oxide has been demonstrated to be an effective strategy for shortening the bandgap of TiO<sub>2</sub> and positively affecting the electrocatalytic performance of catalysts.38-41

Guided by the above rules, we herein developed a facile method for the fabrication of a novel class of Pt–CuO–TiO<sub>2</sub>/C nanotubes with modified electronic structure, which could function as promising catalyst supports for boosting the electrocatalytic performance of Pt–C–H. Consequently, a mass activity as high as 1537.3 mA mg<sub>Pt</sub><sup>-1</sup> could be achieved at peak potential, being correspondingly 6.0 and 2.75 times higher than those of Pt–C–H (256.2 mA mg<sub>Pt</sub><sup>-1</sup>) and Pt–TiO<sub>2</sub>/C (558.7 mA mg<sub>Pt</sub><sup>-1</sup>). More importantly, such a Pt–CuO–TiO<sub>2</sub>/C catalyst also displayed excellent electrochemical stability, with good tolerance to CO poisoning and resistance to agglomeration for long-duration electrochemical operations.

## 2. Experimental

#### 2.1. Chemicals and materials

Vulcan XC-72R carbon black, trisodium citrate dehydrate, sulfuric acid ( $\geq$ 95%), methanol, TiO<sub>2</sub> nanopowder, ethanol (C<sub>2</sub>H<sub>5</sub>OH, 99.7%), sodium borohydride, copper nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) and other chemical agents were all brought from Kelong Chemical Reagent Company (Chengdu, China). Hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O, 99.9%) was provided by the First Reagent Factory (Shanghai, China). Nafion solution was purchased from Chongqing Ruixing Co. Ltd. All Chemicals are analytical reagent grade.

#### 2.2. Material preparations

**2.2.1. Preparation of CuO-TiO**<sub>2</sub> **nanotubes.** 6 g of NaOH was dissolved in 20 mL of ultrapure water, followed by the addition of 0.5 g of TiO<sub>2</sub> and 2.265 g of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O. The above suspension was ultrasonicated for 40 min. After that, the slurry was transferred to a 100 mL Teflon-lined autoclave and maintained at 150 °C for 24 h. Subsequently, the as-prepared brown product was collected by centrifugation and washed with ethanol and ultrapure water. The obtained product was dried at 55 °C overnight. Similar procedures were employed for the synthesis of Pt–TiO<sub>2</sub>@C, but in the absence of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O.

**2.2.2.** Preparation of Pt–CuO–TiO<sub>2</sub>/C hybrid material. 20 mg of the mixture of CuO–TiO<sub>2</sub> and carbon black was uniformly

dispersed into 20 mL of H<sub>2</sub>O, followed by ultrasonication for 30 min to form a homogeneous CuO–TiO<sub>2</sub>/C slurry; 25 mg of trisodium citrate dehydrate was dissolved into 6 mL of distilled water with magnetic stirring for 15 min to form a uniform solution. After that, 0.525 mL of 48.803 mM H<sub>2</sub>PtCl<sub>6</sub>–ethylene glycol was injected into the above solution dropwise to obtain an aqueous H<sub>2</sub>PtCl<sub>6</sub> solution; 3.5 mg of NaBH<sub>4</sub> was added into 8 mL of H<sub>2</sub>O to form an NaBH<sub>4</sub> water solution. Secondly, the H<sub>2</sub>PtCl<sub>6</sub> mixed solution was injected dropwise into the CuO–TiO<sub>2</sub>/C suspension, and then sodium borohydride aqueous solution was mixed with the above solution, followed by constant stirring for 24 h. The collected precipitate was dried at 60 °C for 4 h to obtain Pt–CuO–TiO<sub>2</sub>/C. Furthermore, the identical procedure was also employed to obtain Pt–TiO<sub>2</sub>/C and Pt–C–H (home-made).

#### 2.3. Electrochemical measurements

Electrochemical measurements were carried out using a CHI 760E electrochemical instrument equipped with a classic threeelectrode system. The catalytic inks were prepared as follows: 2 mg of the catalyst was poured into 1 mL of solution ( $V_{H_2O}$ :  $V_{C_2H_3OH} = 1:1$ ), and then 50 µL of 5 wt% Nafion solution was dripped into the solution. After sonicating to obtain a uniform ink, 5 µL of the catalyst ink was carefully dripped onto the working electrode. All electrolytes were purified for at least 15 min in high-purity N<sub>2</sub> before measurement.

#### 2.4. Physical characterization

A scanning electron microscope (FE-SEM, JEOL JSM-7800F) and a field emission transmission electron microscope (FE-TEM, Talos F200S) were utilized to explore the morphological and structural features. The surface element compositions and chemical states of the samples were detected by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi) measurement using a monochromatic Al-K $\alpha$  X-ray source. Powder X-ray diffraction (XRD) patterns were obtained using an XRD instrument (RINT2000, Rigaku) with Cu-K $\alpha$  radiation.

## Results and discussion

Pt-CuO-TiO<sub>2</sub>/C was synthesized through a facile two-step wet chemical method, in which the CuO-TiO<sub>2</sub> was firstly synthesized through a simple hydrothermal method. Subsequently, the Pt-CuO-TiO<sub>2</sub>/C was prepared by reducing the Pt precursor employing NaBH<sub>4</sub> as the reductant. A series of advanced characterizations, including SEM, TEM, elemental EDS mapping, XRD, and XPS, was conducted to systematically analyze the morphological and structural features. From Fig. S1 (ESI†), it can be clearly seen that the as-obtained TiO<sub>2</sub> treated by NaOH features the typical nanotube-like structure. After the deposition of the carbon and Pt nanoparticles, the SEM images show many unique clusters, suggesting the successful formation of Pt-CuO-TiO<sub>2</sub>/C (Fig. S2, ESI†). In addition to the SEM images, TEM images were also obtained. As shown in Fig. 1A and B, the as-prepared samples were composed of the distinctive nanotubes and carbon



Fig. 1 Morphology and chemical composition characterizations of the Pt-CuO-TiO<sub>2</sub>/C catalyst. (A-C) Representative TEM images of the Pt-CuO-TiO<sub>2</sub>/C catalyst. (D) HAADF-STEM and TEM-EDS elemental mapping images of the Cu (blue), O (green), Ti (purple),and Pt (yellow) atoms in the Pt-CuO-TiO<sub>2</sub>/C composite.

black that were loaded with the uniform nanoparticles, suggesting that the Pt nanoparticles were uniformly dispersed on the surface of carbon black to not only expose rich surface active centers, but also greatly stabilize the Pt nanoparticles. The HRTEM image is displayed in Fig. 1C; the measured lattice spacings of 0.2254 nm, 0.2195 nm, 0.2239 nm and 0.1939 nm originated from the  $TiO_2$ 

(200), TiO<sub>2</sub>(111), Pt(111) and Pt(200) planes, respectively. The HAADF-STEM image also shows the TiO2 nanotube-supported Pt nanocatalyst, which was consistent with the TEM and SEM results. In order to further confirm the formation of the Pt-CuO-TiO<sub>2</sub>/C composite, we also conducted TEM-EDS characterization. As shown in Fig. 1D, the elemental EDS mapping suggested that Cu (blue), O (green), Ti (purple) and Pt (yellow) elements were uniformly scattered throughout the whole sample. The TEM-EDS spectrum of the Pt-CuO-TiO<sub>2</sub>/C composite is shown in Fig. 2A. As illustrated in Fig. 2A, the typical peaks for C, O, Pt, Ti, and Cu atoms could be clearly observed, being consistent with the TEM-EDS elemental mapping results. Besides, the crystal phase of the Pt-CuO-TiO2/C composite was characterized by XRD (Fig. 2B), showing many strong XRD diffraction peaks, which could be assigned to the TiO<sub>2</sub> (JCPDS no. 82-0514), CuO (PDF#80-1916), and Pt (JCPDS no. 87-0647).42 The crystal phase results from the XRD analysis are consistent with the SAED results (Fig. S3, ESI<sup>†</sup>). For comparison, the XRD pattern of the CuO-TiO<sub>2</sub> nanotubes was also obtained. From Fig. S4 (ESI<sup>+</sup>), it can be clearly seen that the XRD peaks of the sample could be assigned to the CuO (PDF#80-1916) and TiO<sub>2</sub> (PDF#82-0514), further indicating the successful fabrication of the CuO-TiO<sub>2</sub> nanotubes.

As is well known, the surface composition as well as the chemical state are crucial for determining the ultimate electrocatalytic properties.43,44 Therefore, gaining insight into the surface composition and chemical oxidation state of the Pt-CuO-TiO2/C is essential for understanding their influence on the electrocatalytic properties. In this case, we used XPS technology to detect the surface composition and oxidation state. Fig. 3A shows the XPS survey spectrum of the Pt-CuO-TiO<sub>2</sub>/C. As can be seen in Fig. 3A, the typical XPS peaks at the binding energies around 70, 460, 530, and 940 eV are assigned to the Pt 4f, Ti 2p, O 1s, and Cu 2p, respectively, which also indicated the formation of the Pt-CuO-TiO<sub>2</sub>/C composite. Besides the survey spectrum, the high-resolution XPS spectra of Pt 4f, Cu 2p, Ti 2p, and O 1s are also shown in Fig. 3. As can be seen in Fig. 3B, the XPS spectrum of Pt 4f can be deconvoluted into two strong peaks and four weak peaks, in which the two strong peaks at the binding energies of 71.3 and 74.7 can be assigned to the metallic Pt of Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$ , while the other weak peaks are associated with the oxidative Pt.45,46 Fig. 3C shows the Pt 4f XPS spectra of Pt-TiO<sub>2</sub>/C and Pt-CuO-TiO<sub>2</sub>/C. As observed, the Pt 4f spectrum of Pt-CuO-TiO<sub>2</sub>/ C is positively shifted to higher binding energy as compared to the



Fig. 2 Composition and structure characterization of the  $Pt-CuO-TiO_2/C$ . (A) TEM-EDS spectrum of the  $Pt-CuO-TiO_2/C$ . (B) XRD pattern of the  $Pt-CuO-TiO_2/C$ .



**Fig. 3** Surface composition and oxidation state characterizations. (A) Survey XPS spectrum of the  $Pt-CuO-TiO_2/C$ . (B) High-resolution XPS spectra of the Pt 4f in  $Pt-CuO-TiO_2/C$ . (C) Pt 4f comparison of  $Pt-TiO_2/C$  and  $Pt-CuO-TiO_2/C$ . High-resolution XPS spectra for (D) Cu 2p, (E) Ti 2p, and (F) O 1s in  $Pt-CuO-TiO_2/C$  composition.

Pt–TiO<sub>2</sub>/C, suggesting that the introduction of Cu could greatly optimize the electronic structure of Pt. Fig. 3D shows the Cu 2p XPS spectrum, which can be divided into two strong peaks presented at the binding energies of 932.6 and 952.6 eV, corresponding to the Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$ , and one oscillating satellite peak (942.5 eV), suggesting the successful doping of Cu into TiO<sub>2</sub>.<sup>47</sup> Furthermore, the high-resolution XPS spectrum of Ti 2p was also obtained and is shown in Fig. 3E. The two peaks at the binding energies of 458.6 and 464.3 eV are assigned to the Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$ , respectively.<sup>48–50</sup> The high-resolution XPS spectrum of O 1s is displayed in Fig. 3F, showing that the O 1s XPS peaks are associated with the TiO<sub>2</sub>. The XPS analyses further demonstrated the successful fabrication of Pt–CuO–TiO<sub>2</sub>/C and suggested that the doping of Cu could effectively modify the electronic structure of TiO<sub>2</sub> and thus boost the electrocatalytic performance.

The electrochemical properties of the resulting Pt–CuO–TiO<sub>2</sub>/C catalyst were systematically investigated and benchmarked against the Pt–TiO<sub>2</sub>/C and Pt–C–H catalysts. The cyclic voltammogram (CV) measurements for the Pt–CuO–TiO<sub>2</sub>/C, Pt–TiO<sub>2</sub>/C, and Pt–C–H catalysts were firstly conducted in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at a scan rate of 50 mV s<sup>-1</sup>. The electrochemical active surface areas (ECSAs) of these electrocatalysts were calculated according to the hydrogen adsorption/desorption peaks in the CV curves.<sup>19,51,52</sup> As shown in Fig. 4B, Pt–CuO–TiO<sub>2</sub>/C possessed the highest ECSA of up to 103.2 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup>, relatively larger than those of Pt–TiO<sub>2</sub>/C (73.3 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup>) and Pt–C–H (59.7 m<sup>2</sup> g<sub>Pt</sub><sup>-1</sup>). Therefore, the



Fig. 4 (A) CV curves of the Pt-C-H, Pt-CuO-TiO<sub>2</sub>/C, and Pt-TiO<sub>2</sub>/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. (B) The corresponding ECSA values per catalyst. (C) MOR curves of the Pt-C-H, Pt-CuO-TiO<sub>2</sub>/C, and Pt-TiO<sub>2</sub>/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution. (D) Histogram of the mass activities of the Pt-C-H, Pt-CuO-TiO<sub>2</sub>/C, and Pt-TiO<sub>2</sub>/C for the MOR.

specific activity can be calculated and the results are shown in Table 1. Obviously, Pt-CuO-TiO2/C possessed the best specific activity, which is 1.96 times and 3.4 times higher than those of the Pt-TiO<sub>2</sub>/C and Pt-C-H catalysts, respectively. This enhancement in ECSA and specific activity can be ascribed to the optimization of the electronic structure after the CuO doping, and the synergistic contributions of the TiO<sub>2</sub> nanotubes and carbon black. The anodic MOR was also employed as the model reaction to evaluate the electrocatalytic performances of different catalysts. Fig. 4C shows the MOR curves of the Pt-C-H, Pt-CuO-TiO<sub>2</sub>/C, and Pt-TiO<sub>2</sub>/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 1 M CH<sub>3</sub>OH. As shown in Fig. 4C, the MOR curves included two typical oxidation peaks, in which the peak that appeared at the potential of around 0.7 V (versus SCE) was assigned to the oxidation of methanol, while the other one at the potential of around 0.4 V is associated with the further oxidation of intermediates. Pt-CuO-TiO<sub>2</sub>/C clearly shows much higher oxidation peaks as compared to the benchmarked Pt-C-H and Pt-TiO<sub>2</sub>/C. For comparison, the mass activities of these three electrocatalysts are summarized in Fig. 4D. As shown in Fig. 4D, Pt-CuO-TiO<sub>2</sub>/C could deliver a high mass activity of 1537.3 mA mg<sub>Pt</sub><sup>-1</sup>, giving 6.0- and 2.75-fold enhancements compared to Pt-C-H (256.2 mA mg<sub>Pt</sub><sup>-1</sup>) and Pt-TiO<sub>2</sub>/C (558.7 mA  $mg_{Pt}^{-1}$ ), suggesting the outstanding electrocatalytic performance of the Pt-CuO-TiO2/C catalyst. Table 2 lists the mass activity from other relevant research in methanol electrooxidation for comparison. The high electrocatalytic activity of

Table 1 Summary of the ECSA and specific activity of Pt–CuO–TiO<sub>2</sub>/C, Pt–TiO<sub>2</sub>/C and Pt–C–H catalysts

| Sample                     | $ECSA \left(m^2 \ g^{-1}\right)$ | Specific activity (mA $\text{cm}_{\text{Pt}}^{-2}$ ) |  |
|----------------------------|----------------------------------|--|--|
| Pt-TiO <sub>2</sub> -CuO/C | 103.2                            | 1.49   |  |
| Pt-TiO <sub>2</sub> /C     | 73.3                             | 0.76   |  |
| Pt-C-H                     | 59.7                             | 0.43   |  |

Table 2 Summary of the mass activity for Pt-TiO<sub>2</sub>-CuO/C and Pt-TiO<sub>2</sub>/C catalysts and other correlative work reported recently in methanol electrooxidation

| Catalyst                                | Mass activity (mA $mg_{Pt}^{-1}$ ) | Conditions   | Ref.      |
|---|------------------------------------|--|-----------|
| Pt-TiO <sub>2</sub> -CuO/C              | 1537.3                             | $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$                       | This work |
| Pt-TiO <sub>2</sub> /C                  | 558.7                              | $0.5 \text{ M H}_2 \text{SO}_4 + 1 \text{ M CH}_3 \text{OH}$                     | This work |
| Pt- <sub>NR</sub> CeO <sub>2</sub> /GNs | 498                                | 0.5 M H <sub>2</sub> SO <sub>4</sub> + 0.5 M CH <sub>3</sub> OH                  | 53        |
| Pt/CeO <sub>2</sub> /PANI               | 400                                | $0.5 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$                     | 54        |
| Pt/TiO2@NC-NCNTs                        | 577                                | 0.5 M H <sub>2</sub> SO <sub>4</sub> + 1 M CH <sub>3</sub> OH                    | 55        |
| Pt/Co@NCNTs-MC                          | 700.3                              | $1 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$                         | 56        |
| Pt/DSCT                                 | 462                                | $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$                       | 57        |
| Pt/LP-TiO <sub>2</sub> /CFP             | 1182.8                             | $0.5 \text{ M H}_2 \text{SO}_4 + 1 \text{ M CH}_3 \text{OH}$                     | 58        |
| Pt/TiC NWs                              | 360                                | $0.5 \text{ M H}_2 \text{SO}_4 + 1 \text{ M CH}_3 \text{OH}$                     | 59        |
| PtNi CNCs                               | 696                                | $0.5 \text{ M H}_2 \text{SO}_4 + 1 \text{ M CH}_3 \text{OH}$                     | 60        |
| Pt-HPCS@CoP/NC                          | 688                                | $0.5 \text{ M H}_2 \text{SO}_4 + 1 \text{ M CH}_3 \text{OH}$                     | 61        |
| Pt/WN/CNT-rGO                           | 702.4                              | $1 \text{ M H}_2 \overline{\text{SO}}_4 + 1 \text{ M CH}_3 \overline{\text{OH}}$ | 62        |

Pt–CuO–TiO<sub>2</sub>/C is ascribed to the exposure of rich surface active sites, optimization of the electronic structure after the Cu doping, and the synergistic contributions of the  $TiO_2$  nanotubes and carbon black.

In addition to the MOR activity, the electrochemical durability is also another crucial factor determining the future prospects of the developed catalyst in fuel cells.<sup>63</sup> To this end, we herein conducted chronoamperometric (CA) tests to evaluate its electrochemical stability by utilizing the Pt-C-H and Pt-TiO<sub>2</sub>/C catalysts as benchmarks. Fig. 5A shows the CA curves of the different catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution. As can be seen, the Pt-CuO-TiO<sub>2</sub>/C showed much higher current density as compared to the Pt-C-H and Pt-TiO<sub>2</sub>/C catalysts over time, indicating the high electrochemical stability. For easy comparison, the retained current densities of these electrocatalysts after a continuous 3600 s CA test are also summarized in Fig. 5B. As shown in Fig. 5B, the Pt-CuO-TiO<sub>2</sub>/ C retained a current density of 70.6 mA  $mg_{Pt}^{-1}$  after the 3600 s test, being much higher than those of Pt-C-H (9.8 mA  $mg_{Pt}^{-1}$ ) and Pt-TiO<sub>2</sub>/C (16.5 mA mg<sub>Pt</sub><sup>-1</sup>), revealing the enhanced electrochemical stability of the Pt-CuO-TiO2/C catalyst. Meanwhile, the catalytic durability of the Pt-CuO-TiO<sub>2</sub>/C and Pt-C-H catalysts was researched using the accelerated durability test (ADT), as shown in Fig. 6A and B. Fig. 6C shows that the Pt-CuO-TiO<sub>2</sub>/C catalyst exhibits a lower ECSA loss ratio compared to the Pt-C-H catalyst after the 1000 cycles CV test, which further verified the better durability of the Pt-CuO-TiO<sub>2</sub>/C.

TEM was used to probe the morphology and structure of the  $Pt-CuO-TiO_2/C$  catalyst after the ADT. As can be seen in



Fig. 5 (A) CA curves of Pt–C–H, Pt–CuO–TiO<sub>2</sub>/C, and Pt–TiO<sub>2</sub>/C in 0.5 M H<sub>2</sub>SO<sub>4</sub> + 1 M CH<sub>3</sub>OH solution. (B) Magnified CA curves of Pt–C–H, Pt–CuO–TiO<sub>2</sub>/C, and Pt–TiO<sub>2</sub>/C.

Fig. 7A–C, Pt–CuO–TiO<sub>2</sub>/C showed no obvious changes or serious Pt NP aggregation. In conclusion, the introduction of CuO–TiO<sub>2</sub> can enhance the interaction between the catalytic species and the carrier, and thus alleviate catalytic aggregation.

Furthermore, the origin of the promoted MOR stability for Pt–CuO–TiO<sub>2</sub>/C was studied in detail. Normally, the durability of the anode electrocatalysts toward MOR is easily destroyed by some poisonous intermediates, such as CO and HCHO. Therefore, we conducted CO stripping experiments to evaluate the antipoisoning capability of the electrocatalyst.<sup>64–66</sup> As seen in Fig. 8, the Pt–CuO–TiO<sub>2</sub>/C exhibited a peak potential of CO oxidation at 633 mV, which was much lower than those for Pt–C–H (659 mV) and Pt–TiO<sub>2</sub>/C (649 mV), suggesting the great tolerance of CO by Pt–CuO–TiO<sub>2</sub>/C. More importantly, we found that the onset potential of CO oxidation on Pt–CuO–TiO<sub>2</sub>/C was 575 mV, which was more negative than those for Pt–C–H (611 mV) and Pt–TiO<sub>2</sub>/C (599 mV), further demonstrating the strong antipoisoning ability of Pt–CuO–TiO<sub>2</sub>/C for CO.

The improvement of CO tolerance mainly depends on the synergistic mechanism of the catalyst. The feasible reaction mechanism of methanol oxidation on Pt–CuO–TiO<sub>2</sub>/C can be described *via* the following reaction equations:

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$$Pt + CH_3OH \rightarrow Pt-(CO)_{ads} + 4H^+ + 4e^-$$
(1)

$$\operatorname{TiO}_2 + \operatorname{H}_2 O \to \operatorname{TiO}_2 - OH + H^+ + e^- \qquad (2)$$

$$TiO_2-OH + Pt-(CO)_{ads} \rightarrow Pt + TiO_2 + CO_2 + H^+ + e^-$$
(3)

Primarily, methanol dehydrogenates mainly on Pt active sites, producing many intermediate products CO and chemisorbing



Fig. 6 CVs of the (A)  $Pt-CuO-TiO_2/C$  and (B) Pt-C-H catalysts before and after 1000 cycles in 0.5 M  $H_2SO_4$  solution. (C) Comparison of ECSA remaining and loss ratio for the  $Pt-CuO-TiO_2/C$  and Pt-C-H catalysts after 1000 cycles CV test.



Fig. 7 TEM images of Pt-CuO-TiO<sub>2</sub>/C (A-C) after 1000 cycles CV test.



Fig. 8 CO stripping experiments for (A) Pt–C–H, (B) Pt–TiO<sub>2</sub>/C, and (C) Pt–CuO–TiO<sub>2</sub>/C in 0.5 M  $H_2SO_4$  solution.

on Pt surface (Pt–(CO)<sub>ads</sub>) (eqn (1)).<sup>67,68</sup> In the meantime, Because TiO<sub>2</sub> is naturally a hydrophilic substance, H<sub>2</sub>O molecules can be dissociated. Owing to water decomposition on the surface of the TiO<sub>2</sub>, abundant hydroxyl groups are adsorbed to the surface of TiO<sub>2</sub> in acidic electrolytes (TiO<sub>2</sub>–OH) (eqn (2)).<sup>69</sup> The TiO<sub>2</sub>–OH can quickly oxidize CO<sub>ads</sub> species to CO<sub>2</sub> (eqn (3)), which is conducive to the release of free Pt active sites in the electrooxidation process of methanol.<sup>58</sup>

Thus, the Pt–CuO–TiO<sub>2</sub>/C catalyst displays not only high electrocatalytic activity but also excellent electrochemical stability toward MOR in acidic solution. After a series of advanced characterizations and mechanism studies, have found that the excellent electrocatalytic properties were attributed to the introduction of CuO–TiO<sub>2</sub> nanotubes. For one thing, the nanotube-like TiO<sub>2</sub> could provide rich surface active sites available for reactants and intermediates. For another, the Cu doping lowered the bandgap and modified the electronic structure of the TiO<sub>2</sub>,<sup>38–41</sup> leading to enhanced electrocatalytic activity and stability toward the MOR in a harsh environment.

## 4. Conclusions

To summarize, we have developed a facile wet chemical method for the synthesis of a Pt–CuO–TiO<sub>2</sub>/C nanocatalyst, in which the CuO doping in the TiO<sub>2</sub> could greatly modify its electronic structure and significantly promote the tolerance of CO-like intermediates. Moreover, the nanotube-like structure enabled the TiO<sub>2</sub> to anchor Pt nanoparticles to expose more surface active sites, thereby contributing to substantial enhancement in the electrocatalytic performance toward the MOR. Furthermore, the synergistic effects between the CuO–TiO<sub>2</sub> and the carbon material greatly promoted the stability of the Pt nanocatalyst for the electrocatalytic MOR. All of these electronic and geometric structure advantages greatly promoted the electrocatalytic performance of the Pt–CuO–TiO<sub>2</sub>/C nanocatalyst, thereby making it a promising electrocatalyst for fuel cells. It is believed that these results can boost the study of metal oxide-supported catalysts for fuel cell reactions and accelerate the rapid development of fuel cells.

## Conflicts of interest

There are no conflicts to declare.

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