

## PAPER

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# Pt<sub>3</sub>Sn nanoparticles enriched with SnO<sub>2</sub>/Pt<sub>3</sub>Sn interfaces for highly efficient alcohol electrooxidation†

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Pt<sub>3</sub>Sn nanoparticles (NPs) enriched with Pt<sub>3</sub>Sn/ultra-small SnO<sub>2</sub> interfaces (Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG) were synthesized through a thermal treatment of Pt<sub>2</sub>Sn/NG in a H<sub>2</sub> atmosphere, followed by annealing under H<sub>2</sub> and air conditions. The unique structure of Pt<sub>3</sub>Sn NPs enriched with Pt<sub>3</sub>Sn/SnO<sub>2</sub> interfaces was observed on the Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG catalyst based on HRTEM. The optimized Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG catalyst achieves high catalytic activity with an ethanol oxidation reaction (EOR) activity of 366 mA mg<sub>Pt</sub><sup>-1</sup> and a methanol oxidation reaction (MOR) activity of 503 mA mg<sub>Pt</sub><sup>-1</sup> at the potential of 0.7 V, which are eight-fold and five-fold higher than those for the commercial Pt/C catalyst (44 and 99 mA mg<sub>Pt</sub><sup>-1</sup>, respectively). The Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG catalyst is found to be 3 times more stable and have higher CO tolerance than Pt/C. The outstanding performance of the Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG catalyst should be ascribed to the synergetic effect induced by the unique structure of Pt<sub>3</sub>Sn NPs enriched with Pt<sub>3</sub>Sn/SnO<sub>2</sub> interfaces. The synergetic effect between Pt<sub>3</sub>Sn NPs and ultra-small SnO<sub>2</sub> increases the performance for alcohol oxidation because the Sn in both Pt<sub>3</sub>Sn and SnO<sub>2</sub> favors the removal of CO<sub>ads</sub> on the nearby Pt by providing OH<sub>ads</sub> species at low potentials. The present work suggests that the Pt<sub>3</sub>Sn@u-SnO<sub>2</sub> is indeed a unique kind of efficient electrocatalyst for alcohol electrooxidation.

Received 28th April 2021  
Accepted 2nd July 2021

DOI: 10.1039/d1na00314c

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## 1. Introduction

During the past few decades, direct alcohol fuel cells (DAFCs) have emerged as an attractive alternative energy technology for portable electronics and vehicles due to their high energy density, low pollutant emission and easy storage and transportation.<sup>1–3</sup> Pt/C catalysts are the most popular electrocatalysts to accelerate the kinetics of the methanol oxidation reaction (MOR) and ethanol oxidation reaction (EOR) at the anode in DAFCs.<sup>4–6</sup> However, the practical adoption of DAFCs is limited by the high cost, low activities and poor durability of Pt/C catalysts.<sup>6,7</sup> Furthermore, Pt is highly susceptible to being poisoned by intermediates such as CO, which easily adsorb on Pt and block the active sites of Pt catalysts, thus leading to the deactivation of Pt NPs.<sup>8,9</sup>

To address the above issues, Pt alloying with other transition metals is an effective strategy to promote the oxidation of

methanol/ethanol.<sup>2,10–12</sup> Different bimetallic PtM (M = Ru, Rh, Co, Ni, Fe, Sn) catalysts with different structures have been explored to improve the Pt activity and stability towards oxidation of methanol/ethanol.<sup>13–19</sup> The improvement in the performance of Pt alloys is attributed to a bifunctional and/or electronic effect of transition metals on Pt.<sup>20–22</sup> Among these Pt alloys, Pt alloyed with Sn has received considerable attention for alcohol oxidation mainly due to its superior performance with high CO-poisoning tolerance.<sup>23–26</sup> For example, compared with pure nanowires, ultrathin Pt<sub>x</sub>Sn<sub>1–x</sub> nanowires were found to not only achieve superior activity and stability towards the MOR and EOR, but also exhibit much lower onset potentials.<sup>27–29</sup> Furthermore, Pt<sub>3</sub>Sn NPs are reported to have higher EOR activity than PtSn NPs.<sup>30</sup>

The design of interfacial Pt–metal oxide structures in DAFC anode catalytic systems is believed to be another effective strategy.<sup>31–34</sup> The interfacial Pt–metal oxide structures not only improve the stability resulting from the strong metal–support interaction (SMSI) effect, but also improve the Pt activity through the bifunctional mechanism, wherein metal oxides provide adsorbed hydroxyl groups for adjacent Pt active sites to facilitate the oxidation and removal of the reaction intermediates (e.g., CH<sub>x</sub> and CO) at a lower potential and thus improve the Pt activity towards the MOR and EOR.<sup>35</sup> For example, SnO<sub>2</sub> NPs were widely used to provide hydroxyl groups for helping the removal of adsorbed CO on the surface of Pt, leading to

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/d1na00314c

improved electrocatalytic performance for methanol/ethanol oxidation.<sup>36,37</sup> Recently, Cheng *et al.*<sup>38</sup> annealed Pt–Sn on N-doped graphene under air conditions to ensure that each generated Pt<sub>3</sub>Sn NP is in close contact with one or more SnO<sub>2</sub> NPs, resulting in high activity towards the MOR and EOR due to the formation of the interfacial Pt<sub>3</sub>Sn–SnO<sub>2</sub> structures. However, designing enough interfacial Pt–metal oxides around Pt-based catalysts is still a big challenge.

In this work, we developed highly active and stable Pt<sub>3</sub>Sn NPs enriched with SnO<sub>2</sub>/Pt<sub>3</sub>Sn interfaces through surface restructuring in Pt<sub>2</sub>Sn NPs under H<sub>2</sub> and air conditions. As shown in Scheme 1, Pt<sub>2</sub>Sn/NG catalysts were firstly obtained by deposition of Pt<sub>2</sub>Sn NPs on nitrogen-doped graphene (NG) using the polyol method<sup>39</sup> with the nominal Pt/Sn atomic ratio of 2 : 1. The Pt<sub>3</sub>Sn NPs enriched with SnO<sub>2</sub>/Pt<sub>3</sub>Sn interfaces on the NG (Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG) were achieved through thermal treatment of Pt<sub>2</sub>Sn/NG in a H<sub>2</sub> atmosphere, followed by annealing under air conditions. Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG catalysts display superior activity and excellent stability for the EOR and MOR.

## 2. Results and discussion

### 2.1 Structure of the catalyst

X-ray diffraction (XRD) was firstly applied to monitor the transformation of Pt<sub>2</sub>Sn/NG to Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG. Three broad peaks centered at 38.9°, 45.2° and 66.5° were detected for the Pt<sub>2</sub>Sn/NG catalyst (Fig. 1), owing to the reflections of (111), (200) and (220) planes of Pt NPs with a face-centered cubic (fcc) structure, respectively.<sup>40</sup> After treatment of Pt<sub>2</sub>Sn/NG in H<sub>2</sub>/N<sub>2</sub> at 300 °C for 1 h, stronger and sharper diffraction peaks appear, which indicates the formation of a large particle size in the Pt<sub>2</sub>Sn–H/NG catalyst. Compared with commercial Pt/C and Pt<sub>2</sub>Sn–H/NG catalysts, it is obvious that diffraction peaks in the Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG catalyst negatively shift to 38.8°, 45.5° and 66.1°, which are close to (111), (200) and (220) planes of the Pt<sub>3</sub>Sn NPs (PDF# 35-1360). Furthermore, small and broadened diffraction peaks of SnO<sub>2</sub> were observed, which demonstrate the ultra-small feature of SnO<sub>2</sub> NPs. A strong diffraction peak at about *ca.* 25.5° was observed, originating from the (002) reflections of NG.

Transmission electron microscopy (TEM) was further performed to investigate the structural evolution upon the thermal treatment of the Pt<sub>2</sub>Sn/NG sample. Fig. S1† shows that Pt<sub>2</sub>Sn NPs with 2–4 nm in diameter were highly dispersed on NG. A

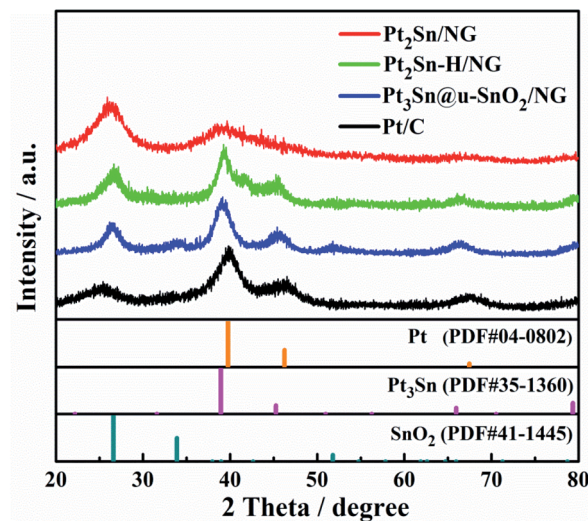


Fig. 1 XRD patterns of the Pt<sub>2</sub>Sn/NG, Pt<sub>2</sub>Sn–H/NG, Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG and Pt/C catalysts.

larger particle size of Pt<sub>2</sub>Sn NPs is found to be formed after treatment of Pt<sub>2</sub>Sn/NG in H<sub>2</sub>/N<sub>2</sub> at 300 °C for 1 h as shown in Fig. S2.† After contiguous annealing of the Pt<sub>2</sub>Sn–H/NG sample in air at 300 °C for 1 h, the interplanar spacings were measured to be 0.200 and 0.231 nm, as shown in Fig. 2b, corresponding to the spacings between the (200) and (111) facets of fcc Pt<sub>3</sub>Sn, respectively. The Pt<sub>3</sub>Sn formation in Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG was further displayed by the selected diffraction pattern as shown in Fig. S3.† In addition to the typical (111) and (200) planes, we found Pt<sub>3</sub>Sn specific superlattice diffraction rings with diameters of 11.17 nm<sup>–1</sup>, 14.08 nm<sup>–1</sup> and 16.65 nm<sup>–1</sup>. The corresponding crystal plane spacing was 0.179 nm, 0.142 nm and 0.120 nm, respectively, which are attributed to (210), (220) and

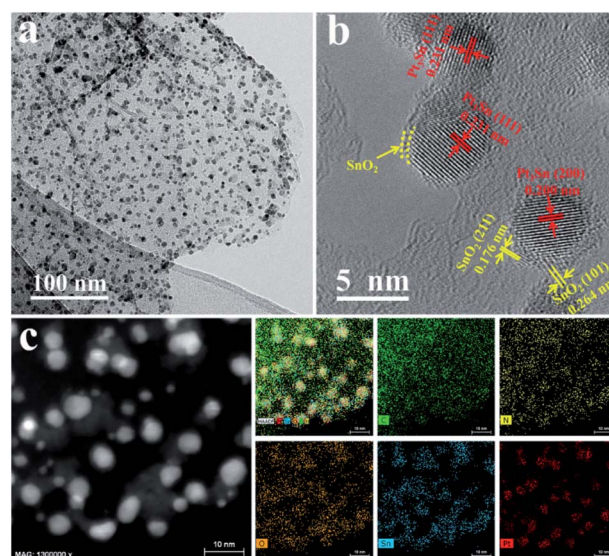
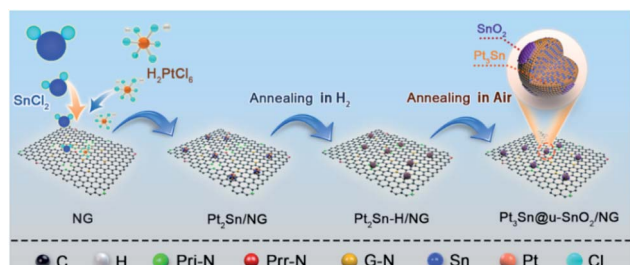


Fig. 2 (a) TEM and (b) HRTEM images of the Pt<sub>3</sub>Sn@u-SnO<sub>2</sub>/NG catalyst. (c) STEM image and the corresponding elemental maps of C, N, O, Sn and Pt.



Scheme 1 Schematic diagram of the synthesis of Pt<sub>3</sub>Sn@u-SnO<sub>2</sub> on N-doped graphene.

(311) of  $\text{Pt}_3\text{Sn}$ , respectively. More importantly, ultra-small  $\text{SnO}_2$  NPs on the  $\text{Pt}_3\text{Sn}$  NPs were found, in accordance with the analysis of XRD. This result suggests the formation of the interfacial  $\text{Pt}_3\text{Sn-SnO}_2$  structures on  $\text{Pt}_3\text{Sn}$  NPs through surface restructuring in  $\text{Pt}_2\text{Sn}$  NPs under air conditions. Pt-based catalysts enriched with Pt/metal oxides have proved to increase the EOR due to the enhanced C-C bond cleavage.<sup>41</sup> The elemental mapping images as shown in Fig. 2c also indicate that the Sn element is distributed around the  $\text{Pt}_3\text{Sn}$  NPs, which confirms that there are abundant ultra-small  $\text{SnO}_2$  NPs around the  $\text{Pt}_3\text{Sn}$  NPs.

X-ray photoelectron spectroscopy (XPS) was carried out to observe the effect of thermal treatment in  $\text{H}_2$  and air on the surface properties of the  $\text{Pt}_2\text{Sn}/\text{NG}$  sample shown in Fig. 3. The high resolution XPS spectrum of  $\text{Pt}_2\text{Sn}/\text{NG}$  in the Pt 4f region (Fig. 3b) clearly shows the binding energies of Pt 4f<sub>5/2</sub> at 74.77 eV and Pt 4f<sub>7/2</sub> at 71.49 eV, which are a little lower than those of the Pt/C catalyst (75.10 and 71.76 eV). After thermal treatment of the  $\text{Pt}_2\text{Sn}/\text{NG}$  sample in  $\text{H}_2$ , the binding energies of Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub> for the  $\text{Pt}_2\text{Sn-H}/\text{NG}$  sample were negatively shifted to 74.59 eV and 71.23 eV. The thermal treatment in  $\text{H}_2$  changed the crystal structure and degree of ordering of the alloy, which leads to the tuning of the Pt surface electronic structure and thus the downshift of Pt 4f.<sup>42</sup> After annealing of the  $\text{Pt}_2\text{Sn-H}/\text{NG}$  sample in air, the binding energies of Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub> for the  $\text{Pt}_3\text{Sn@u-SnO}_2/\text{NG}$  sample positively shift to 74.61 eV and 71.32 eV. The deconvoluted Pt 4f spectrum of the  $\text{Pt}_3\text{Sn@u-SnO}_2/\text{NG}$  sample as shown in Fig. 3b indicates that two doublets are located at binding energies of 71.32/74.61 eV and 72.50/75.90 eV, corresponding to metal Pt and the bivalent Pt ion, respectively. The binding energies of Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub> for the other samples are summarized in Table S2.† Fig. 3c shows the

deconvoluted Sn 3d spectra of  $\text{Pt}_2\text{Sn}/\text{NG}$ ,  $\text{Pt}_2\text{Sn-H}/\text{NG}$  and  $\text{Pt}_3\text{Sn@u-SnO}_2/\text{NG}$  samples. The main two bands located at about 486.93/495.34 eV and 485.51/494.04 eV were observed for these three samples (Table S3†), which should be attributed to  $\text{Sn(II/IV)}$  and  $\text{Sn(0)}$ . As given in Table S4,† the  $\text{Sn(0)}$  content in  $\text{Pt}_2\text{Sn-H}/\text{NG}$  is higher than that of  $\text{Pt}_2\text{Sn}/\text{NG}$ , which is mainly due to the change in the crystal structure and degree of ordering of the alloy.<sup>43</sup> Compared with  $\text{Pt}_2\text{Sn-H}/\text{NG}$ , the  $\text{Pt}_3\text{Sn@u-SnO}_2/\text{NG}$  sample has a lower content of  $\text{Sn(0)}$  due to the formation of  $\text{SnO}_2$ . There is no significant change observed for N configurations and content in NG after the thermal treatment at 300 °C in  $\text{H}_2$  and air atmospheres (Fig. 3d).

## 2.2 Evaluation of electrochemical activity

The cyclic voltammograms (CVs) of the as-prepared  $\text{Pt}_3\text{Sn@u-SnO}_2/\text{NG}$  were recorded prior to evaluating its EOR activity. The CVs of  $\text{Pt}_3\text{Sn@u-SnO}_2/\text{NG}$ ,  $\text{Pt}_2\text{Sn-H}/\text{NG}$  and  $\text{Pt}_2\text{Sn}/\text{NG}$  as shown in Fig. S4a† showed different adsorption/desorption peaks compared with the Pt/C catalyst, which arise from the insertion of Sn into the Pt lattice.<sup>42</sup> The EOR performance of our samples was characterized as shown in Fig. 4 and the current densities were normalized with respect to the Pt loading. It is observed from polarization curves for ethanol oxidation in Fig. 4a that the peak EOR current densities of different catalysts decrease in the

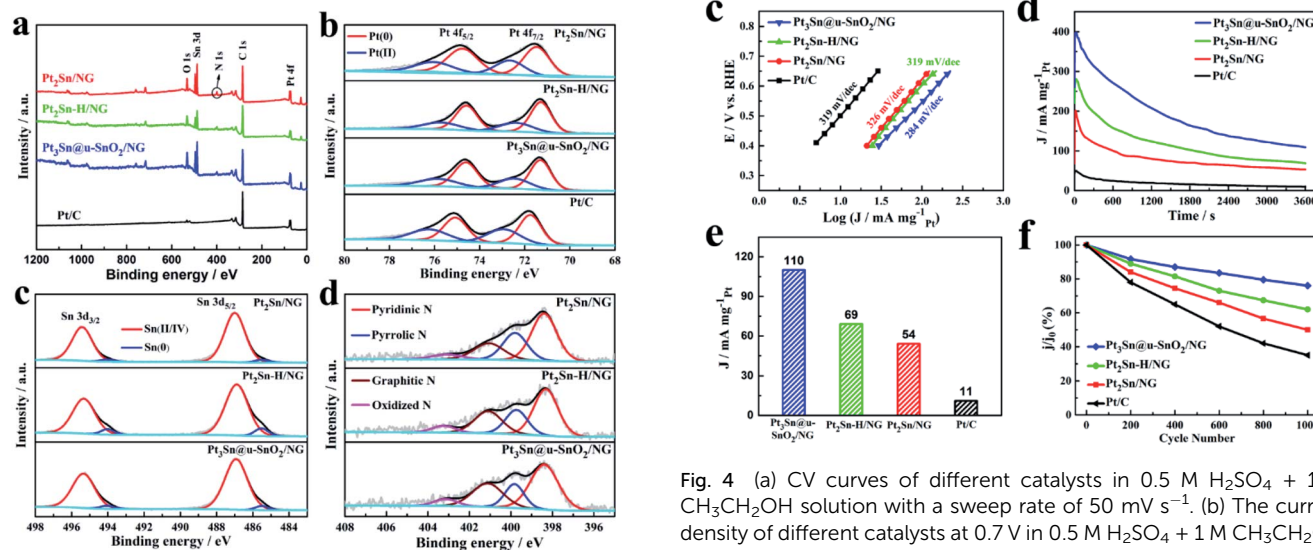


Fig. 3 (a) XPS survey spectra of  $\text{Pt}_2\text{Sn}/\text{NG}$ ,  $\text{Pt}_2\text{Sn-H}/\text{NG}$ ,  $\text{Pt}_3\text{Sn@u-SnO}_2/\text{NG}$  and Pt/C catalysts. (b) High-resolution Pt 4f spectra of  $\text{Pt}_2\text{Sn}/\text{NG}$ ,  $\text{Pt}_2\text{Sn-H}/\text{NG}$ ,  $\text{Pt}_3\text{Sn@u-SnO}_2/\text{NG}$  and Pt/C catalysts. High-resolution (c) Sn 3d and (d) N 1s spectra of  $\text{Pt}_2\text{Sn}/\text{NG}$ ,  $\text{Pt}_2\text{Sn-H}/\text{NG}$  and  $\text{Pt}_3\text{Sn@u-SnO}_2/\text{NG}$  catalysts.

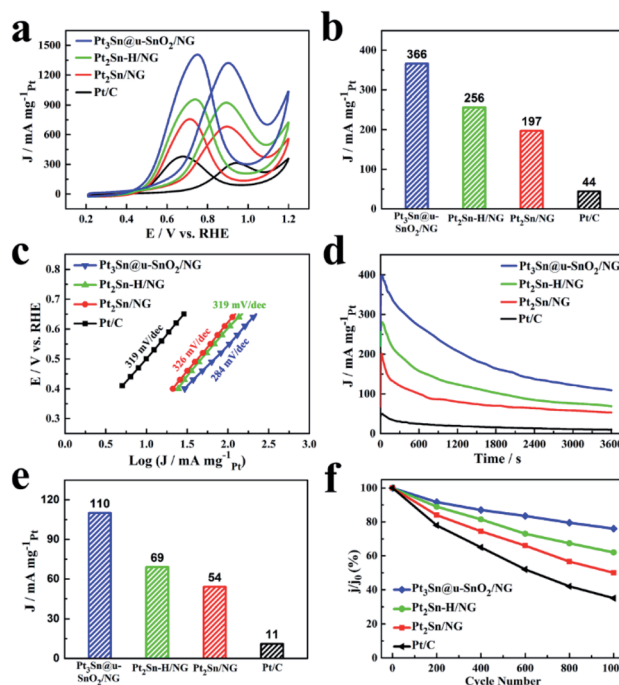


Fig. 4 (a) CV curves of different catalysts in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{CH}_2\text{OH}$  solution with a sweep rate of 50  $\text{mV s}^{-1}$ . (b) The current density of different catalysts at 0.7 V in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{CH}_2\text{OH}$  solution. (c) Corresponding Tafel plots for the EOR on different catalysts. (d) Chronoamperometric curves of  $t$  of different catalysts in  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{CH}_2\text{OH}$  solution at constant voltage 0.7 V for 3600 s. (e) The current density at 0.7 V at 3600 s for different catalysts obtained from Fig. 4d. (f) Changes of peak current densities of the EOR during potential cycling of different catalysts.



order of  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG} > \text{Pt}_2\text{Sn-H}/\text{NG} > \text{Pt}_2\text{Sn}/\text{NG} > \text{Pt}/\text{C}$  (30%, JM). We also find that the onset potential of the EOR on different catalysts follows the same trend as shown in Fig. S4†. More importantly,  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  shows higher EOR activity compared with the other samples during 0.45–0.7 V vs. RHE (Fig. S5†) for the practical applications of direct ethanol fuel cells (DEFCs).<sup>44</sup> The mass activity of  $366 \text{ mA mg}_{\text{Pt}}^{-1}$  was achieved on  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  at 0.7 V (Fig. 4b), which is 1.4, 1.9, and 8.3 times greater than that of  $\text{Pt}_2\text{Sn-H}/\text{NG}$  ( $256 \text{ mA mg}_{\text{Pt}}^{-1}$ ),  $\text{Pt}_2\text{Sn}/\text{NG}$  ( $197 \text{ mA mg}_{\text{Pt}}^{-1}$ ) and  $\text{Pt}/\text{C}$  ( $44 \text{ mA mg}_{\text{Pt}}^{-1}$ ), respectively. The high EOR activity of  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  was further confirmed by the Tafel plots as shown in Fig. 4e. The Tafel slope on  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  is  $284 \text{ mV dec}^{-1}$ , much lower than that of commercial  $\text{Pt}/\text{C}$  ( $319 \text{ mV dec}^{-1}$ ), indicating that  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  prepared by our strategy can obviously promote the EOR kinetics on the Pt surface. The very high EOR activity of the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst mainly should be attributed to the unique structure of  $\text{Pt}_3\text{Sn}$  NPs enriched with  $\text{Pt}_3\text{Sn}/\text{SnO}_2$  interfaces, which make the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst one of the most promising EOR catalysts towards the EOR compared with the most recently reported catalysts (Table S5†).

The chronoamperometric technique was firstly applied to monitor the stabilities of different electrocatalysts. As shown in Fig. 4c, the EOR activities on all catalysts running at the potential of 0.7 V gradually decay with time because the generated intermediates like CO poison the active sites of Pt-based catalysts during the ethanol oxidation. The  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst achieves higher mass activity in comparison with the  $\text{Pt}_2\text{Sn-H}/\text{NG}$ ,  $\text{Pt}_2\text{Sn}/\text{NG}$  and  $\text{Pt}/\text{C}$  catalysts during a period of 3600 s (Fig. 4d). After operating the reaction for 3600 s, the retained mass activity on the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst is found to be  $110 \text{ mA mg}_{\text{Pt}}^{-1}$  at the potential of 0.7 V, outperforming the  $\text{Pt}_2\text{Sn-H}/\text{NG}$  ( $69 \text{ mA mg}_{\text{Pt}}^{-1}$ ),  $\text{Pt}_2\text{Sn}/\text{NG}$  ( $54 \text{ mA mg}_{\text{Pt}}^{-1}$ ) and  $\text{Pt}/\text{C}$  ( $11 \text{ mA mg}_{\text{Pt}}^{-1}$ ), respectively. The stability of the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst was further investigated by the accelerated durability tests (ADTs). The  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst retains the highest proportion of its initial activity among all catalysts after 1000 cycles (Fig. 4f and S6†). The  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst exhibits superior long-term stability with the loss of 24% of its initial activity, which is about 2.7 times higher than that of the  $\text{Pt}/\text{C}$  catalyst (65%). The  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  did not show significant agglomeration, and the ultra-small  $\text{SnO}_2$  around  $\text{Pt}_3\text{Sn}$  NPs was still visible (Fig. S7†). These findings indicate that the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst possesses excellent performance due to the formation of the interfacial  $\text{Pt}_3\text{Sn-SnO}_2$  structures on  $\text{Pt}_3\text{Sn}$  NPs.

In addition to the high EOR activity, the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst also shows excellent performance for methanol oxidation as shown in Fig. 5 and Table S6.† The  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst has higher MOR peak activity compared with the  $\text{Pt}_2\text{Sn-H}/\text{NG}$ ,  $\text{Pt}_2\text{Sn}/\text{NG}$  and  $\text{Pt}/\text{C}$  catalysts (Fig. 5a).  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  is found to have higher MOR activity compared with the other samples during 0.45–0.7 V vs. RHE (Fig. S8†). Besides the main oxidation peak at about 0.84 V for the MOR, a shoulder peak at 0.72 V was observed for the methanol oxidation reaction, attributed to the different types of active sites for methanol oxidation.<sup>45</sup> As shown in Fig. 5b, the mass activity of the MOR on

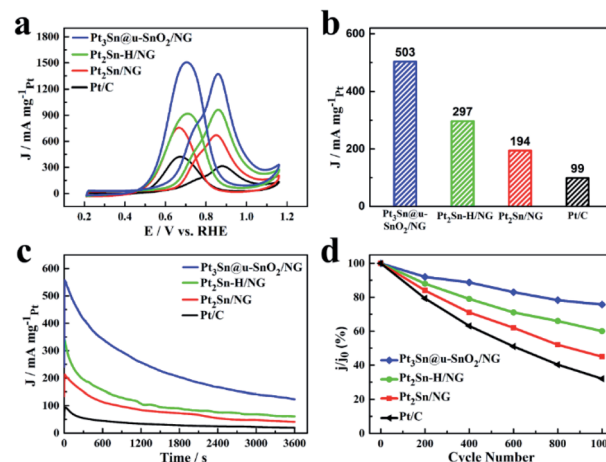


Fig. 5 (a) CV curves of different catalysts in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$  solution with a sweep rate of  $50 \text{ mV s}^{-1}$ . (b) The current density of different catalysts at 0.7 V in 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$  solution. (c) Chronoamperometric curves of different catalysts in  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$  solution at constant voltage 0.7 V for 3600 s. (d) Changes of peak current densities of the MOR during potential cycling of different catalysts.

the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst is  $503 \text{ mA mg}_{\text{Pt}}^{-1}$  at the potential of 0.7 V, outperforming  $\text{Pt}_2\text{Sn-H}/\text{NG}$  ( $297 \text{ mA mg}_{\text{Pt}}^{-1}$ ),  $\text{Pt}_2\text{Sn}/\text{NG}$  ( $194 \text{ mA mg}_{\text{Pt}}^{-1}$ ) and  $\text{Pt}/\text{C}$  ( $99 \text{ mA mg}_{\text{Pt}}^{-1}$ ), respectively. The MOR mass activity on the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst is 5.1 times higher than that of the  $\text{Pt}/\text{C}$  catalyst. The excellent MOR activity of  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  was also supported by the Tafel plots (Fig. S9†). The chronoamperometric measurements (Fig. 5c) show that the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst has higher current density and lower current decay in comparison with the other samples, indicating the high stability of the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst for methanol oxidation. The high stability of the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst during the MOR is also confirmed by the ADTs. After ADT (Fig. 5d, S10 and S11†), the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst losses only 25% of its initial activity while the activity of the  $\text{Pt}/\text{C}$  catalyst decreases by 68% under the same operating conditions.

The ability of the CO tolerance on different catalysts was evaluated by CO stripping voltammograms as shown in Fig. 6. It is obvious that the onset potential for CO oxidation on the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst is 0.36 V, lower than that of  $\text{Pt}_2\text{Sn-H}/\text{NG}$  (0.55 V),  $\text{Pt}_2\text{Sn}/\text{NG}$  (0.64 V) and  $\text{Pt}/\text{C}$  (0.81 V), respectively. The lowest onset potential of  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  (0.36 V) should be ascribed to the unique structure of  $\text{Pt}_3\text{Sn}$  decorated with ultra-small  $\text{SnO}_2$ , helping the CO oxidation on the Pt surface at relatively low potentials by the bifunctional effects. Furthermore, the main peak of CO oxidation on the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst has the lowest potential of 0.73 V compared with the other catalysts. This result indicates that the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst possesses high CO tolerance.

The enhanced activity and stability of the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst may be related to the unique structure of  $\text{Pt}_3\text{Sn}$  NPs enriched with  $\text{Pt}_3\text{Sn}/\text{SnO}_2$  interfaces. The  $\text{Pt}_3\text{Sn}$  NPs not only possesses high activity but also stability during the MOR and



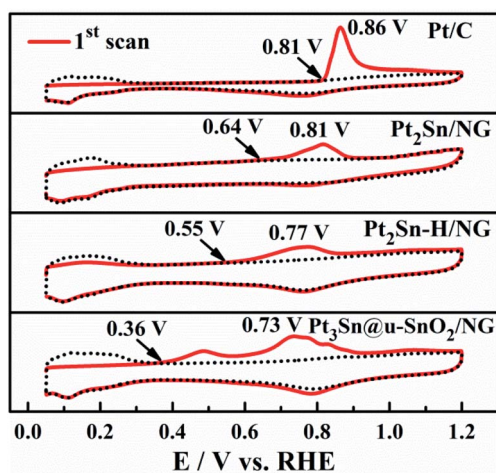


Fig. 6 CO stripping patterns recorded on  $\text{Pt}_2\text{Sn}/\text{NG}$ ,  $\text{Pt}_2\text{Sn-H}/\text{NG}$ ,  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  and  $\text{Pt}/\text{C}$  in 0.5 M  $\text{H}_2\text{SO}_4$ .

EOR process. The incorporation of Sn into Pt lattices is believed to not only tune the Pt electronic structure but also increase the Pt–Pt distance, which results in the enhanced performance for alcohol oxidation by inhibiting CO adsorption and lowering the CO affinity on Pt active sites.<sup>46</sup> Furthermore, the surface decorated ultra-small  $\text{SnO}_2$  can generate OH species at low potentials, which can improve the kinetics of CO electro-oxidation on the Pt NPs.

### 3. Conclusion

In conclusion, we have successfully synthesized  $\text{Pt}_3\text{Sn}$  NPs enriched with  $\text{Pt}_3\text{Sn}/\text{SnO}_2$  interfaces on NG through thermal treatment of  $\text{Pt}_2\text{Sn}/\text{NG}$  in a  $\text{H}_2$  atmosphere, followed by annealing under  $\text{H}_2$  and air conditions. The  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst exhibits superior mass activities of  $366 \text{ mA mg}_{\text{Pt}}^{-1}$  for the EOR and  $503 \text{ mA mg}_{\text{Pt}}^{-1}$  for the MOR at 0.7 V, which are 8.3 and 5.1 times better than those of commercial  $\text{Pt}/\text{C}$ , respectively. CO-stripping profiles obtained on the  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst showed higher CO tolerance in comparison with  $\text{Pt}/\text{C}$ . The outstanding performance of  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalysts should be ascribed to the synergetic effect induced by the unique structure of  $\text{Pt}_3\text{Sn}$  NPs enriched with  $\text{Pt}_3\text{Sn}/\text{SnO}_2$  interfaces.

### 4. Methods

#### 4.1 Chemicals

All chemicals were utilized as received without further purification. Chloroplatinic acid hexahydrate [ $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ], tin(II) chloride dehydrate [ $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ], urea [ $\text{CO}(\text{NH}_2)_2$ ] and ethylene glycol (EG) were of analytical reagent (A.R.) grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Commercial 30 wt%  $\text{Pt}/\text{C}$  was purchased from Johnson Matthey. Deionized water (DI water, Millipore,  $18.2 \text{ M}\Omega$  at  $25^\circ\text{C}$ ) was used in all processes.

#### 4.2 Synthesis of the $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$

The N-doped GO (NG) was synthesized by pyrolysis of the mixture of graphene oxide (GO) prepared by a modified Hummers method<sup>47</sup> and urea in an  $\text{N}_2$  atmosphere at  $600^\circ\text{C}$  for 30 minutes.  $\text{Pt}_2\text{Sn}/\text{NG}$  was prepared using  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  as precursors with the Sn/Pt atomic ratio of 1 : 2 by the polyol method.<sup>39</sup> The  $\text{Pt}_2\text{Sn-H}/\text{NG}$  catalyst was obtained by direct heat treatment of  $\text{Pt}_2\text{Sn}/\text{NG}$  at  $300^\circ\text{C}$  for 1 h in a 10%  $\text{H}_2/90\% \text{ N}_2$  atmosphere. The  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$  catalyst was obtained by direct heat treatment of  $\text{Pt}_2\text{Sn-H}/\text{NG}$  at  $300^\circ\text{C}$  for 1 h in an air atmosphere. The Pt loading on  $\text{Pt}_3\text{Sn}@u\text{-SnO}_2/\text{NG}$ ,  $\text{Pt}_2\text{Sn-H}/\text{NG}$  and  $\text{Pt}_2\text{Sn}/\text{NG}$  catalysts was 14.5 wt%, 16.2 wt% and 15.8 wt%, respectively according to the ICP test.

#### 4.3 Material characterization and electrochemical measurements

The composition, structure and morphology of the prepared catalysts were investigated by transmission electron microscopy (TEM, TECNAL G2F20) and X-ray powder diffraction (XRD, ULTIMA III). X-ray photoelectron spectroscopy (XPS) spectra were studied with a K-Alpha spectrometer. The Pt loading was obtained using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) (iCAP7000, Thermo Fisher Scientific). Electrochemical measurements were performed with an Autolab electrochemistry station using a standard three-electrode cell at  $25^\circ\text{C}$ . More detailed information regarding electrochemical testing is provided in the ESI.<sup>†</sup>

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21875039), Minjiang Professorship (XRC-1677), and Fujian Province's High Level Innovative and Entrepreneurial Talents (50012709).

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