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# High performance layer-by-layer Pt<sub>3</sub>Ni(Pt-skin)-modified Pd/C for the oxygen reduction reaction†

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Bimetallic Pt–Ni with Pt on the outermost layer and an innermost layer enriched in Ni, referred to as Pt<sub>3</sub>Ni(Pt-skin), is a promising configuration of an electrocatalyst for the oxygen reduction reaction (ORR) in fuel cells. We prepare a core (Pd)/shell (Pt<sub>3</sub>Ni(Pt-skin)) catalyst (Pt<sub>3</sub>Ni(Pt-skin)/Pd/C) from Zn underpotential deposition (UPD) on a Ni UPD modified Pd/C catalyst, facilitating Pt atomic layer-by-layer growth on the Ni surface through the galvanic replacement process. Pt<sub>3</sub>Ni(Pt-skin)/Pd/C shows the best ORR performance, with a Pt specific activity of 16.7 mA cm<sup>−2</sup> and Pt mass activity of 14.2 A mg<sub>Pt</sub><sup>−1</sup>, which are 90- and 156- fold improvements over commercial Pt/C catalysts. The Pt<sub>3</sub>Ni(Pt-skin) structure effectively inhibits Ni leaching to improve the durability in two accelerated durability test modes mimicking the catalyst lifetime and start-up/shut-down cycles.

## Introduction

Cathodic oxygen reduction reaction ORR electrocatalysts play a crucial role in fuel cell performance.<sup>1–3</sup> The Pt catalyzed ORR has sluggish kinetics and requires a high overpotential, causing lower Pt specific activity ( $j_{\text{kPt}}$ , the catalytic activity normalized by the Pt electrochemically active surface area (ECSA)) and Pt mass activity ( $i_{\text{mPt}}$ , the catalytic activity per Pt mass). The high cost and the low durability of Pt ORR electrocatalysts remain a challenge for the widespread commercialization of fuel cells.<sup>4–18</sup> Alloying Pt with another transition metal (Co, Ni, Fe, *etc.*) has attracted much attention in the design of advanced electrocatalysts, as this approach not only decreases the Pt content but also enhances the catalytic activity and durability.<sup>8,19–23</sup> These designs include core-shell structured nanoparticles (NPs),<sup>24,25</sup> as well as de-alloyed<sup>26–28</sup> and porous structured NPs.<sup>6,26</sup> The Pt alloys may tailor the electronic (affecting the Pt–OH bond energetics) and geometric structures (affecting the Pt–Pt bond distance and coordination number) to enhance the catalytic activity.<sup>8</sup> The highest recorded  $j_{\text{kPt}}$  values were achieved on single crystal surfaces or well-defined NPs with a specifically engineered facet structure and alloy composition. For example, Stamenkovic *et al.* found that single-crystal Pt<sub>3</sub>Ni (111) with Pt-skin had a  $j_{\text{kPt}}$  value 10 times higher than the corresponding Pt (111) surface and 90 times higher than the commercial Pt/C catalysts used for the ORR.<sup>8</sup> Pt<sub>3</sub>Ni octahedral NPs were shown to exhibit favorable microstructures for greatly enhanced activity in the ORR,<sup>28–30</sup> but were still limited by their

insufficient stability due to Ni leaching from the alloys and decreased ECSA from the agglomeration of the NPs during electrochemical cycling.<sup>31</sup> Core-shell NPs represent a multi-metallic structure with tunable properties to enhance ORR catalytic activity.<sup>32–38</sup> A promising structure to optimize  $i_{\text{mPt}}$  and Pt utilization is a thin shell or skin layers of Pt or Pt alloys over a non-Pt NP core. As reported by Adzic *et al.*, Cu underpotential deposition (UPD) is used as a sacrificial coating on the core, followed by galvanic replacement (Gal) with noble metal ions for the final shell metal.<sup>7,39–41</sup> UPD-Gal is one of the most successful methods to specifically coat Pt monolayers on different metals, but the commonly used Cu UPD (Cu<sub>u</sub>) limits the options of Pt coating substrates due to its high work function,  $\Phi_{\text{Cu}}$  (~4.94 eV).<sup>42</sup> It is known that when the  $\Phi$  of an electrodeposited metal,  $\Phi_{\text{M}}$ , is lower than that of the substrate metal,  $\Phi_{\text{S}}$ , UPD may occur at a potential more positive than the equilibrium potential. The Kolb–Gerischer equation,  $\Delta E = 0.5\Delta\Phi$  ( $\Delta E$  is the underpotential shift in V and  $\Delta\Phi$  is  $\Phi_{\text{M}} - \Phi_{\text{S}}$  of the electron in eV), has been used to evaluate the level of underpotential shift.<sup>43</sup> Despite numerous attempts to synthesize Pt alloying nanocatalysts with Pt-skin surfaces on transition metals,<sup>28,44–50</sup> it still remains a challenge to demonstrate their existence at the nanoscale. To resolve this issue, we attempted to improve the elegant UPD-Gal approach, also referred to as electrochemical atomic layer deposition (E-ALD) or electrochemical atomic layer epitaxy EC-ALE.<sup>51,52</sup> In UPD-Gal, the UPD adlayer enables a type of surface limited reaction (SLR). SLRs occur only at the substrate or deposit surface and specifically form an atomic layer or a monolayer coverage. The “atomic layer” refers to a coverage less than a monolayer, a monolayer being a unit of deposit coverage. Zn UPD (Zn<sub>u</sub>) was used to replace the Cu<sub>u</sub> in the UPD-Gal due to its lower value of  $\Phi_{\text{Zn}}$  (~3.95 eV) compared to  $\Phi_{\text{Cu}}$ ,<sup>42</sup> and the more negative standard

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reduction potential,  $E^0(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$ .<sup>53</sup> The lower  $\Phi_{\text{Zn}}$  makes  $\text{Zn}_{\text{u}}$  occur on a greater variety of substrates, particularly Ni.  $\text{Zn}_{\text{u}}$  can therefore replace many metals that are nobler than Zn in the Gal process thanks to its more negative  $E^0$ .

We report  $\text{Zn}_{\text{u}}$  assisted UPD-Gal ( $\text{ZnUPD-Gal}$ ) in a Ni UPD ( $\text{Ni}_{\text{u}}$ ) process of constructing a layer-by-layer  $\text{Pt}_3\text{Ni}(\text{Pt-skin})$  thin layer on a carbon-supported Pd electrocatalyst ( $\text{Pd}_{20}/\text{C}$ ) (20 wt% Pd on XC-72 Vulcan carbon, E-TEK) ( $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$ ). The  $\text{Pt}_3\text{Ni}(\text{Pt-skin})$  structure retains the advantages of the ultra-thin layer structure and the synergetic effects of the Ni sublayer.  $\text{Pt}_3\text{-Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$  possesses an ultra-high  $j_{\text{kPt}} = 16.7 \text{ mA cm}^{-2}$  and  $i_{\text{mPt}} = 14.2 \text{ A mg}_{\text{Pt}}^{-1}$  (Pt loading =  $2.97 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ ), at  $0.9 \text{ V}$  vs. RHE, which are 90-fold and 156-fold improvements, respectively, over commercial Pt/C catalysts ( $0.185 \text{ mA cm}^{-2}$  and  $0.091 \text{ A mg}_{\text{Pt}}^{-1}$ , Pt loading =  $24 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ ). We also show that the perfect  $\text{Pt}_3\text{Ni}(\text{Pt-skin})$  structure effectively inhibits Ni leaching, significantly improving the durability of catalysts.

## Results and discussion

Fig. 1 shows the CVs of  $\text{Ni}_{\text{u}}$  and  $\text{Zn}_{\text{u}}$  on  $\text{Pd}_{20}/\text{C}@GC$  in an Ar-saturated  $0.5 \text{ M Na}_2\text{SO}_4$  aqueous solution ( $\text{Na}_2\text{SO}_{4\text{aq}}$ ). These

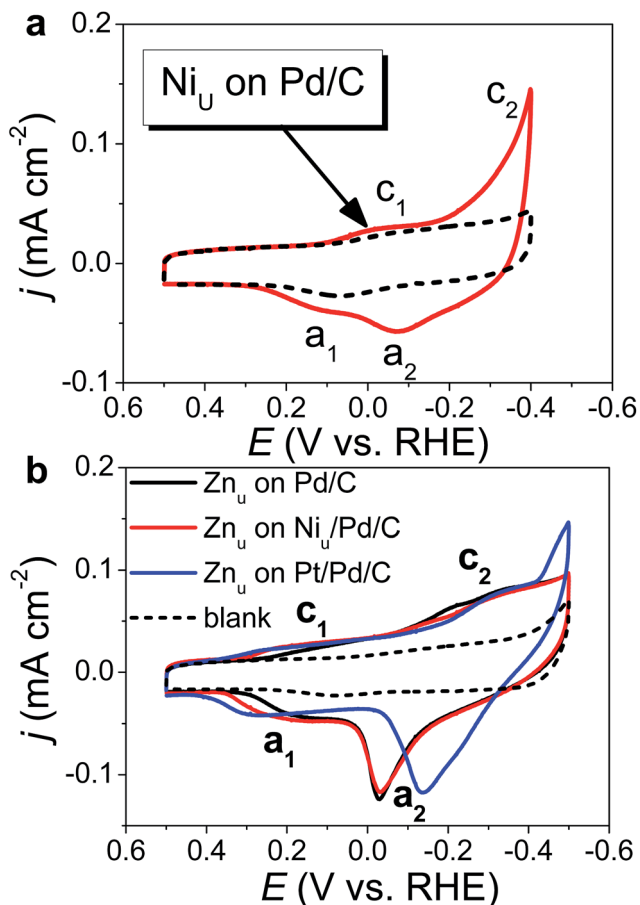
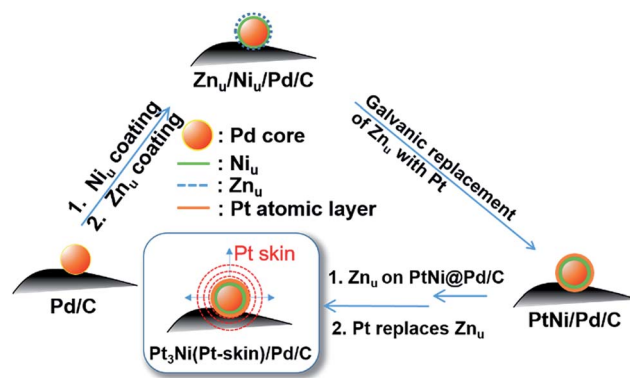


Fig. 1 CVs of (a)  $\text{Ni}_{\text{u}}$  on  $\text{Pd}_{20}/\text{C}@GC$  and (b)  $\text{Zn}_{\text{u}}$  on  $\text{Pd}_{20}/\text{C}@GC$ ,  $\text{Ni}_{\text{u}}/\text{Pd}_{20}/\text{C}@GC$ , and  $\text{Ni}_{\text{u}}/\text{Pd}_{20}/\text{C}@GC$  recorded in Ar saturated  $0.5 \text{ M Na}_2\text{SO}_{4\text{aq}}$  (solid line) with and (dashed line) without (a)  $20 \text{ mM NiSO}_4$  and (b)  $20 \text{ mM Zn}(\text{ClO}_4)_2$  at a sweep rate of  $50 \text{ mV s}^{-1}$ .

voltammograms both show two pairs of redox waves,  $c_1/a_1$  and  $c_2/a_2$ , which correspond to UPD/stripping and bulk deposition (OPD)/bulk stripping, respectively. These indicate that  $\text{Ni}_{\text{u}}$  or  $\text{Zn}_{\text{u}}$  can modify the Pd surface through controlled potential electrodeposition. Herein  $\text{Zn}_{\text{u}}$  was used to assist in the selective growth of Pt atomic layers on a given metallic surface, here Ni and Pt.  $\text{Zn}_{\text{u}}$  was further studied on  $\text{Ni}_{\text{u}}/\text{Pd}_{20}/\text{C}@GC$  and Pt atomic layer covered  $\text{Pd}_{20}/\text{C}@GC$  ( $\text{Pt}/\text{Pd}_{20}/\text{C}@GC$ ) (Fig. 1b).  $\text{Ni}_{\text{u}}/\text{Pd}_{20}/\text{C}$  was from direct electrodeposition of  $\text{Ni}_{\text{u}}$  on  $\text{Pd}_{20}/\text{C}$  in  $0.5 \text{ M Na}_2\text{SO}_{4\text{aq}}$  containing  $20 \text{ mM NiSO}_4$ .  $\text{Pt}/\text{Pd}_{20}/\text{C}$  was prepared by UPD-Gal to deposit a Pt atomic layer on  $\text{Pd}_{20}/\text{C}$ . The  $\text{Zn}_{\text{u}}$  redox waves,  $c_1/a_1$ , on  $\text{Pd}_{20}/\text{C}$  positively shifted from  $\sim 0.18 \text{ V}$  to  $\sim 0.2 \text{ V}$  and  $\sim 0.3 \text{ V}$  after the modification of the  $\text{Ni}_{\text{u}}$  and Pt layer, respectively. The changes in CVs are ascribed to  $\text{Zn}_{\text{u}}$  and are surface dependent. Although  $\text{Zn}_{\text{u}}$  on Pt has been reported in the literature,<sup>54</sup>  $\text{Zn}_{\text{u}}$  on Ni has not been observed until now as the  $\text{Ni}_{\text{u}}$  was freshly produced without serious oxide or hydroxide surface inhibitors. The  $\text{Zn}_{\text{u}}$  on Pd, Ni, and Pt surfaces is related to the higher  $\Phi_s$  of these substrates,  $\Phi_{\text{Pd}}$  ( $\sim 5.0 \text{ eV}$ ),  $\Phi_{\text{Ni}}$  ( $\sim 4.91 \text{ eV}$ ) and  $\Phi_{\text{Pt}}$  ( $\sim 5.4 \text{ eV}$ ), in comparison with the lower  $\Phi_{\text{Zn}}$  ( $\sim 3.95 \text{ eV}$ ).<sup>42</sup> Based on the Kolb–Gerischer equation, we could approximately calculate  $\Delta E$  for the metal couples, Pd substrate/Zn, Ni substrate/Zn and Pt substrate/Zn, as  $\sim 0.53 \text{ V}$ ,  $\sim 0.48 \text{ V}$  and  $\sim 0.7 \text{ V}$ , respectively. This provides grounds for realizing that  $\text{Zn}_{\text{u}}$  on Pd, Ni and Pt is possible. In comparison,  $\text{Cu}_{\text{u}}$  cannot occur on Ni surfaces due to  $\Phi_{\text{Cu}}$  ( $\sim 4.94 \text{ eV}$ ) being close to  $\Phi_{\text{Ni}}$ . This implies that  $\text{Zn}_{\text{u}}$  is a more suitable candidate to promote the Pt atomic layer to specifically form on a Ni surface.

Based on the findings of  $\text{Zn}_{\text{u}}$  on Ni, Pd and Pt surfaces and  $\text{Ni}_{\text{u}}$  on Pd and Pt surfaces,  $\text{ZnUPD-Gal}$  was used to prepare a  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$  electrocatalyst (Scheme 1). First,  $\text{Ni}_{\text{u}}$  was electrodeposited on the Pd surface of  $\text{Pd}_{20}/\text{C}$ , followed by modification of  $\text{Zn}_{\text{u}}$  on  $\text{Ni}_{\text{u}}/\text{Pd}_{20}/\text{C}$ . Subsequently,  $\text{Zn}_{\text{u}}$  was replaced by Pt in the Gal process, leading to Pt atomic layer covered  $\text{Ni}_{\text{u}}/\text{Pd}_{20}/\text{C}$  ( $\text{PtNi}/\text{Pd}_{20}/\text{C}$ ). The repetitive  $\text{ZnUPD-Gal}$  continually introduced the second and the third Pt atomic layers onto  $\text{PtNi}/\text{Pd}_{20}/\text{C}$  to obtain the desired electrocatalyst,  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$ . The micromorphology and elemental composition distribution of  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$  were examined by high-resolution transmission electron microscopy (HRTEM) combined with energy dispersive X-ray spectroscopy



Scheme 1 The preparation process of  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$  electrocatalysts through  $\text{ZnUPD-Gal}$  on  $\text{Ni}_{\text{u}}$ .



(EDS) (Fig. 2a and b and S1†). In Fig. S1a–c,† typical bright-field TEM images of pristine Pd<sub>20</sub>/C reveal a relatively uniform dispersion of Pd NP (Pd<sub>nano</sub>) with sizes of approximately 4.8–5.6 nm (diameter). After Pt<sub>3</sub>Ni(Pt-skin) modification, the growth of the particle size occurred as expected (diameter increased to ~6.8 nm) (Fig. S1d–f†). The core of Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>nano</sub> shows clear fringe orientations of the Pd (111) single-crystal structure (Fig. 2a). The EDS line profile analysis shows the distribution of Pt, Ni, and Pd components in a single NP (Fig. 2b). The width of Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>nano</sub> examined was 4 nm, as designated by the red line in Fig. 2a. The line profile analysis validates the core-shell structure, which is a Pd core covered by an ultra-thin PtNi shell with a thickness of approximately 1.2 nm. The Pd composition is constant and high in the particle center, and decreases from the edge of the core to the particle surface. Most of the Ni component is located at the interface between the Pd core and PtNi shell. At the exterior of the PtNi shell, the Pt intensity is approximately 2.5 times that of Ni in the interior of the PtNi shell. This analysis demonstrates the formation of

a core (Pd)/shell (Pt<sub>3</sub>Ni(Pt-skin)) structure. To extend the diversity of the ZnUPD-Gal with the Ni<sub>u</sub> process, a three repeated PtNi layer covered Pd core ((PtNi)<sub>3</sub>/Pd<sub>20</sub>/C) was also prepared as a control example. The EDS line profile analysis of (PtNi)<sub>3</sub>/Pd<sub>20</sub>/C confirms that a Pd core/(PtNi)<sub>3</sub> shell structure was successfully obtained using this process (Fig. S2 and S3†).

The CVs of H<sub>2</sub>SO<sub>4aq</sub> were used to track different modified layers grown on the Pd surface. The typical CV of Pd<sub>20</sub>/C shows redox peaks corresponding to the formation and removal of Pd hydroxide (Pd(OH)<sub>x</sub>) (0.6–1.0 V vs. RHE) and H absorption (H<sub>ab</sub>)/desorption (0.3–0.0 V vs. RHE) (Fig. 3a). In comparison with the CV of pristine Pd<sub>20</sub>/C, the first modified layer, Ni<sub>u</sub>, on Pd<sub>20</sub>/C inhibits the formation of Pd(OH)<sub>x</sub> and H<sub>ab</sub>, causing the reduction of related redox charges on Ni<sub>u</sub>/Pd<sub>20</sub>/C. The following Pt atomic layers were grown in turn on the Ni<sub>u</sub> surface by ZnUPD-Gal. With the increase of the Pt layer, characteristic Pt redox

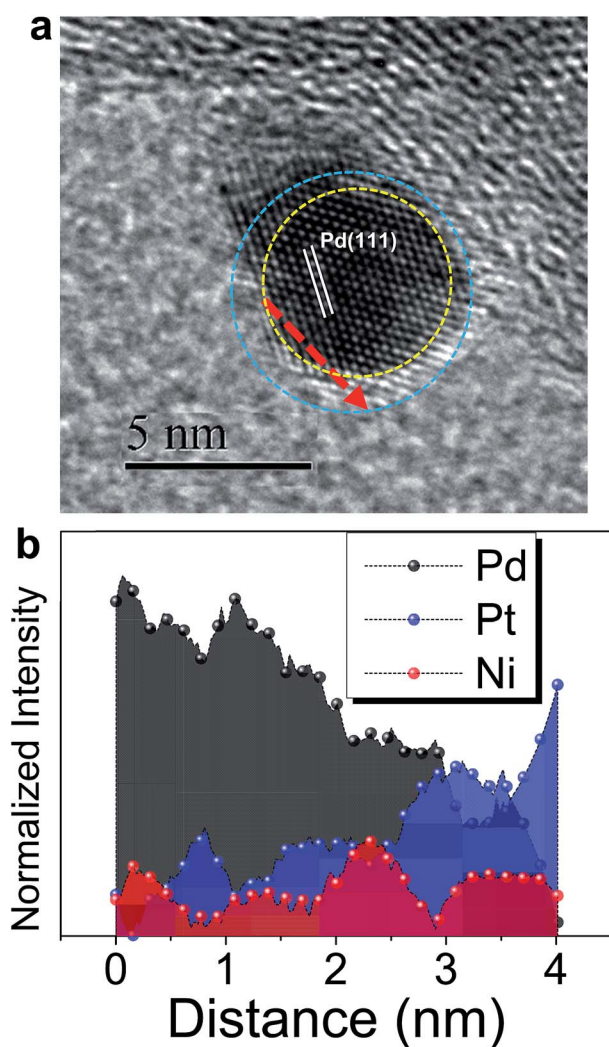


Fig. 2 (a) The representative HRTEM image of a core (Pd)/shell (Pt<sub>3</sub>-Ni(Pt-skin)) nanoparticle; (b) the corresponding EDS line-scan profile along the red dashed line as shown in (a).

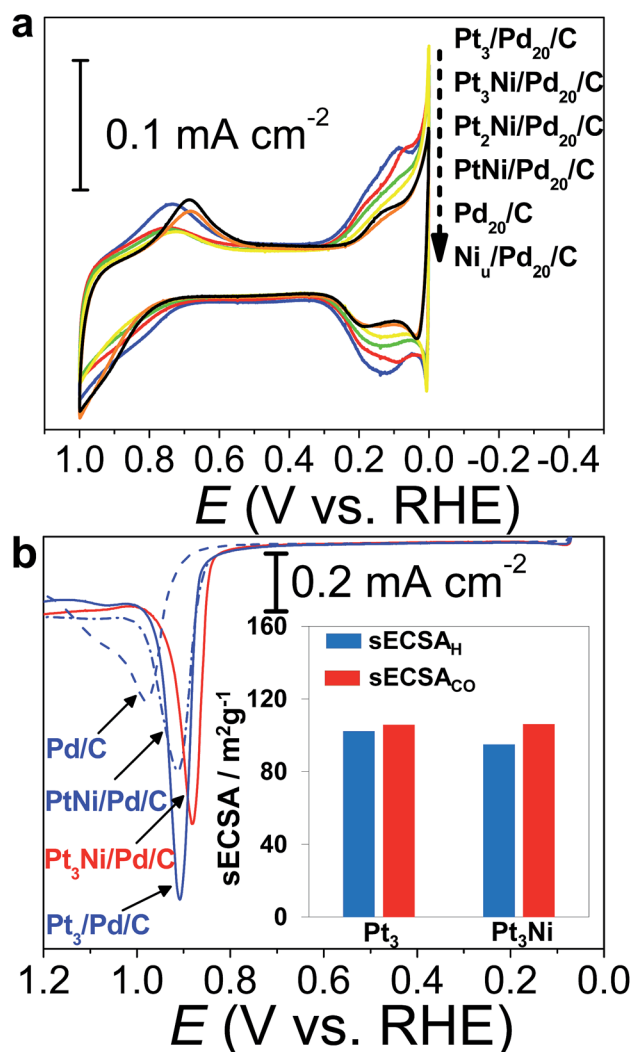


Fig. 3 Electrochemical surface characterization of electrocatalysts by using a GC electrode in 0.1 M H<sub>2</sub>SO<sub>4aq</sub>: (a) cyclic voltammograms of (blue) Pt<sub>3</sub>/Pd<sub>20</sub>/C, (red) Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C, (green) Pt<sub>2</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C, (yellow) PtNi(Pt-skin)/Pd<sub>20</sub>/C, (black) Pd<sub>20</sub>/C, and (orange) Ni<sub>u</sub>/Pd<sub>20</sub>/C; (b) CO stripping curves. The inset shows (blue) sECSA<sub>H</sub> and (red) sECSA<sub>CO</sub> for (Pt<sub>3</sub>) Pt<sub>3</sub>/Pd<sub>20</sub>/C and (Pt<sub>3</sub>Ni) Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C.





waves, including the formation of Pt hydroxide ( $\text{Pt}(\text{OH})_x$ ) occurred at a more negative potential ( $\sim 0.75$  V vs. RHE) and hydrogen adsorption ( $\text{H}_{\text{ad}}$ )/desorption waves gradually grew. For the purpose of comparison, three Pt layer-covered  $\text{Pd}_{20}/\text{C}@\text{GC}$  ( $\text{Pt}_3/\text{Pd}_{20}/\text{C}@\text{GC}$ ) without  $\text{Ni}_{\text{u}}$  was also prepared using UPD-Gal. This indicated that the surface of  $\text{Pt}_3/\text{Pd}_{20}/\text{C}$  was mainly composed of Pt, due to the similar CV features of  $\text{Pt}_3/\text{Pd}_{20}/\text{C}$  and  $\text{Pt}/\text{C}$ . In comparison to the CV features of  $\text{Pt}_3/\text{Pd}_{20}/\text{C}$ , those of  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$  based on the same Pt content showed that the onset potential of  $\text{H}_{\text{ad}}$  shifted towards a more negative potential and the formation of  $\text{Pt}(\text{OH})_x$  occurred at a more positive potential. This is a consequence of the electronically modified structure of Pt for “Pt skin” surfaces by the subsurface Ni atoms, which leads to weakened interactions between Pt and adsorbates such as  $\text{H}_{\text{ad}}$  and surface hydroxides ( $\text{OH}_{\text{ad}}$ ). This is also typical for the  $\text{Pt}_3\text{Ni}(\text{Pt-skin})$  structure.<sup>8,55</sup> The  $\text{H}_{\text{ad}}$  integrated charge is a conventional approach in the estimation of ECSA ( $\text{ECSA}_{\text{H}}$ ).<sup>56</sup> However, the suppression of  $\text{H}_{\text{ad}}$  on the  $\text{Pt}_3\text{Ni}(\text{Pt-skin})$  structure can substantially affect the accurate estimation of the real ECSA. The electro-oxidation of adsorbed carbon monoxide ( $\text{CO}_{\text{ad}}$ ), known as CO stripping, has been suggested as a complementary ECSA evaluation method ( $\text{ECSA}_{\text{CO}}$ ).<sup>55,57</sup> Fig. 3b shows the voltammetric curves of CO stripping obtained for pristine  $\text{Pd}_{20}/\text{C}$ ,  $\text{PtNi}/\text{Pd}_{20}/\text{C}$ , and  $\text{Pt}_3\text{-Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$ . The oxidation of the  $\text{CO}_{\text{ad}}$  takes place in a single peak whose peak potential shifts towards more negative values as the Pt content increases. The broad CO stripping peak for  $\text{Pd}_{20}/\text{C}$  becomes sharper with increasing Pt content in the  $\text{PtNi}$  shell.<sup>58</sup> These results suggest that the  $\text{PtNi}$  shell significantly weakens the interaction of Pd surface atoms with  $\text{CO}_{\text{ad}}$ . Interestingly, the onset of CO stripping on  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$  is more negatively shifted than on  $\text{Pt}_3/\text{Pd}/\text{C}$ , and the shape of the stripping peak is broader due to the weaker interaction of the Pt surface atoms with CO from the Ni sublayer. However, the similar charge of CO oxidation points to an equal coverage of CO. The specific ECSA ( $\text{sECSA} = \text{ECSA}/\text{metal loading}, \text{m}^2 \text{g}^{-1}$ ) for  $\text{Pt}_3\text{Ni}/\text{Pd}/\text{C}$  and  $\text{Pt}_3/\text{Pd}/\text{C}$  electrocatalysts was evaluated from  $\text{ECSA}_{\text{H}}$  ( $\text{sECSA}_{\text{H}}$ ) and  $\text{ECSA}_{\text{CO}}$  ( $\text{sECSA}_{\text{CO}}$ ), respectively (Fig. 3b). Although the suppression of  $\text{sECSA}_{\text{H}}$  on  $\text{Pt}_3\text{Ni}/\text{Pd}/\text{C}$  ( $95.1 \text{ m}^2 \text{g}^{-1}$ ) was observed in comparison with that of  $\text{Pt}_3/\text{Pd}/\text{C}$  ( $102.3 \text{ m}^2 \text{g}^{-1}$ ),  $\text{sECSA}_{\text{CO}}$  shows a similar value of  $\sim 106 \text{ m}^2 \text{g}^{-1}$  on both  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}/\text{C}$  and  $\text{Pt}_3/\text{Pd}/\text{C}$ .

The ORR polarization curves were obtained with  $\text{Pd}_{20}/\text{C}$ ,  $\text{Ni}/\text{Pd}_{20}/\text{C}$ ,  $\text{Pt}_3/\text{Pd}_{20}/\text{C}$ ,  $\text{PtNi}/\text{Pd}_{20}/\text{C}$  and  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$  electrocatalysts as thin films on the GC disc electrode of a RRDE in an  $\text{O}_2$ -saturated  $0.1 \text{ M HClO}_4$  solution at 1600 rpm (Fig. 4a). The Pt ring electrode of the RRDE was potentiostated at 1.1 V to collect the ring current ( $i_r$ ) related to the  $\text{H}_2\text{O}_2$  oxidation reaction. The polarization curves on the disc electrode displayed two distinguishable potential regions: well-defined diffusion limiting currents ( $i_D$ ) for the ORR below 0.7 V and a mixed kinetic-diffusion control region between 0.7 and 1.1 V. In both potential regions,  $i_r$  was a rather small fraction of  $i_D$  for all electrocatalysts, revealing that the ORR proceeds almost entirely through the  $4e^-$  reduction pathway. A quantitative presentation of the  $\text{H}_2\text{O}_2$  production (current efficiency,  $\chi_{\text{H}_2\text{O}_2}$ ) was given using eqn (1):<sup>20</sup>

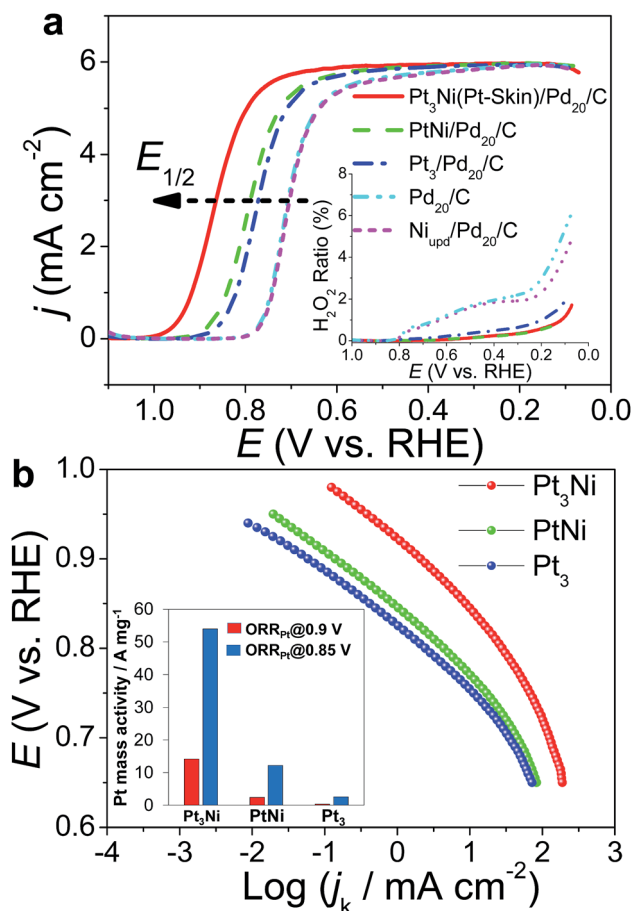


Fig. 4 (a) ORR polarization curves of  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$ ,  $\text{PtNi}/\text{Pd}_{20}/\text{C}$ ,  $\text{Pt}_3/\text{Pd}_{20}/\text{C}$ ,  $\text{Ni}_{\text{u}}/\text{Pd}_{20}/\text{C}$ , and commercial  $\text{Pd}_{20}/\text{C}$  catalysts recorded at room temperature in an  $\text{O}_2$ -saturated  $0.1 \text{ M HClO}_4$  aqueous solution with a scan rate of  $10 \text{ mV s}^{-1}$  and a rotation rate of 1600 rpm. Inset: the corresponding  $\text{H}_2\text{O}_2$  production current efficiency,  $\chi_{\text{H}_2\text{O}_2}$ , from ring current ( $i_r$ ) during the ORR, ring potential = 1.1 V, collection efficiency:  $N = 0.2$ . (b) The corresponding Tafel plots. Inset: (ORR@0.85 V and ORR@0.9 V) mass activities and (ORR<sub>Pt</sub>@0.85 V and ORR<sub>Pt</sub>@0.9 V) Pt mass activities for ( $\text{Pt}_3\text{Ni}$ )  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$ , ( $\text{PtNi}$ )  $\text{PtNi}/\text{Pd}_{20}/\text{C}$ , and ( $\text{Pt}_3$ )  $\text{Pt}_3/\text{Pd}_{20}/\text{C}$  measured at 0.85 V and 0.9 V.

$$\chi_{\text{H}_2\text{O}_2} = \frac{2i_r/N}{i_D + i_r/N} \quad (1)$$

where  $N$  is the collection efficiency of the RRDE. In the potential region of  $0.05 < E < 1$  V, similarly small amounts of  $\text{H}_2\text{O}_2$  were detected on the ring electrode from the  $\text{Pd}_{20}/\text{C}$  and  $\text{Ni}_{\text{u}}/\text{Pd}_{20}/\text{C}$  electrocatalysts, implying that Ni modification does not alter the reaction pathways. Pt-containing shells on the other three electrocatalysts ( $\text{Pt}_3/\text{Pd}_{20}/\text{C}$ ,  $\text{PtNi}/\text{Pd}_{20}/\text{C}$  and  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$ ) effectively inhibited the production of  $\text{H}_2\text{O}_2$  during the ORR, since there was no detectable  $\text{H}_2\text{O}_2$  on the ring electrode in the kinetically controlled potential region, implying that Pt atomic layers perfectly covered the outermost layer of Pt-containing shells. The half-wave potential of an ORR polarization curve,  $E_{1/2}$ , is often used to evaluate the electrocatalytic activity of a catalyst.  $E_{1/2}$  increased in the following sequence:  $\text{Pd}_{20}/\text{C} \sim \text{Ni}_{\text{u}}/\text{Pd}_{20}/\text{C} < \text{Pt}_3/\text{Pd}_{20}/\text{C} < \text{PtNi}/\text{Pd}_{20}/\text{C} \ll \text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$ .  $\text{Pt}_3\text{Ni}(\text{Pt-skin})/\text{Pd}_{20}/\text{C}$  showed a marked positive shift in  $E_{1/2}$  of 200 mV and 100 mV relative to  $\text{Pd}_{20}/\text{C}$  and

Pt<sub>3</sub>/Pd<sub>20</sub>/C, respectively. These data show that the Pt<sub>3</sub>Ni(Pt-skin) structure exhibits marked activity improvements over Pd<sub>20</sub>/C and Pt<sub>3</sub>/Pd<sub>20</sub>/C catalysts. Fig. 4b compares the Tafel plots for the specific activity ( $j_k$ ) towards the ORR obtained by normalizing the kinetic current ( $i_k$ ) to the ECSA<sub>CO</sub> for Pt<sub>3</sub>/Pd<sub>20</sub>/C, PtNi/Pd<sub>20</sub>/C and Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C, at 1600 rpm in the cathodic sweep direction.  $i_k$  was obtained from the measured currents, corrected for mass transport according to eqn (2).<sup>59–61</sup>

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_D} \quad (2)$$

Two Tafel slopes of Pt<sub>3</sub>/Pd<sub>20</sub>/C,  $-60/-119$  mV dec<sup>-1</sup>, were similar to those observed on conventional Pt/C. The values of the Tafel slopes of Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C,  $-70/-122$  mV dec<sup>-1</sup>, showed a slight difference from those of Pt<sub>3</sub>/Pd<sub>20</sub>/C, probably owing to a different state and coverage of Pt(OH)<sub>x</sub> after the insertion of the Ni sublayer. When comparing  $j_k$  for different electrocatalysts at 0.9 V, the specific activity of Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C was 2.34 mA cm<sup>-2</sup>, which is much higher than those of Pt<sub>3</sub>/Pd<sub>20</sub>/C ( $\sim 0.06$  mA cm<sup>-2</sup>) and PtNi/Pd<sub>20</sub>/C ( $\sim 0.16$  mA cm<sup>-2</sup>). Considering the ECSA<sub>CO</sub> contribution from Pt (ECSA<sub>CO</sub>(Pt) = sECSA<sub>CO</sub>  $\times$  the mass of Pt ( $\sim 2.97$   $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>)), Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C shows a very high specific activity  $j_k$  of Pt ( $j_{kPt}$ ) 16.7 mA cm<sup>-2</sup> at 0.9 V, which is 90-fold enhancement over commercial Pt/C catalysts (0.185 mA cm<sup>-2</sup>, Pt loading = 24  $\mu$ g cm<sup>-2</sup>) and even higher than the possibly highest record, 10.3 mA cm<sup>-2</sup>, for octahedral Mo–Pt<sub>3</sub>Ni/C (the particle shape is close to spherical)<sup>62</sup> and 11.5 mA cm<sup>-2</sup>, for jagged Pt nanowires from de-alloying PtNi nanowires with a totally different microstructure.<sup>31</sup> The Pt content was obtained by measuring the charge associated with Zn<sub>u</sub> (after correcting for the double layer charging) on Pd<sub>20</sub>/C and assuming that there was a one-to-one ratio between the UPD adlayer and the Pt atoms. The total amount of Pt on Pt<sub>3</sub>/Pd<sub>20</sub>/C and Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C ( $\sim 2.97$   $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>) was much less than that on the commercial Pt/C ( $\sim 24$   $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>). This finding highlights the advantages of ultra-thin layer electrocatalysts, which contribute to not only the reduction of Pt content but also the enhancement of catalytic activity thanks to their high Pt utilization.<sup>39,40</sup> The Pt mass activities ( $i_{mPt}$ ) at 0.9 and 0.85 V were calculated based on the ORR polarization curves and the amount of Pt on the electrodes. The Pt<sub>3</sub>Ni(Pt-skin) structure retained the advantages of the ultra-thin layer structure and the synergetic effect of the Ni sublayer presented an ultra-high  $i_{mPt}$  of 14.2 A mg<sub>Pt</sub><sup>-1</sup> based on Pt loading (2.97  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>) at 0.9 V. The  $i_{mPt}$  of the Pt<sub>3</sub>Ni(Pt-

skin)/Pd<sub>20</sub>/C catalyst achieved a 37- and 156-fold improvement over Pt<sub>3</sub>/Pd<sub>20</sub>/C (0.381 A mg<sub>Pt</sub><sup>-1</sup>,  $\sim 2.97$   $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>) and commercial Pt/C catalysts (0.091 A mg<sub>Pt</sub><sup>-1</sup>,  $\sim 24$   $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>), respectively. The  $i_{mPt}$  is more than an order of magnitude greater than the U.S. Department of Energy's 2017 goal (0.44 A mg<sub>Pt</sub><sup>-1</sup>). The  $i_{mPt}$  of Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C is even higher than those of the state-of-the-art Pt–Ni catalysts, including the recently reported PtNi nanoframe catalysts (5.7 A mg<sub>Pt</sub><sup>-1</sup>),<sup>28</sup> Mo–Pt<sub>3</sub>Ni/C (6.98 A mg<sub>Pt</sub><sup>-1</sup>, Pt loading = 4.08  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>)<sup>62</sup> and jagged Pt nanowires (13.6 A mg<sub>Pt</sub><sup>-1</sup>, Pt loading = 2.2  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup>) (Table 1).<sup>31</sup> Two accelerated durability test (ADT) modes further examined the Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C lifetime (Fig. 5).

One was a commonly used test mode (ADT<sub>s</sub>) which applied a linear potential sweep from 0.6 to 1.0 V vs. RHE at a scan rate of 50 mV s<sup>-1</sup> for 20 000 cycles in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>. Recently, another ADT mode (ADT<sub>on-off</sub>), start-up/shut-down cycles, has gradually received attention.<sup>63,64</sup> The ADT<sub>on-off</sub> performed a linear potential sweep from 1.0 to 1.5 V vs. RHE for 20 000 cycles at a scan rate of 500 mV s<sup>-1</sup> in an O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>. After ADT<sub>s</sub>, Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C retained its ECSA and high activity (Fig. 5a and c), exhibiting only an  $\sim 2$  mV shift for its  $E_{1/2}$ . This result is also consistent with the pioneering work by Adzic's group in which the modification of Pt<sub>nano</sub> surfaces with Au clusters through UPD-Gal improved the stability of catalysts.<sup>7</sup> Our previous studies also demonstrated that nonspecific noble metal cluster (Pt, Pd or Au) modification through UPD-Gal enhanced the interaction between Pt<sub>nano</sub> and the carbon support to improve catalyst durability during ADT<sub>s</sub>.<sup>11</sup> Interestingly, Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C shows the highest durability during ADT<sub>on-off</sub> (Fig. 5b and d). In the ADT<sub>on-off</sub>, Pt dissolution and Ni leaching were serious issues for typical Pt/C or PtNi catalysts owing to their operation at a higher anodic potential. The superior stability of Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C during the ADT<sub>on-off</sub> may be a result of the perfect Pt<sub>3</sub>Ni(Pt-skin) structure. The Pt-skin located on the exterior of the PtNi shell effectively inhibits the dissolution of the Pd core and interior Ni sublayer leaching. The issue of Pt dissolution may have been improved due to the enlargement of the particle sizes of Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>nano</sub> in comparison with pristine Pd<sub>nano</sub> (from  $\sim 5$  nm to  $\sim 6.8$  nm). It has previously been demonstrated that the Pt dissolution is significantly dependent on particle size and environmental acidity.<sup>65</sup> A larger particle size ( $>5$  nm) could both reduce the trend of Pt dissolution and its activity. However, the ultra-thin layer Pt<sub>3</sub>Ni(Pt-skin) modification not only stabilizes Pt from particle size enlargement but also significantly

**Table 1** Performance of the Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C catalyst and some representative results with high performance from recent published studies<sup>a</sup>

Catalysts	Pt loading ( $\mu$ g cm <sup>-2</sup> )	sECSA <sub>CO</sub> (m <sup>2</sup> g <sup>-1</sup> )	$j_{kPt}$ (mA cm <sup>-2</sup> )	$i_{mPt}$ (A mg <sub>Pt</sub> <sup>-1</sup> )	
Pt <sub>3</sub> Ni(Pt-skin)/Pd <sub>20</sub> /C	2.97	106	16.7	14.2	This work
Mo–Pt <sub>3</sub> Ni/C	4.08	83.9	8.2	6.98	Ref. 62
Pt <sub>3</sub> Ni/C nanoframes	N/A	N/A	1.48	5.7	Ref. 28
Jagged Pt nanowires	2.2	118	11.5	13.6	Ref. 31
Commercial Pt/C	24	91	0.185	0.091	This work

<sup>a</sup> N/A: not available.



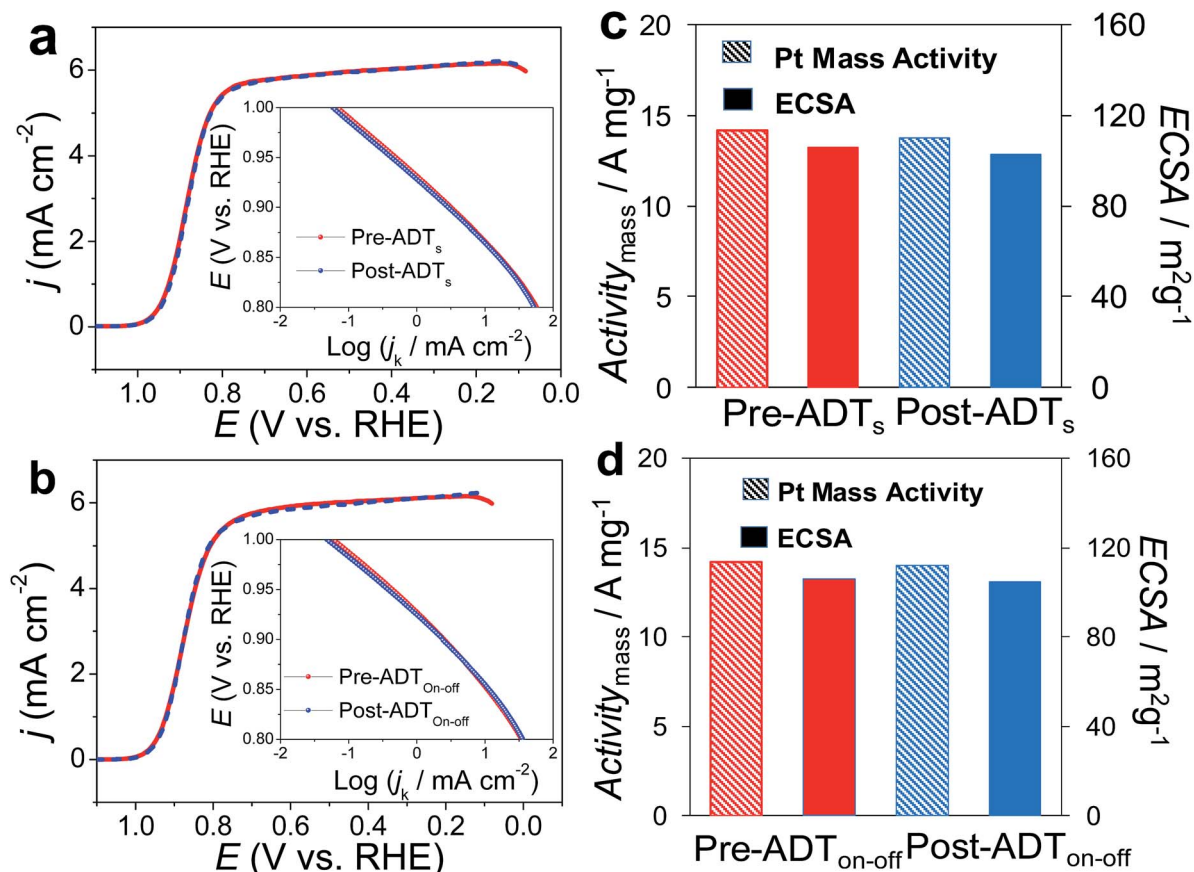


Fig. 5 ORR polarization curves of the Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C catalyst on a GC RDE (0.196 cm<sup>2</sup>, ~2.97 μg cm<sup>-2</sup> Pt loading) (dashed line) before and (solid line) after accelerated durability tests include (a) ADT<sub>s</sub>: a linear potential polarization from 0.6 to 1.0 V vs. RHE at a scan rate of 50 mV s<sup>-1</sup> for 20 000 cycles and (b) ADT<sub>on-off</sub>: a linear potential polarization from 1.0 to 1.5 V vs. RHE for 20 000 cycles at a scan rate of 500 mV s<sup>-1</sup> in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>. Insets: the corresponding Tafel plots. (c) and (d) (solid pattern) sECSA<sub>CO</sub>, and (slash pattern) Pt mass activities for (blue) before and (red) after accelerated durability tests.

enhances catalytic activity owing to the full exposure of Pt active sites on the surface of Pd/C.

## Conclusions

In conclusion, considering that the Pt<sub>3</sub>Ni(Pt-skin) structure exhibited the highest catalytic activity ever recorded, in this work, the challenge of preparing a nanocatalyst mimicking the Pt<sub>3</sub>Ni(Pt-skin) structure was mitigated by growing a Ni<sub>u</sub> covered Pd<sub>nano</sub> core using the ZnUPD-Gal procedure. ZnUPD-Gal is an improvement to common CuUPD-Gal that offers more options of coating surfaces and facilitates more metal growth in the Gal process owing to the intrinsic lower  $\Phi_{Zn}$  and more negative  $E^0$  (Zn<sup>2+</sup>/Zn). The Pt<sub>3</sub>Ni(Pt-skin) thin layer with ultra-low Pt loading presents not only a breakthrough in Pt specific activity and Pt mass activity, both of which were superior to those of state-of-the-art Pt-Ni catalysts, but also in high durability owing to the perfect Pt<sub>3</sub>Ni(Pt-skin) construction.

## Experimental

### Chemicals

Carbon-supported palladium (Pd<sub>20</sub>/C) (20 wt% Pd on XC-72 Valcan carbon (E-TEK)), Pt<sub>20</sub>/C (20 wt% Pt on XC-72 Valcan

carbon (E-TEK)), 70% HClO<sub>4</sub> (JT-Baker), 95–98% H<sub>2</sub>SO<sub>4</sub> (Aldrich), 98% NiSO<sub>4</sub>·6H<sub>2</sub>O (Aldrich), 98% Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (Aldrich), 99.7% Cu(NO<sub>3</sub>)<sub>2</sub> (JT-Baker), 99.9% K<sub>2</sub>PtCl<sub>4</sub> (Alfa), and 5% Nafion (NF) perfluorinated resin in a mixture of lower aliphatic alcohols and water (Aldrich) were used as received.

### Electrochemical experiments

The electrochemical experiments were conducted using a CHI 760C potentiostat/galvanostat and a three-electrode electrochemical cell. To prevent Cl<sup>-</sup> interference from the typical Ag/AgCl reference electrode, Hg/HgSO<sub>4</sub> (0.5 M H<sub>2</sub>SO<sub>4</sub>) was used as the reference electrode and Pt wire was used as the counter electrode. The potentials were measured against the reference electrode and converted to the reversible hydrogen electrode (RHE) reference scale by  $E_{RHE} = E_{Hg/HgSO_4} + 0.68 + 0.059pH_{electrolyte}$ . All potentials in this paper were stated with reference to the RHE. A glassy carbon (GC) electrode (Pine, 5.0 mm diameter, 0.196 cm<sup>2</sup> for the fabrication of electrocatalysts or the examination of electrocatalyst performance for the ORR) served as the substrate electrode for the Pd<sub>20</sub>/C electrocatalyst suspension. The Pd<sub>20</sub>/C catalyst suspension was prepared by mixing 10 mg of commercial Pd<sub>20</sub>/C electrocatalyst powder in 5 mL of deionized water (with specific resistivity =





18.2 M $\Omega$  cm), followed by the gradual addition of 1 ml of isopropyl alcohol and 20 min of ultrasonication to obtain a Pd<sub>20</sub>/C suspension. The Pd<sub>20</sub>/C@GC electrode was fabricated using a drop coating procedure. Briefly, a GC electrode was polished successively with 1.0, 0.3, and 0.05  $\mu$ m alumina powder cloth (Buchler) followed by sonication in deionized water and drying prior to use. 2–7  $\mu$ l of the Pd<sub>20</sub>/C suspension was pipetted onto the surface of the GC electrode as a circle with a geometric area of 0.01–0.05 cm<sup>2</sup>. Pd<sub>20</sub>/C@GC was obtained after drying under an Ar flow at room temperature ( $\sim$ 28  $^{\circ}$ C) for solvent evaporation.

#### Preparation of Ni<sub>u</sub>/Pd<sub>20</sub>/C, PtNi/Pd<sub>20</sub>/C, Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C, Pt<sub>3</sub>/Pd<sub>20</sub>/C, and (PtNi)<sub>3</sub>/Pd<sub>20</sub>/C electrocatalysts

Pd<sub>20</sub>/C@GCE was used as a working electrode to prepare relative catalysts. The microstructure of the post-modified Pd<sub>20</sub>/C electrocatalysts was examined by the electrochemical characterization and image analysis. High-resolution transmission electron microscopy (TEM) images (HRTEM) and elemental composition micro-distribution of post-modified Pd<sub>20</sub>/C electrocatalysts were obtained using a JEOL JEM-2100F field emission TEM (FE-TEM) equipped with an energy dispersive X-ray spectrometer (EDS).

**Preparation of Ni<sub>u</sub>/Pd<sub>20</sub>/C.** The Ni underpotential deposition (Ni<sub>u</sub>) covered Pd<sub>20</sub>/C@GC (Ni<sub>u</sub>/Pd<sub>20</sub>/C@GC) electrocatalyst was prepared by direct electrodeposition of Ni<sub>u</sub> on the Pd surface of the Pd<sub>20</sub>/C@GC electrode from a 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (Na<sub>2</sub>SO<sub>4aq</sub>) containing 20 mM NiSO<sub>4</sub>. The potential was stopped at  $-0.1$  V vs. RHE for 20 min to allow the Ni<sub>u</sub> to completely cover the entire Pd surface. All operations were carried out in a three-electrode electrochemical cell under an Ar atmosphere.

**Preparation of PtNi/Pd<sub>20</sub>/C.** The Pt atomic layer was prepared by ZnUPD-Gal on the Ni surface of the as-prepared Ni<sub>u</sub>/Pd<sub>20</sub>/C@GC from 0.5 M Na<sub>2</sub>SO<sub>4aq</sub> containing 20 mM Zn(ClO<sub>4</sub>)<sub>2</sub>. The potential was stopped at 0.05 V vs. RHE for 10 min to allow the Zn<sub>u</sub> to completely cover the whole surface of the Ni surface. All of these operations were carried out in a three-electrode electrochemical cell under an Ar atmosphere. The as-prepared Zn<sub>u</sub> modified Ni<sub>u</sub>/Pd<sub>20</sub>/C@GC was rinsed with deionized water and immersed in a 0.2 M H<sub>2</sub>SO<sub>4</sub> solution containing 1.0 mM K<sub>2</sub>PtCl<sub>4</sub> for about 5 min to displace the Zn<sub>u</sub> with Pt and to obtain Pt atomic layer modified Ni<sub>u</sub>/Pd<sub>20</sub>/C@GC (PtNi/Pd<sub>20</sub>/C@GC).

**Preparation of Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C.** The repetitive ZnUPD-Gal process was continually used to introduce the second and the third Pt atomic layers onto the as-prepared PtNi/Pd<sub>20</sub>/C@GC to obtain Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C@GC.

**Preparation of Pt<sub>3</sub>/Pd<sub>20</sub>/C.** The repetitive ZnUPD-Gal process continually introduced three Pt atomic layers on Pd<sub>20</sub>/C@GC to obtain Pt<sub>3</sub>/Pd<sub>20</sub>/C@GC.

**Preparation of (PtNi)<sub>3</sub>/Pd<sub>20</sub>/C.** To extend the diversity of the ZnUPD-Gal on Ni<sub>u</sub>, a Pt atomic layer and Ni<sub>u</sub> repetitively overlapped shell, which was three repeated PtNi layers on a Pd core ((PtNi)<sub>3</sub>/Pd<sub>20</sub>/C), was prepared as a control example. Ni<sub>u</sub> was electrodeposited on the Pt surface of the as-prepared PtNi/Pd<sub>20</sub>/C@GC from 0.5 M Na<sub>2</sub>SO<sub>4aq</sub> containing 20 mM NiSO<sub>4</sub> (Ni<sub>u</sub>/PtNi/Pd<sub>20</sub>/C@GC) at a controlled potential of  $-0.05$  V vs. RHE for

20 min to allow the Ni<sub>u</sub> to completely cover the whole surface of the Pt surface. The Zn<sub>u</sub> was electrodeposited on the as-prepared Ni<sub>u</sub>/PtNi/Pd<sub>20</sub>/C@GC from 0.5 M Na<sub>2</sub>SO<sub>4aq</sub> containing 20 mM Zn(ClO<sub>4</sub>)<sub>2</sub>, while controlling the potential at 0.05 V vs. RHE for 10 min. Subsequently, the Zn<sub>u</sub> was replaced by more noble Pt in the Gal process, leading to Pt atomic layer covered Ni<sub>u</sub>/PtNi/Pd<sub>20</sub>/C@GC ((PtNi)<sub>2</sub>/Pd<sub>20</sub>/C@GC). The ZnUPD-Gal on Ni<sub>u</sub> was used to introduce the third PtNi layer on (PtNi)<sub>2</sub>/Pd<sub>20</sub>/C@GC and obtain (PtNi)<sub>3</sub>/Pd<sub>20</sub>/C@GC.

#### Electrochemical characterization of the ORR

A commercial (Pine Instruments) rotating ring-disk electrode (RRDE) was used with a Pt ring and an interchangeable disk. The disk electrode was a GC rod modified by a thin layer of as-prepared electrocatalyst covered by a Nafion polymer thin film used as the working electrode for ORR measurements. The as-prepared working electrode was electrochemically cleaned using a cycling potential between 0.0 and 1.0 V (vs. RHE) 10 times in Ar-purged 0.1 M H<sub>2</sub>SO<sub>4</sub>, except for Ni<sub>u</sub>/Pd<sub>20</sub>/C owing to Ni<sub>u</sub> leaching. The electrochemical surface areas (ECSA) of the electrocatalysts were determined by measuring the areas (charges) under the hydrogen adsorption peaks (H<sub>ad</sub>) (ECSA<sub>H</sub>) and the electro-oxidation of adsorbed carbon monoxide (CO<sub>ad</sub>), otherwise known as CO stripping (ECSA<sub>CO</sub>), respectively, in the cyclic voltammograms. A conversion factor of 0.21 mC cm<sup>-2</sup> was used to determine ECSA<sub>H</sub>. For CO stripping experiments, CO was adsorbed onto the pre-cleaned electrode by holding the potential at 0.05 V for 10 min in CO saturated 0.1 M HClO<sub>4</sub> solution. The CO stripping curve was taken after purging with Ar for 30 min. A conversion factor of 0.42 mC cm<sup>-2</sup> was used to determine ECSA<sub>CO</sub>. The specific ECSA values (sECSA = ECSA/metal loading, m<sup>2</sup> g<sup>-1</sup>) of the electrocatalysts were evaluated from ECSA<sub>H</sub> (sECSA<sub>H</sub>) and ECSA<sub>CO</sub> (sECSA<sub>CO</sub>). When considering the ECSA<sub>CO</sub> contribution from Pt (ECSA<sub>CO(Pt)</sub> = sECSA<sub>CO</sub>  $\times$  the mass of Pt ( $\sim$ 2.97  $\mu$ g<sub>Pt</sub> cm<sup>-2</sup> for Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C and Pt<sub>3</sub>/Pd<sub>20</sub>/C)), the Pt content was obtained by measuring the charge associated with Zn<sub>u</sub> (after correcting for the double layer charging) on Pd<sub>20</sub>/C and assuming that there was a one-to-one ratio between the UPD adlayer and Pt atoms. ORR experiments were performed in oxygen-saturated 0.1 M HClO<sub>4</sub> aqueous solution. The solution was purged for at least 30 min to ensure oxygen saturation. The ORR electrochemical experiments were conducted in a three-electrode electrochemical cell. Hg/HgSO<sub>4</sub> (0.5 M H<sub>2</sub>SO<sub>4</sub>) and a Pt wire were used as the reference and counter electrodes, respectively; however, all potentials are quoted with respect to a RHE. The scan rate was 0.01 V s<sup>-1</sup>. A Pine Model AFMSR electrode rotator controlled the electrode rotation for the ORR electrochemical experiments. During measurement of the polarization curves for the ORR on the disk electrode, the Pt ring electrode was potentiostated at 1.1 V vs. RHE, a potential where the peroxide oxidation reaction is under pure diffusion control; the collection efficiency, N, for the ring-disk assembly was  $\sim$ 0.2.

#### Accelerated durability test (ADT, linear potential scanning)

The durability of the Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C catalyst was investigated in two ADT modes. In the ambient temperature potential



polarization, Pt<sub>3</sub>Ni(Pt-skin)/Pd<sub>20</sub>/C@GC was used as the working electrode.

**Accelerated durability tests related to catalyst lifetime (ADT<sub>s</sub>).** The ADTs were conducted by linear potential sweeping from 0.6 to 1.0 V vs. RHE at a scan rate of 50 mV s<sup>-1</sup> for 20 000 cycles in an O<sub>2</sub>-saturated 0.1 M HClO<sub>4aq</sub> at room temperature.

**Accelerated durability test related start-up/shut-down cycles (ADT<sub>on-off</sub>).** The ADT<sub>on-off</sub> was conducted by linear potential sweeping from 1.0 to 1.5 V vs. RHE for 20 000 cycles at a scan rate of 500 mV s<sup>-1</sup> in O<sub>2</sub>-saturated 0.1 M HClO<sub>4aq</sub> at room temperature.

## Conflicts of interest

There are no conflicts to declare.

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