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## Sophisticated Construction of Binary PdPb Alloy Nanocubes as Robust Electrocatalysts toward Ethylene Glycol and Glycerol Oxidation

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*ACS Appl. Mater. Interfaces*, **Just Accepted Manuscript** • DOI: 10.1021/acsami.8b00532 • Publication Date (Web): 28 Mar 2018

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4 **Sophisticated Construction of Binary PdPb Alloy Nanocubes as**  
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6 **Robust Electrocatalysts toward Ethylene Glycol and Glycerol**  
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8 **Oxidation**  
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34  
35 **ABSTRACT**  
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38 The design of nanocatalysts by controlling pore size and particle characteristics is  
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40 crucial to enhance the selectivity and activity of the catalysis. Thus, we have  
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42 successfully demonstrated the synthesis of binary PdPb alloy nanocubes (PdPb NCs)  
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44 by controlling pore size and particle characteristics. In addition, the as-obtained  
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46 binary PdPb NCs exhibited superior electrocatalytic activity of 4.06 A mg<sup>-1</sup> and 16.8  
47  
48 mA cm<sup>-2</sup> towards ethylene glycol oxidation reaction (EGOR) and 2.22 A mg<sup>-1</sup> and 9.2  
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50 mA cm<sup>-2</sup> towards glycerol oxidation reaction (GOR) when compared to the  
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52 commercial Pd/C. These astonishing characteristics are attributed to the attractive  
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3 nanocube structures as well as the large number of exposed active areas. Furthermore,  
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5 the bifunctional effects originated from Pd and Pb interactions help to display high  
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7 endurance with less activity decay after 500 cycles, showing a great potential in fuel  
8  
9 cells applications.  
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13 **KEYWORDS:** Binary PdPb nanocubes; Catalysts; Fuel cells; High performance;  
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15 Electrooxidation  
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## 17 18 **1. INTRODUCTION** 19

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21 Currently, fuel cells have attracted lots of interest due to their wide application  
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23 prospect in our daily lives.<sup>1-2</sup> Ethylene glycol and glycerol, due to their high boiling  
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25 point, low toxicity, and less obvious crossover, have attracted considerable attention  
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27 for serving as potentially alternative fuels.<sup>3-6</sup> In the research of highly-active  
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29 electrocatalysts towards liquid fuels, noble metal platinum has been regarded as the  
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31 significant and commonly used material, due to its high activity.<sup>7-8</sup> Nevertheless, there  
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33 are some disadvantages associated with Pt such as: high cost, low durability and scare  
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35 natural abundance, which have seriously limited its large-scale production.<sup>9-10</sup> To  
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37 break this bottleneck, tremendous efforts have been focused on developing an  
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39 appropriate substitute for Pt catalysts.<sup>11-13</sup>  
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46 Recently, well-defined Pd nanocrystals have been of vital significance for  
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48 applications in sensing, hydrogen storage and especially in fuel cells due to its high  
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50 activity and great tolerance to some CO-like intermediate species in the alkaline  
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52 media.<sup>14-18</sup> Regardless of these favorable terms, there are still some problems related  
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54 to the Pd nanocrystals such as particle aggregation and poor durability, all of which  
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3 greatly impede the commercial development of fuel cells technologies.<sup>19-21</sup> Therefore,  
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5 considerable attentions have been focused on designing Pd or Pd-based catalysts with  
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7 improved electrocatalytic performances.<sup>22</sup> The most promising strategy is to alloy Pd  
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9 with a second transition metal, for which can not only gain a higher utilization of Pd,  
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11 but also lift the electrocatalytic performances of Pd to a higher level through the  
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13 bifunctional, electronic or surface effects.<sup>23-24</sup> Among them, alloying Pd with Pb has  
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15 been demonstrated to show excellent electrocatalytic performances due to the  
16  
17 geometric, and electronic effect, as well as the bifunctional mechanism.<sup>25-26</sup> Besides,  
18  
19 the incorporation of Pb into Pd could also offer high resistance to toxic CO-like  
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21 species by weakening the bond energy of Pd-CO or by enhancing the electrooxidation  
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23 of CO-like species.<sup>27-28</sup>  
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30 Along with this strategy, morphology control has also been demonstrated to be  
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32 an advanced approach for modifying the catalytic properties of Pd nanocrystals,  
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34 therefore, enhancing the electrocatalytic performances. Up-to-date, significant  
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36 advances have been achieved in the fabrication of Pd-based nanocrystals with  
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38 fascinating morphologies. A lot of Pd-based nanocatalysts with unique shapes have  
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40 been engineered such as nanowires,<sup>29-30</sup> nanoflowers,<sup>31-32</sup> and nanoframes<sup>33-35</sup>.  
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42 Among others, the binary nanocubes with rough surface in particular, have been  
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44 proved to expose more active areas,<sup>36-37</sup> which promote the electron mobility and  
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46 efficient mass transfer of liquid fuel.<sup>38</sup> In this regard, if we can integrate the  
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48 morphology and composition superiorities to fulfill the design of Pd-based  
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50 nanocatalysts over size and morphology, it would greatly boost the commercial  
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development of fuel cells.<sup>39-40</sup>

Herein, we have developed for the first time an advanced method for the synthesis of binary Pd<sub>2</sub>Pb alloy NCs. The key parameter for synthesizing such fascinating Pd<sub>2</sub>Pb NCs structures is the successful introduction of hexadecyltrimethylammonium bromide (CTAB) in the reaction system. In addition, the Pd<sub>2</sub>Pb NCs structures presented unique characteristics such as: highly-dispersed properties as well as synergistic effect. Furthermore, the resulted Pd<sub>2</sub>Pb NCs exhibited greatly enhanced electrocatalytic activities of 4.06 A mg<sup>-1</sup> and 16.8 mA cm<sup>-2</sup>, 2.22 A mg<sup>-1</sup> and 9.2 mA cm<sup>-2</sup> towards EGOR and GOR when compared to Pd/C. Finally, the 500 cycles CV have also demonstrated its superior durability with negligible decay.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials and reagents

Palladium (II) acetylacetonate (Pd(acac)<sub>2</sub>, reagent grade, 99.0%) and oleylamine (OAm) were all purchased from Sigma-Aldrich. Lead (II) acetate (PbAc<sub>2</sub>, analytical reagent, 99.5%), lead (II) chloride (PbCl<sub>2</sub>, analytical reagent, 99%), CTAB (CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>N(Br)(CH<sub>3</sub>)<sub>3</sub>, analytical reagent, 99.0%), and tetra-n-butylammonium bromide (TBAB, analytical reagent, 99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Cetyltrimethylammonium chloride (CTAC, reagent grade, 97%) was purchased from Alfa Aesar (Shanghai, China).

### 2.2 Preparation of PdPb nanocubes (PdPb NCs)

Experimentally, OAm (5 mL), Pd(acac)<sub>2</sub> (7.6mg), PbAc<sub>2</sub> (2.4 mg), and CTAB (36 mg) were added into a vial. After sonicating for 2 h, the glass vial was then transferred

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3 to the oil bath and heated to 160 °C in 30 min and kept reacting at 160 °C for another  
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6 5 h. The syntheses of Pd<sub>3</sub>Pb NCs and Pd<sub>4</sub>Pb NCs could also be prepared *via* changing  
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8 the amounts of PbAc<sub>2</sub> to 3.2 mg and 4.8 mg, respectively while keeping other reaction  
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10 conditions the same.

### 13 **2.3 Characterizations**

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16 The morphologies and structures of the PdPb NCs were firstly characterized by a  
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18 HITACHIHT7700 transmission electron microscope. The FEITecnai F20 transmission  
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20 electron microscope was also employed to record the high-angle annular dark field  
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22 scanning transmission electron microscopy (HAADF-STEM), high-resolution TEM  
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24 (HR-TEM), and energy-dispersive X-ray spectroscopy (EDS) mapping images. A  
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26 Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer using 300 W  
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28 Al K $\alpha$  radiation was used to recorded the X-ray photoelectron spectroscopy (XPS).  
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30 The powder X-ray diffraction (PXRD) patterns were obtained by using X'Pert-Pro  
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32 MPD diffractometer (Netherlands PANalytical) with a Cu K $\alpha$  X-ray source ( $\lambda =$   
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34 1.540598 Å).

### 40 **2.3 Electrochemical measurements**

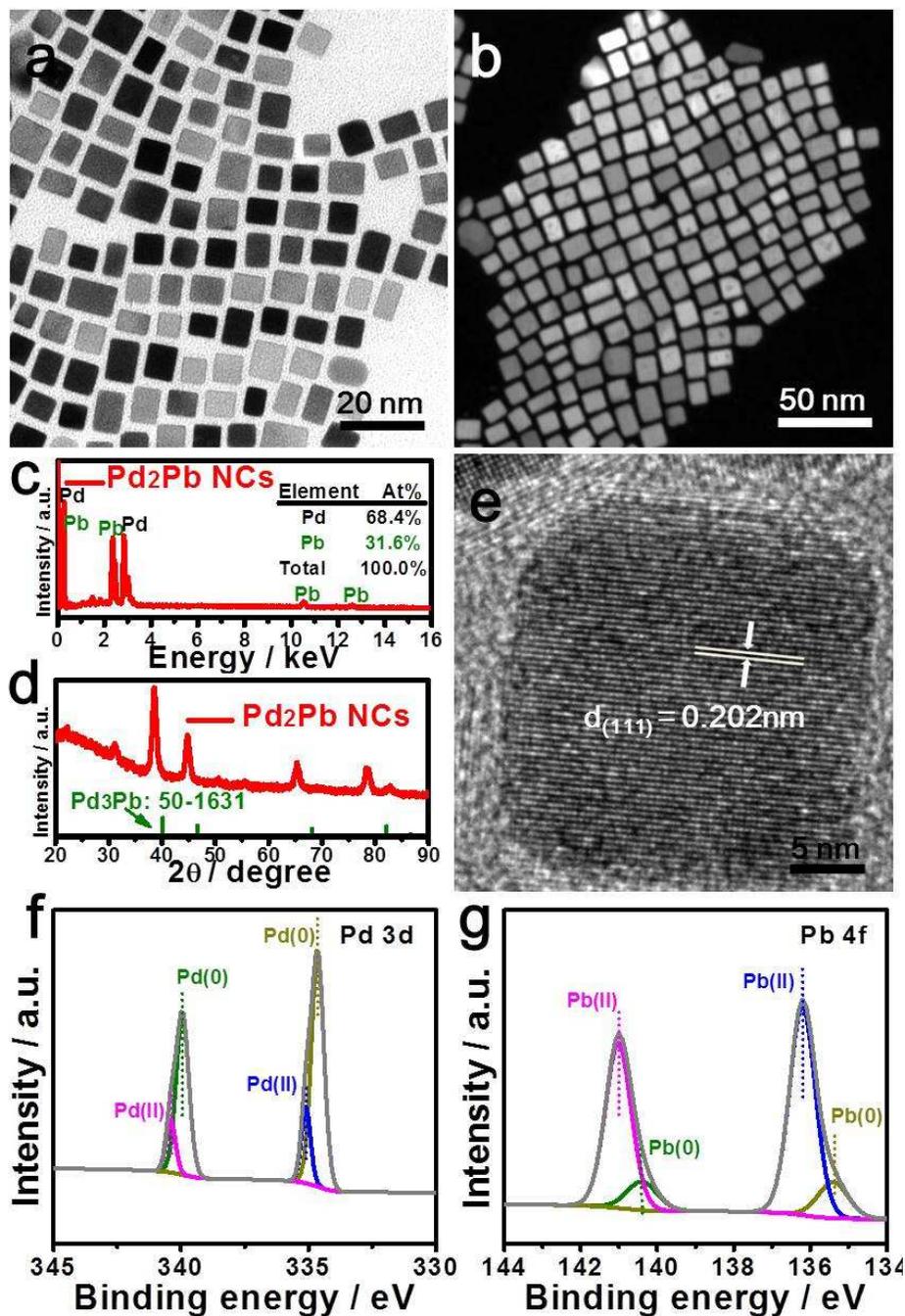
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43 A standard three-electrode system was employed to perform all the  
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45 electrochemical measurements. The electrochemical active surface area (ECSA) was  
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47 related to the surface active sites,<sup>1</sup> Therefore the ECSA can be calculated from the  
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49 coulombic charge for the reduction of palladium oxide using the following equation:  
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51  $ECSA = Q / 0.405 \times Pd_m$ .<sup>41</sup> EGOR was conducted in 1 M KOH + 1 M EG solution and  
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53 GOR in 1 M KOH + 1 M glycerol solution. The durability was evaluated by  
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3 performing the CV for 500 cycles at the sweep rate of  $50 \text{ mV s}^{-1}$ . For comparison, the  
4 commercial Pd/C was used as the reference catalyst.  
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### 8 **3. RESULTS AND DISCUSSION**

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10 A simple wet-chemical method has been employed to create a novel class of PdPb  
11 NCs with tunable compositions. The morphological and structural features of Pd<sub>2</sub>Pb  
12 NCs were firstly investigated employing a TEM. The typical TEM images (Figure 1a)  
13 and HAADF-STEM images (Figure 1b) showed that the as-obtained nanocubes are  
14 uniform with a high yield approaching 100%. Through statistics on the size of 50  
15 particles, it was found that the resulted Pd<sub>2</sub>Pb NCs followed a narrow size distribution  
16 with a mean diameter around 10.2 nm (Figure S1). SEM-EDS has been employed also  
17 to confirm the structural compositions and morphologies.  
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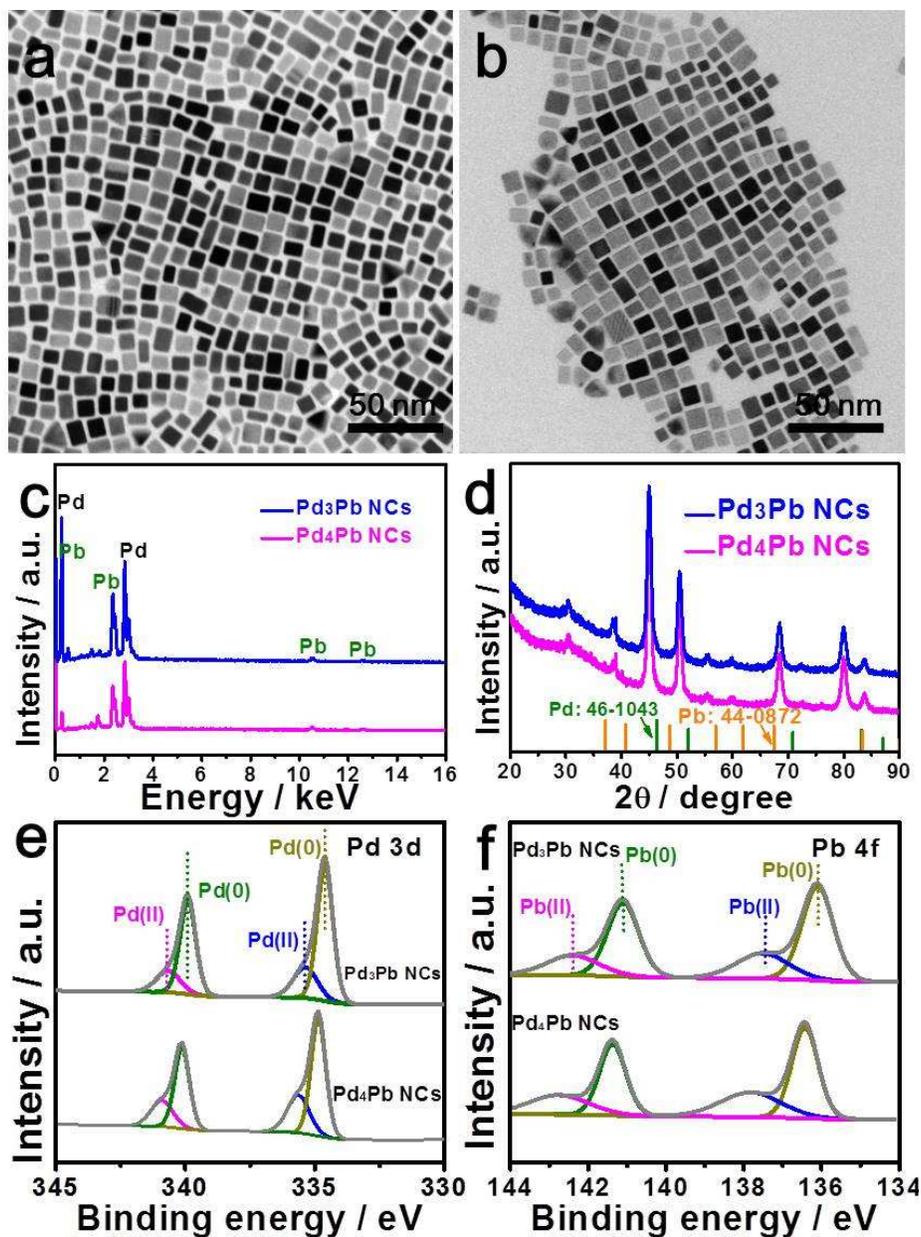


**Figure 1.** (a) TEM, (b) low-magnification HAADF-STEM, (c) SEM-EDS images, (d) PXRD pattern, and (e) HRTEM image. XPS spectra of (f) Pd 3d and (g) Pb 4f in Pd<sub>2</sub>Pb NCs.

Figure 1c illustrates that the atomic ratio of Pd/Pb in Pd<sub>2</sub>Pb NCs is 68.4/31.6,

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3 being consistent with the feed ratio. The phase crystals of the samples were  
4 investigated by PXRD (Figure 1d). The PXRD patterns of Pd<sub>2</sub>Pb NCs showed the  
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6 approached face-center-cubic (fcc) structure of PdPb alloy, confirming the presence of  
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8 PdPb alloy phase in such Pd<sub>2</sub>Pb NCs.<sup>25</sup> In addition, the alloy phase of PdPb was  
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10 analyzed by HRTEM (Figure 1e). It was revealed that the adjacent fringe of the NCs  
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12 is 0.202 nm, which is associated with the Pd<sub>2</sub>Pb (111) facet, further demonstrating the  
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14 alloy phase formation of PdPb.<sup>42</sup> Moreover, the elemental valences and the electronic  
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16 coupling effect among Pd and Pb were studied by XPS. As it is displayed in Figure 1f  
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18 and g, the binding energy of Pd slightly shift to a higher degree while Pb shift to a  
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20 smaller degree when compared with both monometals of Pd and Pb, indicating the  
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22 occurrence of charger transfer between Pd and Pb.<sup>43</sup>  
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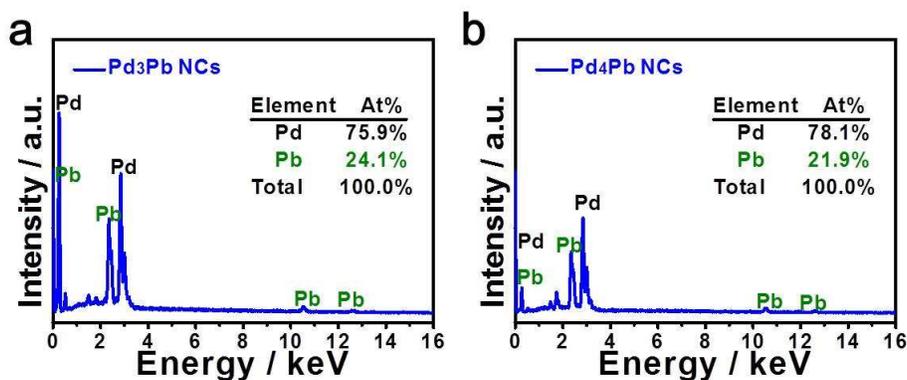
30 To further investigate their properties, the Brunauer–Emmett–Teller (BET)  
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32 measurements have also been conducted. From the N<sub>2</sub> adsorption–desorption  
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34 isotherms in Figure S2, we can find that the as-prepared Pd<sub>2</sub>Pb NCs possessed high  
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36 surface area, which is consistent with the analysis of TEM. These results have  
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38 revealed that the as-prepared Pd<sub>2</sub>Pb NCs possess a high surface area, thus exposing  
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40 more surface active sites available for EG and glycerol.  
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**Figure 2.** TEM images of (a) Pd<sub>3</sub>Pb, (b) Pd<sub>4</sub>Pb NCs, SEM-EDS of (c) Pd<sub>3</sub>Pb and (d) Pd<sub>4</sub>Pb NCs, PXRD patterns of (e) Pd<sub>3</sub>Pb and Pd<sub>4</sub>Pb NCs, (f) XPS spectra of (e) Pd 3d and (f) Pb 4f for Pd<sub>3</sub>Pb and Pd<sub>4</sub>Pb NCs.

It has been demonstrated that the composition can greatly affect the final shape of the nanocrystals. In this regard, we have also taken into consideration the influences of compositions on the morphology, and we have therefore prepared the Pd<sub>3</sub>Pb and

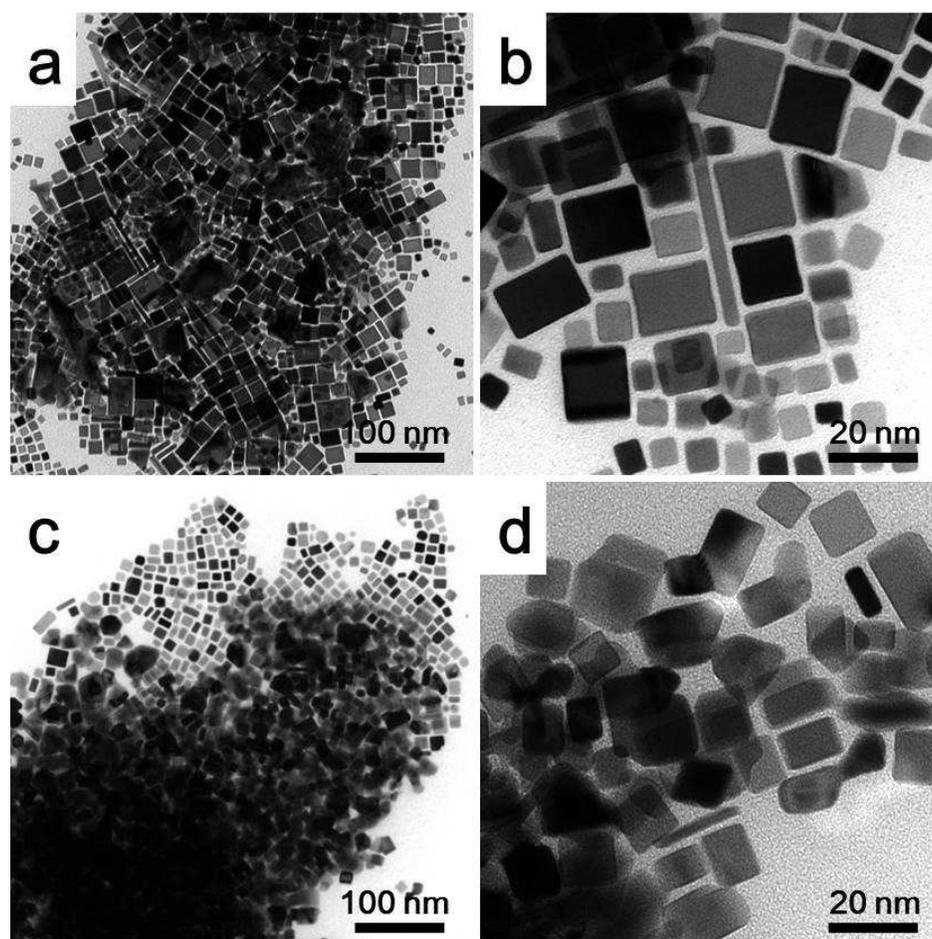
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3 Pd<sub>4</sub>Pb NCs *via* the same strategy while adjusting the amount of PbAc<sub>2</sub>. Figure 2a and  
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6 b showed that both Pd<sub>3</sub>Pb and Pd<sub>4</sub>Pb nanocrystals also displayed the typical cubic  
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8 structure like that of Pd<sub>2</sub>Pb, demonstrating that the large-scale synthesis regardless of  
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10 the atomic ratio variation. Through detailed statistics, it was found that the average  
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12 diameter of the obtained Pd<sub>3</sub>Pb NCs and Pd<sub>4</sub>Pb NCs were about 12.33 nm and 10.99  
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14 nm, respectively. (Figure S3b, d). In addition, the SEM-EDS analyses for Pd<sub>3</sub>Pb and  
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16 Pd<sub>4</sub>Pb NCs in Figure 2c and Figure 3 have also revealed that the atomic ratios are also  
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18 close to the theoretical values. The PXRD of Pd<sub>3</sub>Pb and Pd<sub>4</sub>Pb NCs were also  
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20 analyzed (Figure 2d) to confirm their alloy phase. In addition, both the XRD patterns  
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22 of Pd<sub>3</sub>Pb and Pd<sub>4</sub>Pb displayed a slight shift when compared to the standard Pd. The  
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24 result indicates the formation of PdPb alloy phases in both Pd<sub>3</sub>Pb and Pd<sub>4</sub>Pb NCs. The  
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26 XPS spectra (Figure 2e, f) also illustrated that both metallic states of Pd<sup>0</sup> and Pb<sup>0</sup> play  
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28 predominant roles in the composite structures.<sup>28</sup> Pd<sub>1.5</sub>Pb NCs and PdPb NCs have also  
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30 been synthesized for comparison purposes. The morphology of the as-prepared  
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32 Pd<sub>1.5</sub>Pb NCs and PdPb NCs are characterized by TEM (Figure S4). Pd<sub>1.5</sub>Pb and PdPb  
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34 NCs do not have typical cubic structure, which may be ascribed to the addition of  
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36 excess amount of lead in the synthesis reaction. Therefore, the amount of lead plays a  
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38 significant role in the synthesis of the ideal PdPb NCs.  
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**Figure 3.** The SEM-EDS of (a) Pd<sub>3</sub>Pb NCs and (b) Pd<sub>4</sub>Pb NCs

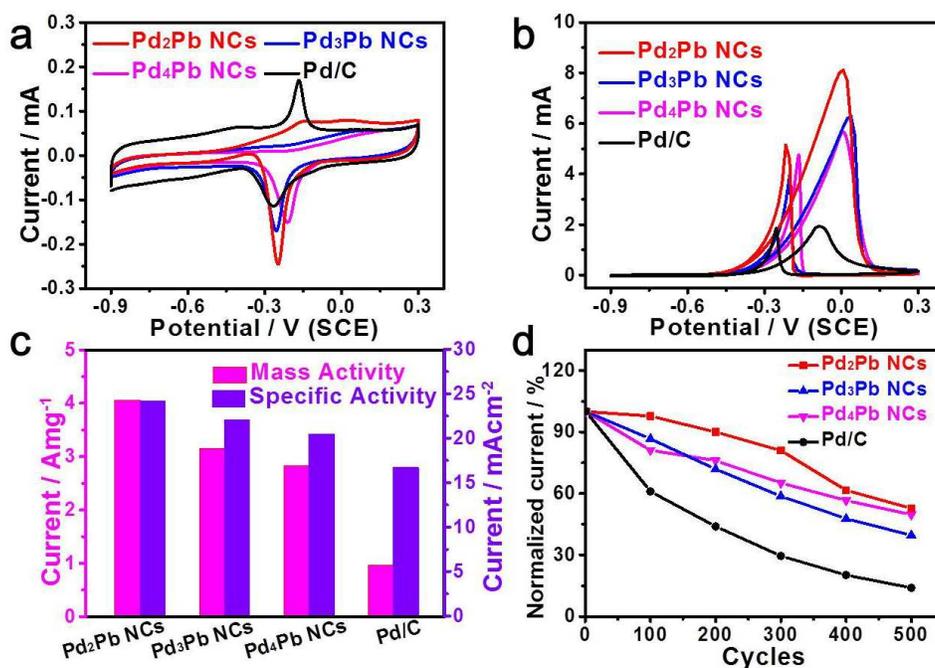
To uncover the formation mechanism, the controlled experiments regarding the reaction parameters have been conducted, and the intermediates from the controlled experiments have also been analyzed by TEM. Among all the experimental parameters, CTAB appears to play a crucial role in controlling the synthesis of PdPb NCs. This can be further demonstrated by the selective adsorption onto specific crystalline surfaces *via* the Van der Waals' forces. In addition, the addition of CTAB significantly decreases the growth rates as well as inducing the anisotropic growth of PdPb NCs with high surface active areas.<sup>44-46</sup> Figure 4a and b showed that the products structures changed dramatically when substituted CTAB with CTAC. When CTAB was changed into TBAB, the morphology of the as-prepared samples changed from NCs to irregular shapes (Figure 4c, d). Therefore, it has been proved that the selective use of CTAB played a significant role in the high-yield production of PdPb NCs. The addition of PbAc<sub>2</sub> was proven to be another significant parameter in the successful preparation of PdPb NCs. As seen in Figure S5, only irregular nanoparticles were obtained when PbAc<sub>2</sub> was replaced with PbCl<sub>2</sub>. These results have revealed that the selective use of CTAB and PbAc<sub>2</sub> was crucial for the successful

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4 synthesis of the desirable PdPb NCs.



35 **Figure 4.** TEM images of PdPb nanocrystals prepared in the same condition while  
36 replacing the CTAB with CTAC (a, b) and TBAB (c, d).  
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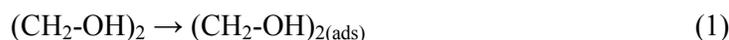
39  
40 Highly uniform PdPb NCs are expected to exhibit outstanding electrocatalytic  
41 performances towards fuel cells. Accordingly, we conducted the EGOR and GOR to  
42  
43 performances towards fuel cells. Accordingly, we conducted the EGOR and GOR to  
44 evaluate their electrocatalytic properties.<sup>47-49</sup> For comparison, the PdPb NCs with  
45 different compositions of Pd<sub>2</sub>Pb NCs, Pd<sub>3</sub>Pb NCs, and Pd<sub>4</sub>Pb NCs were also evaluated.  
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47 The commercial Pd/C was also used as benchmark electrocatalysts for further  
48 comparison. The ECSA values of Pd<sub>2</sub>Pb, Pd<sub>3</sub>Pb, Pd<sub>4</sub>Pb and Pd/C were found to be  
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50 24.2, 22.1, 20.5, and 16.7 m<sup>2</sup> g<sup>-1</sup>, respectively.  
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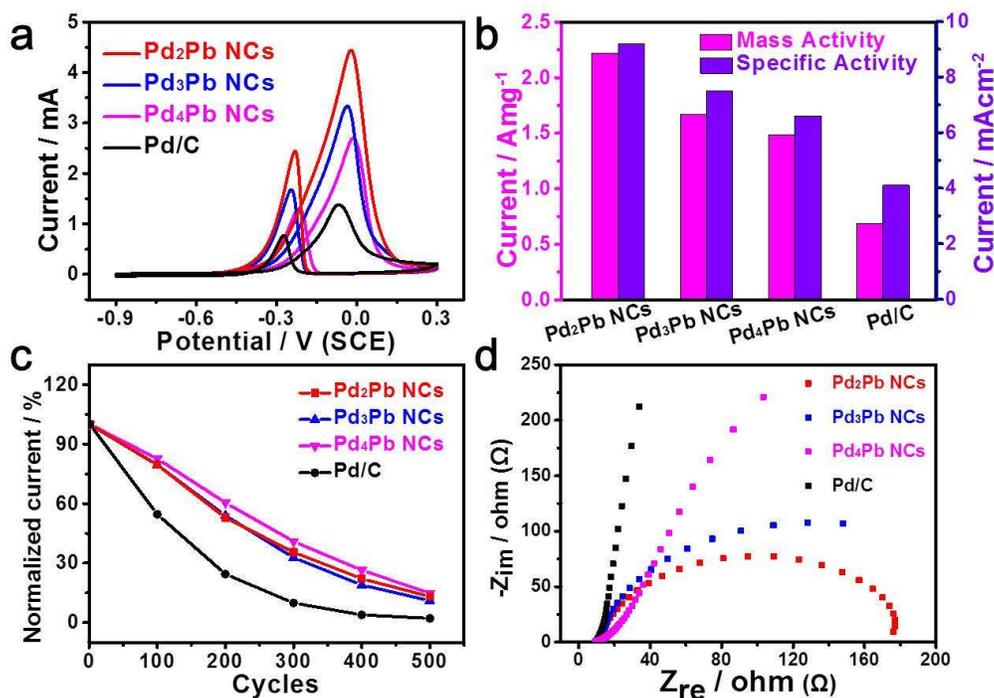


**Figure 5.** CV curves of Pd<sub>2</sub>Pb NCs, Pd<sub>3</sub>Pb NCs, Pd<sub>4</sub>Pb NCs, and Pd/C catalysts in (a) 1 M KOH solution and (b) 1 M KOH + 1 M EG solution. (c) The catalytic activities of these four electrocatalysts. (d) Durability comparisons of these four types of electrocatalysts for 500 cycles.

The EG electrooxidation measurements were conducted in 1 M KOH + 1 M EG solution. Figure 5b displayed the typical CV of these four nanocatalysts. The oxidation peaks for the electrocatalysts were found to be at the potential around -0.05 V. Figure 5c illustrates the mass and specific activities of Pd<sub>2</sub>Pb NCs, Pd<sub>3</sub>Pb NCs, Pd<sub>4</sub>Pb NCs and commercial Pd/C. The Pd<sub>2</sub>Pb NCs exhibited the highest peak current density value of 4.06 A mg<sup>-1</sup> in comparison to all the investigated electrocatalysts. The aforementioned value is therefore, 4.23, 1.43, and 1.29 times greater than that of Pd/C (0.96 A mg<sup>-1</sup>), Pd<sub>4</sub>Pb NCs (2.83 A mg<sup>-1</sup>), and Pd<sub>3</sub>Pb NCs (3.15 A mg<sup>-1</sup>), respectively. Besides, the resulted Pd<sub>2</sub>Pb NCs also displayed superior specific activity

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3 of 16.8 mA cm<sup>-2</sup> towards EGOR which was superior than that of Pd/C (5.8 mA cm<sup>-2</sup>),  
4 Pd<sub>4</sub>Pb NCs (13.8 mA cm<sup>-2</sup>), and Pd<sub>3</sub>Pb NCs (14.3 mA cm<sup>-2</sup>). Moreover, the  
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6 comparison results from Table S1 further confirmed its superior electrocatalytic  
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8 activity towards EGOR. The superior electrocatalytic activity of Pd<sub>2</sub>Pb towards  
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10 EGOR can be attributed to the electron and surface effect in the PdPb alloy.<sup>50</sup> Besides,  
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12 it has been demonstrated that the electrocatalytic activity of Pd can also be improved  
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14 to a higher level after the incorporation of Pb because of the formation of sufficient  
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16 oxygen species, which can react with some intermediates and release the surface  
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18 active sites of Pd.<sup>49, 51</sup> However, a redundant Pb will block the exposed surface active  
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20 sites of Pd, thus lowering the activity of Pd.<sup>43</sup> Therefore, the addition of Pb at a certain  
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22 content (Pd : Pb = 2:1) can significantly increase the catalytic activity towards the  
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24 EGOR. The successive CVs of 500 cycles have also been operated in 1 M KOH + 1  
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26 M EG solution to evaluate EGOR durability (Figure S6). The results showed that the  
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28 Pd<sub>2</sub>Pb NCs gave the highest durability. In addition, the mass activity only decayed by  
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30 47.3 % which was much superior than those of commercial Pd/C (86.1%), Pd<sub>4</sub>Pb  
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32 NCs (60.1%) and Pd<sub>3</sub>Pb NCs (50.1%), respectively (Figure 5d), indicating its better  
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34 electrocatalytic durability towards EGOR. The oxidation mechanism of (CH<sub>2</sub>OH)<sub>2</sub> is  
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36 shown below, in which the reaction system can be oxidized to nontoxic C<sub>2</sub>O<sub>4</sub><sup>2-</sup>,  
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38 showing superior electrocatalytic performances.<sup>52-53</sup>

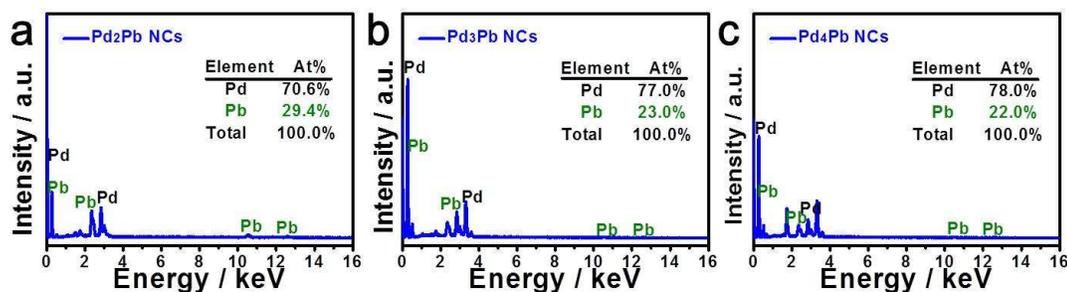
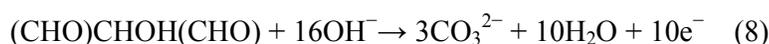
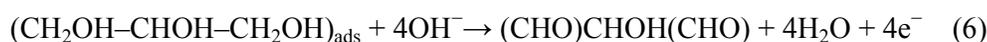
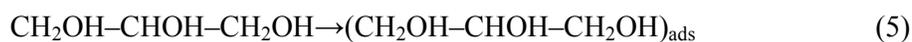




**Figure 6.** CV curves of Pd<sub>2</sub>Pb NCs, Pd<sub>3</sub>Pb NCs, Pd<sub>4</sub>Pb NCs, and commercial Pd/C catalysts in (a) 1 M KOH + 1 M glycerol solution, as well as its (b) corresponding histogram. (c) Durability comparisons of these four types of electrocatalysts for 500 cycles. (d) Nyquist plots of these four electrocatalysts operated in 1 M KOH + 1 M glycerol solution at the potential of -0.1 V.

As for the GOR, the activity variations among these four different catalysts are also similar with that in EGOR (Figure 6a, b). Remarkably, the Pd<sub>2</sub>Pb NCs also showed the highest mass activity of 2.22 A mg<sup>-1</sup> which was much greater than commercial Pd/C (0.69 A mg<sup>-1</sup>), Pd<sub>4</sub>Pb NCs (1.48 A mg<sup>-1</sup>), and Pd<sub>3</sub>Pb NCs (1.67 A mg<sup>-1</sup>). In addition, the Pd<sub>2</sub>Pb NCs also showed the highest specific activity of 9.2 mA cm<sup>-2</sup>, which is 2.24, 1.39, and 1.23 times higher than those of Pd/C (4.1 mA cm<sup>-2</sup>), Pd<sub>4</sub>Pb NCs (6.6 mA cm<sup>-2</sup>) and Pd<sub>3</sub>Pb NCs (7.5 mA cm<sup>-2</sup>), respectively. Moreover, the

durability measurements of these four types of electrocatalysts for the GOR were also conducted *via* repeating the CV scans of 500 cycles. As seen in Figure 4c and Figure S7, after the 500 successive cycles, 14.8% of the initial mass activity was maintained for the nanocubic Pd<sub>2</sub>Pb NCs, which is much better than those of Pd/C (2.1%), Pd<sub>4</sub>Pb NCs (11.0%) and Pd<sub>3</sub>Pb NCs (13.2%). Furthermore, after the 500 successive cycles, the compositions and shapes of PdPb NCs were largely maintained, highlighting the outstanding long-term stability (Figure 7, Figure S8-S10). It has been demonstrated that Pb could lead to the generation of ample oxygenated species and boost the activation of active sites of Pd. All of these fascinating properties have made Pb a perfect catalyst ligand.<sup>54-55</sup> Similar to the EGOR, the main products for GOR were the CO<sub>3</sub><sup>2-</sup>, indicating the complete oxidation of glycerol. The GOR mechanism was shown as follows:<sup>56</sup>



**Figure 7.** The SEM-EDS of (a) the Pd<sub>2</sub>Pb NCs, (b) Pd<sub>3</sub>Pb NCs, and (c) Pd<sub>4</sub>Pb NCs after electrochemical durability test.

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4 The electrochemical impedance spectroscopy (EIS) was carried out at the  
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6 potential of -0.1 V to study their electrochemical reaction processes, where the  
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8 diameter is a crucial parameter for evaluating the electrical conductivity of the  
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10 as-prepared electrocatalysts.<sup>57</sup> As seen in Figure 6d, the order of the diameter  
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12 impedance arc (DIA) of these electrocatalysts was as follows: Pd/C > Pd<sub>4</sub>Pb NCs >  
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14 Pd<sub>3</sub>Pb NCs > Pd<sub>2</sub>Pb NCs. The resulted Pd<sub>2</sub>Pb NCs gave the smallest electron transfer  
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16 resistance and the best electrical conductivity, which was consistent with their  
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18 outstanding electrocatalytic performances.<sup>58</sup> In this work we clearly demonstrated that  
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20 the as-obtained PdPb NCs showed a great enhancement towards electrocatalytic  
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22 activity and reusability. The enhanced performance of the uniform PdPb NCs reported  
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24 herein is likely to be attributed to the integration of the nanocubic structures and  
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26 synergistic effects between the Pd and Pb.  
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#### 32 33 **4. CONCLUSIONS** 34 35

36 In conclusion, an advanced and yet efficient strategy has been developed for the  
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38 design of well-defined cubic PdPb nanocatalysts with a high yield. The controlled  
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40 experiments have revealed that the preparation of PdPb NCs were CTAB-dependent.  
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42 This new class of PdPb nanocatalysts have the distinctive characteristics of being  
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44 ultra-uniform as well as having a nanocubic structure. Those unique characteristics  
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46 are responsible for greatly improving the electrocatalytic performances of fuel cells  
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48 oxidation reactions. Impressively, the optimized Pd<sub>2</sub>Pb NCs gave the best  
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50 electrocatalytic performances towards EGOR and GOR, suggesting a great potential  
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52 for fuel cells. The approach based on tuning the morphology of nanocatalysts can also  
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3 be extended to some other nanomaterials to generate nanocrystals with desirable  
4 nanostructures.  
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#### 7 8 ASSOCIATED CONTENT 9

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11 The Supporting Information is available free of charge on the ACS Publications  
12 website. EDX, XRD, TEM and XPS of the as-prepared samples. CVs, scan cycling  
13 experiments and chronoamperometric curves of Pd<sub>2</sub>Pb NCs, Pd<sub>2</sub>Pb NCs, Pd<sub>2</sub>Pb NCs  
14 and commercial Pd/C modified electrode on electrocatalytic oxidation of ethylene  
15 glycol and glycol.  
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##### 36 37 Author Contributions 38

39 § These authors contributed equally. The manuscript was written through  
40 contributions of all authors. All authors have given approval to the final version of the  
41 manuscript.  
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##### 45 46 Notes 47

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49 The authors declare no competing financial interest.  
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#### 51 52 ACKNOWLEDGMENT 53 54 55 56 57 58 59 60

This work was supported by the National Natural Science Foundation of China (Grant No. 51373111, 21603111), the Suzhou Industry (SYG201636), the project of scientific and technologic infrastructure of Suzhou (SZS201708), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD). In addition, CF would like to express his gratitude to RGU for support.

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