Additive-Free Fabrication of Spherical Hollow Palladium/Copper $A \rightarrow N$ Nanostructures Fuel Cell Application

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S Supporting Information

[AB](#page-3-0)STRACT: [Herein, thro](#page-3-0)ugh tuning the surface energy the surface energy the surface energy of the surface energy difference of the major crystal planes by allowing, π palladium/copper alloyed nanostructures are successfully prepared through a one-pot template-free strategy. Compared ${\bf w}$ th the solid PadCu allowed nanoparticles, the ${\bf w}$ allow ${\bf v}$ alloyed nanostructures exhibit the increased accessible electrochemical active surface area and the enhanced electrocatalytic activity for formic acid oxidation. It is concluded that the aspredated holds \mathbf{w}_i and \mathbf{w}_j allowed nanostructures would be allowed nanostructures would be a set potential candidate as an anomalist indicatalyst indicatalyst in direct formic \mathbf{t}_i $a(t), t, y, t \in \mathbb{R}$, the strategy developed in this strategy developed in this strategy developed in this strategy of study might be expanded to fabricate other metal alloyed $t_{\rm c}$ to

KEYWORDS: palladium/copper alloy, hollow nanostructure, surface energy difference, electrocatalytic activity, direct formic acid fuel cell, formic acid oxidation

owadays, noble metals are extensively utilized as catalysts are extensively utilized as catalysts \mathfrak{r}_i in various fields, including organic chemistry and fuel cells. 1,2 Nevertheless, the rapidly rising price of and rapidly rising price of and rapidly rising price of a \mathfrak{h} is not metals severely limited the applications of the applications of the noble the noble the noble the noble the noble \mathfrak{h} $\left[\begin{array}{ll} \mathbf{t} & \mathbf{t} \end{array} \right]$, therefore, tremendous efforts have been made between \mathbf{t} to solve these issues, in which a general strategy is to form the alloyed nanoparticles of noble and non-noble metals. Previous s tudies demonstrated that some allowed catalysts exhibited that some allowed catalysts exhibited catalysts exhibited values of \mathbb{R}^n s in finitely significant enhancement of the catalytic activity and selectivity and selecti over t and ρ and ρ metals catalysts, and thereby reduce thereby reduce thereby reduce the t c of the costs of the catalysts. c of the other hand, because of the other hand, because of the other hand, because $\mathfrak{g}_\mathbb{C}$ lower densities and higher specific surface areas, hollows $\widehat{\mathfrak{n}}$ nanostructures of nob[le m](#page-3-0)etals exhibited significantly improved catalytic performance and utilization t and t is t and t and t reduced the costs of the costs of the catalogue ϵ therefore, therefore, therefore, therefore, therefore, the construction of hollow metal nanostructures is considered as an

important strategy and [atten](#page-3-0)tion attention. Recently, \mathfrak{m} attention at the central \mathfrak{m} $t_{\rm c}$, preparation of the single or bimetallic noble metal holds metal holds metal holds metal holds metal $\overline{\mathbf{t}}$ structures using a sacrificial temperatures $\overline{\mathbf{t}}$ as sacrificial temperatures was sacrificial temperatures was sacrificial temperatures was satisfied to $\overline{\mathbf{t}}$ represents the rigorous reaction conditions are reacting the rigorous reaction conditions and \mathbf{r}_{max} poor reproducibility seriously limit the applications. Here are the applications, \mathfrak{h} facil[e one](#page-3-0)-pot additive-free synthesis of hollow bimetallic of holds $t - t$ nanoparticles is seldom reported and still remained a great

challenge. In our previous report, we previous report, as additions π allowed nanocubes were prepared through the adjustment of $\mathfrak{g}_{\mathfrak{p}}$ $\mathfrak{t}_{\mathfrak{t}}$ surface energy difference $(\gamma_{\mathfrak{t}})$ of the major crystal planes planes by

by allowing the spherical holds \mathbf{w} allows palladium palladium palladium palladium palladium palladium pal alloyed nanostructures supported on multiwalled carbon nanot \mathfrak{t}_i are \mathfrak{t}_i are \mathfrak{t}_i are prepared by alloying are prepared by all $\mathfrak{g}_{\mathfrak{t},\mathbb{C},\mathbb{C}}$, and a facile one-pot method. It should be noted that this should be noted that this should be noted that this should be noted that the non-point \mathfrak{t} method is additive-free and suitable for one-pot synthesis of \mathfrak{p}_2 hollow nanostructures assembled by allowing nanoparticles of $\mathbf r$ noble and non-noble metals. Moreover, through the introduction of $\mathcal{C}_\mathbf{C}$ of $\mathcal{C}_\mathbf{C}$ and $\mathcal{C}_\mathbf{C}$ the lattice parameter of $\mathcal{C}_\mathbf{C}$ $t_{\rm eff}$ allow $\tilde{\bf f}$ allow $\tilde{\bf f}$ the underlies the undersirable hydrogeneous absorption to improve the free active surface active surface active surface active surface active surface activ small molecules for electrooxidation. This could enhance the electrocatalytic performance significantly, which lowered the loading amount of \mathfrak{g}_∞ and the cost of the cost of the catalyst obviously. For t the facility preparation of the PdCu/MWCNTs, \mathcal{A} t $(11 \t\t t \t\t t \t\t t)$, MWCNTs were simultaneously dispersed into ethylene glycol (\Box) in the standard the pH was adjusted to \mathbf{w} was adjusted to 1 . Then it was search in the 10° for ϵ for ϵ for ϵ the \mathcal{N} and \mathcal{N}

 T , the transmission electron microscopy (TEM) observation $\mathcal{C}(\mathcal{T})$ observation indicates the successful preparation of the \mathcal{J}_max and \mathcal{J}_max $\mathbf{F}_{\mathbf{r}} = \mathbf{F}_{\mathbf{r}}(\mathbf{r},\mathbf$ diameter of ca. 0 of an empty core composed of an $\mathbf{w}(\xi)$ core $\mathbf{w}(\xi)$ uniform shell [wi](#page-1-0)th the average thickness of 4 nm. In addition, \mathbf{t}_i

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Figure 1. (a) TEM and (b) TEM and $\frac{1}{\sqrt{2}}$ temperature of the PdCu/MWCNTs. (c) are the restrictions of the PdCu/MWCNTs. Curve I, \mathcal{A} curve II, Paris II, $\begin{array}{ccc} a & b & d \end{array}$ and $\begin{array}{ccc} a & b & d \end{array}$ at (d) $\begin{array}{ccc} a & b & d \end{array}$ and $\begin{array}{ccc} a & b & d \end{array}$ $\left(\begin{array}{ccc} 0 & 0 & 0 \end{array}\right)$

 $\mathfrak{t}_{\mathbb{R}^n,\mathbb{R}^n}$ resolution $\mathfrak{t}_{\mathbb{R}^n}$ (HRTEM) further indicates the $\mathfrak{t}_{\mathbb{R}^n}$ for a formation of the hollow nanospheres and the hollow π nanospheres are coalesced by small PdCu allowed $\mathbf t$ allowed nanoparticles $\mathbf t$ (Figure 1b). The composition of the PdCu/MWCNTs was was was well was well as \mathcal{N} determined as 1.1 atomic ratio of P and C and C u through energydispersive \mathbf{t} ray spectroscopy (EDS) measurement (see Figure $\mathbb{E}[\mathbf{S}_1]$ in the Supporting Information \mathbf{S}_2 in accordance with the \mathbf{S}_3 theoretical stochiometric proportion.

 P . Power \overline{A} ray diffraction (XRD) results indicate the theorem successful f[ormation](#page-3-0) [of](#page-3-0) [the](#page-3-0) [PdCu](#page-3-0) [a](#page-3-0)lloys. Figure 1c shows the $\mathfrak{h}_\mathcal{S}$ \mathcal{X} attached on \mathcal{X} attached on MWCNTs (Pd/MWCNTs, \mathcal{X} $\zeta(\cdot, \cdot)$, PdCu/MWCNTs (curve I), and PdCu/MWCNTs (curve ζ MMCNTS (Curve III), respectively. For the $\mathcal{C}_\mathbf{r}$ P d/MWC, the first peak at 26.06 is attributed to the first peak at 26.06° is attributed to the to (00) plane of the MWCNTs, the other four peaks at 30.75, the oth $\begin{array}{cccc} 1, & 0, & 1, & 0 \ 0, & (11), & (11), & (11), \end{array}$ \mathfrak{h}_1 , and \mathfrak{h}_2 becomes of t[he](#page-3-0) face-centered-cubic (feed) \mathfrak{h}_2 , respectively. Compared with the $\mathcal{F}_\mathbf{t}$ of \mathbf{t} , the diffraction peaks of the PdCu/MWCNTs slightly shift to the higher θ values. Furthermore, the peak at r \sim \sim \sim \sim characteristic to C (220) plane disappears in curve II and C (0.
 the lattice parameter of the $\langle 0.30 \rangle$ lies $\begin{bmatrix} \mathbf{b} & \mathbf{b} & \mathbf{c} & \mathbf{$ $\begin{array}{ccc} t & t & t & t \\ 10,1 & t & t & t \\ \end{array}$ the successful formation of the PdCu formation of the $\begin{array}{ccccc} &10,1&&&&&\dots& t\\ &\ddots&\ddots&\ddots&\ddots&\ddots&\ddots&\ddots&\ddots \end{array}$ I almost disappears in curve II after the formation of the alloys. $\tan\theta$ the t the attachment through the oriented attachment through t

- (200) plane during the formation of the hollow allow allow allow allow allows allow allows t_{max} t_1
- To determine the formation mechanism of the π nanospheres, we monitored the samples at different intervals during the formation process. The \mathfrak{c}_∞ obviously indicated the formation of $\mathbf{1}_p$ (Figure 1c, Figure S2, Supporting Information). From the TEM images π in Figure 1d, only PdCu allowed nanoparticles are $f_{\rm eff}$ after $f_{\rm eff}$ after reacted for $f_{\rm eff}$ the tendency of the tenden formation of \mathbf{w} is very observation of \mathbf{f}_1 , \mathbf{f}_2 , \mathbf{f}_3 , \mathbf{f}_4 , \mathbf{f}_5 , \mathbf{f}_6 , \mathbf{f}_7 , \mathbf{f}_8 , \mathbf{f}_9 , \mathbf{f}_9 , \mathbf{f}_9 inset of Figure 1e clearly reveals the oriented attachment of t P dcu allowed nanoparticles. After reacted for $\mathfrak{g}_\mathcal{A}$, the hollowed for \mathfrak{m} nanospheres are formed and the internal void space in nanospheres becomes more distinct. Therefore, it can be proposed that the initial formation of the PdCu alloyed nanoparticles and the subsequent oriented attachment play the subsequent play the subsequent play the play the important roles in the formation of the holds \mathbf{w} allows \mathbf{w} allows \mathbf{w}

nanospheres. To better understand the formation $\mathfrak{h}_\mathbb{C}$

hollow $\overline{\mathbf{w}}$ alloyed nano-leads by coalescence of the alloyed nanoparticles, we can relate the theoretical calculations using the theoretical calculations using \mathbf{r}_i density functional theory introducing the surface $\mathfrak{t}_\mathbb{C}$ by introducing the surface $\mathfrak{t}_\mathbb{C}$ energy (γ) , \mathbf{w}_i is the surface energy per unit area energy per uni of a certain crystal plane and plane and plane and plays the important roles in contract $\mathbf r$ π the results, the surface energies of the surface energies of the α (111) (100) (111) (100) and 1.2, 1.3, 1.4, and 1.[48](#page-3-0) $\frac{1}{\sqrt{2}}$, respectively, in coincidence with the previous with the previous $\frac{1}{\sqrt{2}}$ $r=\frac{10,1}{2}$ The $\gamma_{(111)}$ of the values of Cu and PdCu and Pd. While the values of Cu and Pd. While the values of Cu and Pd. While the values of Cu and Pd. While the values of C u and Pd. While the values of C u and the $\gamma_{(100)}$ of the PdCu allows (1.59 J mga allows (1.59 J mga allows (t_1, t_2, t_3)) is much higher than the pure counterparts (Figure 2a). Therefore the therefore the therefore the therefore the t

Figure 2. (b) $\sqrt{ }$ Surface energies of the (111) and (100) planes of the $\sqrt{ }$ C_{eff} and C_{eff} and C_{eff} are C_{eff} and C_{eff} between (100) and (111) planes of the Cu, Pd, and $\mathcal{O}(n)$ \mathcal{A}

 γ and tw between t_i and (111) and (100) planes of the PdCu allowedus of the PdCu allowedus nanoparticles is much higher than those of the pure counterparts. Consequently, after the formation of the allowed nanoparticles, the metastable allowed nanoparticles $\mathbf w$ $_{\infty}$ are selfassemble and coalesce through the oriented attachment of the oriented attachment of the oriented attachment of high energy (100) plane, $\overline{\mathbf{w}}$ reduction \mathbf{t} reduction of \mathbf{t} \mathfrak{h}_i of the system. This might be the system the system of the driving force \mathfrak{h}_i for t the formation of the hollow PdCu nanospheres. Indeed, the hollow t holds π and π nanospheres obtained in the typical experiment in the typical experiment mainly present to (111) plane (Figure 2b). In addition, compared with the XRD pattern of the PdCu allowed allowed nanoparticles (curve $(0, \alpha, \beta)$, (α, β, β) , (α, β, β) affraction peak of α \mathfrak{t}_i , (200) plane of \mathfrak{t}_i alloys almost d[isa](#page-1-0)ppears after the PdCu almost distribution of \mathfrak{t}_i for a \mathfrak{b}_i alloyed \mathfrak{w}_i allowed [na](#page-1-0)nospheres (curve II, Figure 1). This further confirms the oriented attachment of the (100) plane during the formation of the formation of the hollow allows allow allows \mathbf{r}_i [F](#page-1-0)urthermore, through the oriented attachment of the \mathfrak{t}_1 \in (100) planes of the model PdCu allowed nanoparticles, a π model similar to the experimental result can be constructed \mathfrak{t}_i and \mathfrak{t}_{i+1} (see Figures S3 and S4 in the Supporting S4 in the Supporting S4 in the Supporting S4 in the Supporting S4 in the Supportion \mathfrak{t}_i Information). This confirms the reasonability of the abovedescribed theoretical explanation.

[The appli](#page-3-0)cation of the as-prepared PdCu/MWC[NTs](#page-3-0) [as](#page-3-0)-prepared $\mathfrak{h}_\mathbb{R}$ electrocatalyst of the direction of the direct formic acid fuel fuel $(\textcolor{red}{\bullet} - \textcolor{red}{\bullet})$ was evaluated. From the carbon monocide (CO) stripping voltammetry studies (Figure 3), $t_{\rm c}$ active $t_{\rm c}$ active $t_{\rm c}$ negative direction compared with the Pd/MWCNTs. This \mathcal{A} reveals that the \mathfrak{t}_1 the \mathfrak{t}_2 of the PdCu/MWCNTs is significantly is significantly in higher that that of the Pd/MWCNTs, which may be attributed \mathbf{t}_max to two different reasons. First, comparisons with the PdCu allowed \mathbf{r}_i nanoparticles, the internal void space of the hollow allow allows \mathbf{w} nanosphere can be considered as the additional internal s urface. $\frac{1}{\sqrt{2}}$ This can enhance the EAS accessible by small

molecules (e.g., formic acid,) singletic activities $f_{\rm eff}$ improv[ed](#page-3-0) utilization efficiency and thereby the higher electrocatalytic activity. Second, electronic effect between \mathcal{C}_max might be another reason. Parameter t in the catalogue d electrons from ζ alloys, which can relieve the allows, ζ a adsorption for \mathfrak{t}_0 , the important reaction \mathfrak{t}_0 is contributed reaction. intermediates in formic acid oxidation. $\mathbf{t} = \mathbf{t}$

Electrochemical measurements in the t th t the \mathcal{L} $M_{\rm tot}$, the set of the theory of the better ele[ctr](#page-3-0)ocatalytic activity for the better electrocatalytic activity for the ϵ for acid electronomic than $\mathfrak{h}=\mathfrak{h}$ and $\mathfrak{h}=\mathfrak{h}$. From the PdC results shown in Figure 4, the two main of the two main oxidation peaks of the the theorem

catalysts locate at $c=0.30$ in both the positive and negative an directions. The corresponding peak current density of the type \mathfrak{p}_1 P and P is 166.7 mA/cm , 167.7 mA/c much higher than that of the $(10-4)$. $\mathcal{F}_\mathcal{A}$ furthermore, the onset potential of formic acid electro-onset potential of formic acid electro-onset $\mathbf{f}_\mathcal{A}$ out the locates -0.0 99 V, much more thanks −0.012 V of the Pd/MWCNTs. The higher oxidation current current and the lower onset potential demonstrate the much better $\zeta_{\rm eff}$ and the much better electroon activity of the PdCu/MWCNTs.

 $s_{\mathcal{A}}$ are area (EAS) of the \mathcal{A} is much larger than \mathcal{A} is much larger than \mathcal{A} t_1 that $t_2 \in \mathcal{N}$ and \mathcal{N} is furthermore, the onset potential of potential of potential of potential of $\mathfrak{t}_\mathbb{C}$. The Co-stripping on $\mathcal{N}_\mathbb{C}$ shifts toward the $\mathfrak{t}_\mathbb{C}$ expanded to the fabricate other metal allow native \mathfrak{h}_∞ tures. For example, through the preliminary results that t from the ongoing studies on the preparation of the preparation of the preparation of the PtCu and $\mathfrak{p}_\mathcal{A}$ $R_{\rm{max}}$ allowed holds \mathbf{w} and \mathbf{w} the positive show that

perspectives. ■ ASSOCIATED CONTENT

 \bullet Supporting Information

 $E = \frac{1}{2}$ details and $\frac{1}{2}$ details and $\frac{1}{2}$ and $\frac{1}{2}$ and $\frac{1}{2}$ and $\frac{1}{2}$ and $\frac{1}{2}$ nanoparticles, construction of the model holds of the model holds of the model holds \mathbf{w} nanostructure, and chronoamperometric curves of the samples. This material is available free of charge via the Internet at , it $\frac{1}{2}$, $\frac{1}{2}$. $\frac{1}{2}$

■ AUTHOR INFORMATION

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The authors declare no competing financial interest.

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