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Concavity Tuning of Intermetallic Pd-Pb Nanocubes for Selective Semihydrogenation Catalysis

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ABSTRACT: Although considerable studies on pursuing high-performance Pd-based catalysts for the semihydrogenation of alkynes have been carried out, the creation of catalyst with high activity, selectivity and stability simultaneously towards semihydrogenation reactions remains significant challenge. Herein, for the first time we report a facile synthetic strategy to realize the intermetallic Pd-Pb nanocubes with different concave degree by selectively utilizing small molecules. These obtained Pd-Pb nanocrystals exhibit high activity in the semihydrogenation of alkynes, where their performances are highly shape- and composition-dependent with Pd-Pb concave nanocubes showing the optimized alkene selectivity of 94.6% and activity of 179.2 h⁻¹, much higher than those of 10% Pd/C. Detailed X-ray photoelectron spectroscopy results show that the higher ratio of metallic Pd²⁺

and Pb/Pd contribute to higher styrene selectivity. The density functional theory calculations further reveal that the favorable adsorption energy of phenylacetylene and desirable desorption energy of styrene on the Pd₃Pb surface are critical for the phenylacetylene semihydrogenation with excellent activity and high selectivity. Furthermore, the Pd-Pb concave nanocube can endure at least five cycles with very limited conversion and selectivity decays, representing an efficient Pd-based catalyst for selective hydrogenation and beyond.

INTRODUCTION

Nanomaterials composed of precious metals have drawn great attentions in recent years.^{1,2} In particular, nanostructured palladium (Pd) or platinum (Pt) is an efficient heterogeneous catalyst for fuel cell reactions, organic reactions and series of industrial production of chemicals due to their unique physical/chemical properties.³⁻¹⁵ However, the monometallic Pd catalysts are not highly selective toward the desired products when more than one reducible groups are presented in the reaction system, such as in the acetylenic, furfuralor or nitroaromatic compounds hydrogenations because the other reaction processes may be more likely to occur in dynamics and thermodynamics rather than the target reaction process. To maximally overcome this limitation, introducing the second metal is considered as an efficient strategy to enhance the selectivity of the target products via modifying the electronic structures of Pd.¹⁶⁻¹⁸ Alkynes semihydrogenation is an extremely important reaction in the synthesis of fine chemicals, the target products of this reaction are also an important monomer for synthetic resins as well as ion exchange resins.^{12,16} However, to date, while several PdM nanoparticles (NPs) have been reported with enhanced alkenes selectivity for the alkynes semihydrogenation,²⁰⁻²⁶ the activities are still unsatisfied.^{21,27} The design of catalysts with high selectivity and activity simultaneously for semihydrogenation is highly desirable.^{20,21}

From the view of structure, the unique intermetallic nanocrystals with the specific crystal structures and highly ordered surface atom arrangements can provide the spatial separation of active

sites, which cannot be afforded by the conventional disordered nanocrystals.^{18,28-33} The intermetallic catalyst (IMC) can provide strong interaction, charge transfer and orbital rehybridization to achieve catalysis optimization. In addition, due to the high enthalpy of mixing, the IMCs can usually exhibit outstanding stability in catalytic reactions.^{22,31-34} Nevertheless, pursuing effective structure control on IMCs remains a great challenge,^{22,23,26} not to mention the systematic morphological regulation of IMCs. To this end, the realization of systematic control of intermetallic catalysts is highly challenge yet desirable, especially for catalysis optimization.^{26,35-40}

EXPERIMENTAL SECTION

Chemicals. Palladium(II) acetylacetonate (Pd(acac)₂, 99%), lead(II) acetylacetonate (Pb(acac)₂, 99%), lead(II) formate (Pb(HCOO)₂, 99%), oleylamine (C₁₈H₃₇N, OAm, > 70%), benzoic acid (C₇H₆O₂, reagent grade, 99%), dodecyltrimethylammonium chloride (C₁₅H₃₄NCl, DTAC, 99%) and benzaldehyde (C₇H₆O, 99%) are all purchased from Sigma-Aldrich. Lead(II) chloride (PbCl₂, 99.99%), lead(II) acetate trihydrate (Pb(Ac)₂· 3H₂O, > 99%) were obtained from Aladdin. Benzoic acid (C₇H₆O₂, 99%), benzyl alcohol (C₇H₈O, 99%), aniline (C₆H₇N, 99%), cyclohexane (C₆H₁₂, analytical reagent, ≥ 99.5%) and ethanol (C₂H₆O, analytical reagent, ≥ 99.7%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were used as received without further purification. The water (18 MΩ/cm) used in all experiments was prepared by passing through an ultra-pure purification system.

Synthesis of Pd₃Pb NCs, Pd₃Pb SCNCs and Pd₃Pb CNCs. In a typical synthesis of Pd₃Pb NCs, 7.6 mg Pd(acac)₂, 3.2 mg Pb(Ac)₂·3H₂O, 6.6 mg DTAC and 5 mL OAm were added into a vial (volume: 35 mL). After the vial was capped, the mixture was ultrasonicated for around 1 h. The resulting homogeneous mixture was then heated from room temperature to 180 °C in around 45 min and maintained at 180 °C for 5 h in an oil bath, before it was cooled to room temperature. All the

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 Pd_3Pb nanomaterials were collected by centrifugation and washed three times with ethanol/cyclohexane mixture. For the synthesis of Pd_3Pb SCNCs and Pd_3Pb CNCs, all the conditions are similar to those of Pd_3Pb NCs but changing 6.6 mg DTAC to 40 mg benzoic acid and 0.1 mL benzaldehyde, respectively. Before starting the catalytic reaction, the Pd_3Pb intermetallic nanomaterials were load on commercial carbon black and subjected to thermal annealing in air at 250 °C for 1 h and then in 5% H_2/N_2 atmosphere at 300 °C for 1 h.

Characterizations. Power X-ray diffraction (PXRD) patterns were collected using an X Pert-Pro X-ray powder diffractometer equipped with a Cu radiation source ($\lambda = 0.15406$ nm). The morphology and size of the nanomaterials were determined by transmission electron microscope (TEM, Hitachi, HT7700) with an accelerating voltage of 120 kV. High-resolution TEM (HRTEM), TEM energy dispersive X-ray spectroscopy (TEM-EDS) and high angle annular dark field scanning TEM (HAADF-STEM) were conducted on an FEI Tecnai F20 transmission electron microscope at an acceleration voltage of 200 kV. All the samples were prepared by dropping cyclohexane or ethanol dispersion of samples onto carbon-coated copper grids and dried under ambient condition. Low-resolution energy dispersive X-ray spectroscopy was performed on a scanning electron microscope (SEM, Hitachi, S-4700). All the X-ray photoelectron spectroscopy (XPS) spectra of Pd-Pb NCs, SCNCs and CNCs were collected by XPS (Thermo Scientific, ESCALAB 250 XI). The concentration of each ion for each catalyst was analyzed by the inductively coupled plasma atomic emission spectroscopy (710-ES, Varian, ICP-AES).

Hydrogenation reactions of Pd₃Pb NCs, SCNCs and CNCs. For a typical hydrogenation reaction, 3 wt% Pd of Pd₃Pb/C was added into a 50 mL glass pressure vessel. After the addition of 0.1 mmol phenylacetylene, 10 mL ethanol and 5 mg catalyst into a glass pressure vessel, the vessel was pressurized with H₂ (2 atm). The reaction was conducted at 50 °C under stirring at 400 rpm. After the completion of the reaction, the liquid mixture was collected by centrifugation at 12000 rpm

for 2 min. The liquid samples were detected by gas chromatography with flame ionization detector (GC-FID). Formula for the activity of phenylacetylene hydrogenation reaction:

 $Semihydrogenation \ Activity = \frac{n_{phenylacetylene \ converted}}{n_{Pd} \times h}$

RESULTS AND DISCUSSION

Herein, for the first time we report a wet-chemical way to synthesize well-defined Pd_3Pb intermetallic nanomaterials with different concave degree named nanocubes (NCs), slight concave nanocubes (SCNCs) and concave nanocubes (CNCs), which gave rise to highly active, selective and stable semihydrogenation of alkynes. Significantly, the successful creation of the well-defined Pd_3Pb nanomaterials with same composition provides an ideal frame for exploring the effect of concave degree on semihydrogenation. We found that the Pd_3Pb SCNCs and Pd_3Pb CNCs could deliver high conversion and selectivity as well as outstanding stability compared with 10% Pd/C, in which Pd_3Pb CNCs show the highest conversion of 99.9%, styrene selectivity of 94.6% and the activity of semihydrogenation of 179.2 h⁻¹. The intermetallic structure also makes the Pd_3Pb CNCs highly stable with slight activity decay over five cycles. The high performance of the Pd_3Pb CNCs has also been successfully expanded to other alkynes.

We prepared Pd_3Pb NCs with concave feature through a wet-chemical approach, in which $Pd(acac)_2$ and $Pb(Ac)_2 \cdot 3H_2O$ were used as Pd and Pb precursors, OAm was applied as solvent and surfactant (see Supporting Information for details) and DTAC, benzoic acid or benzaldehyde was chosen as morphology control agent. The synthetic parameters, such as the concentrations of the small molecules, the precursors and the species have been explored in details (**Figures S1-5**), in which the formation of Pd_3Pb NCs can be attributed to the introduction of halogen ions, while the creation of Pd_3Pb CNCs and Pd_3Pb SCNCs can be ascribed to the effects from aldehyde group and

carboxyl group, respectively.



Figure 1. (a, b) TEM images, (c) PXRD pattern, (d) TEM-EDX, (e) HRTEM image, (f) HAADF-STEM image and elemental mappings and (g) the corresponding line-scans of the Pd₃Pb CNCs. The inset in (a) is the 3D structure model of the Pd₃Pb CNCs.

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Typical transmission electron microscopy (TEM) (Figure 1a-b) images of Pd₃Pb CNCs show that the majority of the products have concave cubic profiles with the yield approaching to 100%. The Pd₃Pb CNCs are monodisperse with an average diameter of 13.6 nm, which is similar with the size (15.2 nm) calculated by the Scherrer-equation (Figure S6a-c). As shown in Figure 1c, the PXRD pattern of the Pd₃Pb CNCs can be indexed to the standard XRD pattern of intermetallic Pd₃Pb (Joint Committee on Powder Diffraction Standards, JCPDS, No. 20-0827), where Pb atoms occupy the eight vertexes of the cube and Pd atoms occupy the centers of six faces in one unit cell. The composition ratio of Pd/Pb is $73.1 \pm 0.2/26.9 \pm 0.2$, as revealed by the ICP-AES, which is consistent with the TEM-EDX (73.5 \pm 0.4/26.5 \pm 0.4) (Figure 1d) and SEM-EDX (75.0 \pm 0.2/25.0 \pm 0.2) results (Figure S6d). As shown in the HRTEM image (Figure 1e), the distinct lattice spacings of 0.198, 0.225 and 0.232 nm, corresponding to the (200), (-111) and (111) planes of the ordered Pd₃Pb intermetallic structure, are observed. Furthermore, the high-index steps were frequently observed on the surface of Pd₃Pb CNCs (Figure S7), which are beneficial for the catalysis enhancement.^{41,42} The elemental distributions of Pd and Pb were confirmed by the STEM-EDX elemental mappings, where both Pd and Pb distribute evenly in the whole CNC (Figure 1f). The line-scans verify that both Pd and Pb distribute evenly in the whole CNC with weak element distribution in the center part (Figure **1g**).

Figure 2a and S8a show the representative TEM and STEM images of the Pd₃Pb NCs in which nanocubes are the major product. The Pd₃Pb NCs have uniform edge length distribution of around 12 0 nm and the size calculated by Scherrer-equation calculation is 13.7 nm (**Figure S9**). As shown in **Figure S8c**, the distinct PXRD diffraction peaks of the Pd₃Pb NCs can be consistently indexed to the reflections of the intermetallic Pd-Pb materials (JCPDS, No. 20-0827), similar to the XRD diffraction of Pd₃Pb CNCs. The composition ratio of Pd/Pb is 73.3 \pm 0.3/26.7 \pm 0.3, as revealed by the ICP-AES, which is consistent with the TEM-EDX (73.6 \pm 0.5/26.4 \pm 0.5) (**Figure S8e**) and SEM-EDX (73.9 \pm 0.2/26.1 \pm 0.2) results (**Figure S9d**). The displayed facets in the HRTEM shows

the lattice spacing of 0.402 nm, corresponding to the (100) plane of cubic phase Pd₃Pb (space group: *Pm-3m*) intermetallic structure (**Figure 2c**). Both the line-scans and elemental mappings show the uniform Pd and Pb distributions of the Pd₃Pb NCs (**Figure 2e,g**). When DTAC was replaced with benzoic acid, Pd₃Pb SCNCs was obtained (**Figure 2b, 2d, 2f and 2h**). As shown in **Figure S10c**, the Pd₃Pb SCNCs have an average edge length of 12.5 nm (13.8 nm by the Scherrer-equation). The composition ratio of Pd/Pb is $74.9 \pm 0.2/25.1 \pm 0.2$, as revealed by the ICP-AES, which is consistent with the TEM-EDX ($73.8 \pm 0.6/26.2 \pm 0.6$) (**Figure S8f**) and SEM-EDX ($73.7 \pm 0.5/26.3 \pm 0.5$) results (**Figure S10d**). The lattice spacings of 0.400 and 0.398 nm, corresponding to the (100) plane of cubic phase Pd₃Pb intermetallic structure were observed (**Figure 2d**). The element distributions in the Pd₃Pb SCNCs were revealed by the HAADF-STEM-EDX elemental mapping and STEM line scanning, where the Pd and Pb were distributed evenly through the whole SCNC (**Figure 2f,h**).



Figure 2. (a) TEM image, (c) HRTEM image, (e) corresponding line-scans of the Pd₃Pb NCs and (g) HAADF-STEM image and elemental mappings of Pd₃Pb NCs. (b) TEM image, (d) HRTEM image, (f) corresponding line-scans of the Pd₃Pb NCs and (h) HAADF-STEM image and elemental

mappings of the Pd₃Pb SCNCs. The inset in (a) and (b) are the 3D structure models of the Pd₃Pb NCs and Pd₃Pb SCNCs.

The hydrogenation of alkynes to alkenes is of great significance in the production of polyolefins as well as synthetic rubbers.²⁹ Nanostructured Pd is considered to be one of the most active hydrogenation of alkynes catalysts,²² while it shows low selectivity for alkenes due to overhydrogenation. To this end, the created Pd₃Pb NCs, SCNCs and CNCs with modulated concave degrees were adopted as catalysts for alkyne hydrogenations for investigating whether the Pd₃Pb intermetallic nanomaterials with concave feature can potentially result in the enhanced semihydrogenation performance (**Figure 3a**).

Before starting catalytic reaction, the Pd₃Pb nanomaterials were loaded on commercial carbon (**Figure S11**). The calcining process was carried out to remove the organic compounds on the surface, as well as expose the active components of the catalyst particles, where the intermetallic Pd₃Pd phase of all the Pd₃Pb nanomaterials were largely maintained (**Figure S12-13**). **Figure 3b-e** shows the time profile for the hydrogenation of phenylacetylene by using Pd₃Pb nanomaterials with different concave degree supported on C at 50 °C under 2 atm H₂. All the performances of different Pd₃Pb nanomaterials are compared with that of 10% Pd/C. As shown in **Figure 3b**, Pd₃Pb NCs catalyst shows a very high styrene selectivity of > 99%, whereas a low conversion of phenylacetylene (28%). On the contrary, the Pd₃Pb SCNCs and Pd₃Pb CNCs achieve almost complete conversion (> 99%) with high selectivity of 85.4% and 94.6% toward styrene, respectively (**Figure 3c,d**). It is notable that Pd₃Pb CNCs could greatly hinder the overhydrogenation of styrene and the 94.6% selectivity for styrene was maintained even when prolonging the reaction time to 5 h. In addition, the optimized Pd₃Pb CNCs exhibit the favorable semihydrogenation of phenylacetylene activity with the outstanding activity of 179.2 h⁻¹, 5.4, 10.5 and 8.1 times higher than those of the conventional Pd₃Pb

SCNCs (32.8 h^{-1}), Pd₃Pb NCs (17.0 h^{-1}) and 10% Pd/C (22.1 h^{-1}), respectively (**Table S1**). On the sharp contrast, for 10% Pd/C, a relative high conversion to styrene could be achieved, while the selectivity to styrene was very limited (**Figure 3e**). Therefore, the excellent selectivity of the created Pd₃Pb intermetallic nanomaterials is unique and valuable because many conventional catalysts including the Lindlar catalyst cause the rapid overhydrogenation of alkenes into alkanes at a high conversion. The experimental results confirmed that introducing Pb to Pd was an efficient strategy for inhibiting overhydrogenation.



Figure 3. (a) Hydrogenation of phenylacetylene over different concave degree Pd-Pb catalysts and benchmark catalyst: (b) Pd₃Pb NCs, (c) Pd₃Pb SCNCs, (d) Pd₃Pb CNCs and (e) Pd/C. Reaction conditions: phenylacetylene (0.1 mmol), ethanol (10 mL), H₂ (2 atm), 50 °C, catalysts (5 mg; 10% Pd/C, 5 mg).

Significantly, the enhanced semihydrogenation performance of the Pd₃Pb intermetallic CNCs can also be expanded to other alkynes. As shown in **Table 1**, all the different alkynes can be readily transformed into the corresponding alkenes with excellent conversions at high selectivity. The performances of the Pd₃Pb nanomaterials were further investigated by measuring the stability as a function of the reaction cycles. In all the Pd₃Pb nanomaterials, 98% conversion of the Pd₃Pb CNCs can be maintained even after five cycles (**Figure 4a**). In addition to the outstanding conversion and high styrene-selectivity (94.6%) of the Pd₃Pb CNCs, their styrene selectivity is also very stable with only 0.7% decay after five cycles (**Figure 4b**), showing their unusual structural stability in the mild reaction conditions. No significant loss in catalytic conversion and selectivity is also observed for all Pd₃Pb catalysts. While the structure and composition of the Pd₃Pb CNCs/C can be preserved (**Figures S14**), the 10% Pd/C is not very stable with severe aggregation after five cycles (**Figure S15**).

Er	ntry Substrate	Time	Alkyen	Alkene	
		[min]	conv.[%]	sel. [%]	
1	1-Octyne	300	99.9	96.3	
2	1-Phenyl-1-propyne	300	94.8	92.9	
3	Diphenylacetylene	300	99.9	92.1	
4	1-Phenyl-1-pentyne	300	98.2	90.6	
5	4-Ethynyltoluene	300	92.7	87.3	

Table 1. Semihydrogenation of alkynes using intermetallic Pd₃Pb CNCs/C.^[a]

^[a]Reaction conditions: substrate (0.1 mmol) and 3.04 wt% of Pd₃Pb intermetallic CNCs in 10 mL

ethanol were stirred at 50 °C under 2 atm H₂ pressure.



Figure 4. (a) phenylacetylene conversion and (b) styrene selectivity for five rounds of successive reactions over the as-obtained catalysts.

Generally, the Pd surface atoms cannot selectively absorb phenylacetylene and styrene, and the Pb atoms show weak ability for the activation of H₂ molecules and strong ability for poisoning the metallic Pd.^{21,24} Since the catalytic reactions mainly occur on surfaces of nanomaterials, we performed XPS experiments to investigate the surface properties of the Pd/C, Pd₃Pb NCs/C, Pd₃Pb SCNCs/C and Pd₃Pb CNCs/C for decoding the conversion and selectivity differences (**Figure 5 and Table S2**). As shown in **Figure 5a**, the Pd 3d_{5/2} peak of Pd₃Pb NCs/C (336.0 eV), Pd₃Pb SCNCs/C (336.0 eV) and Pd₃Pb CNCs/C (336.0 eV) shift to higher binding energy by 1.1 eV, 1.1 eV and 1.1 eV than Pd/C (334.9 eV), respectively.^{26,28,43} The results show that, compared with monometallic Pd the introduction of Pb into Pd can greatly modify the electronic structure of Pd due to the presence of intimate interactions between Pd and Pb. **Figure 5a,b** and **Table S2** show that Pd⁰ is the major form among the Pd-Pb catalysts. It should be pointed out that the Pd⁰/Pd²⁺ ratio of Pd₃Pb CNCs/C (7.7) is the highest of all the Pd₃Pb nanomaterials. Since the metallic Pd is active for semihydrogenation of alkynes,²⁰⁻²⁶ it is believed that the higher ratio of Pd⁰ in the Pd₃Pb nanomaterials results in higher conversion (99.9%) for semihydrogenation of alkynes (**Figure 5c**).

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The catalyst surface concentration of Pb and chemical state of Pb of the intermetallic nanomaterials were also analyzed. The fitting analysis shows the coexistence of Pb⁰ and Pb²⁺ among Pd₃Pb nanomaterials, where the peaks at about 142.2 eV and 137.4 eV correspond to Pb⁰ 4f_{5/2} and Pb⁰ 4f_{7/2}, and the peaks at about 144.0 eV and 139.0 eV belong to Pb²⁺ 4f_{5/2} and Pb²⁺ 4f_{7/2}, respectively (**Figure 5d** and **Table S2**). For Pd₃Pb SCNCs/C and Pd₃Pb CNCs/C, the higher ratio of Pb²⁺ is beneficial for improving styrene selectivity since the Pb²⁺ modified Pd prefers to poison the overhydrogenation of styrene (**Table S2**).²⁸ In addition, it revealed that the order for Pb/Pd molar ratio is the Pd₃Pb NCs (0.364) > Pd₃Pb CNCs (0.325) > Pd₃Pb SCNCs (0.307), similar to the tendency of styrene selectivity, where the higher ratio of Pb/Pd for Pd₃Pb CNCs/C (0.325) results in the higher styrene-selectivity (94.6%) (**Figure 5d-f**). All in all, the higher ratio of metallic state Pd results in the higher conversion for semihydrogenation of phenylacetylene and the higher ratio of Pb²⁺ and Pb/Pd contribute to higher styrene selectivity.



Figure 5. (a) Pd 3d XPS spectra, (b) Pd⁰/Pd²⁺ molar ratios, (c) phenylacetylene conversion, (d) Pb 4f XPS spectra, (e) Pb/Pd molar ratios and (f) styrene selectivity.

To illuminate the influence of the different surfaces on the performance of semihydrogenation of phenylacetylene, we used density functional theory (DFT) to calculate catalytic processes on different surfaces. Firstly, as shown in **Table S3** and **Figure S16**, the adsorption energies of H₂ on the (100), (110) and (111) surface are -0.41 eV, -0.15 eV and -0.28 eV, respectively. The adsorption energies of H on the (100), (110) and (111) surfaces are 0.01 eV, -0.29 eV and -0.52 eV. It can be seen from **Figure S16** that the dissociation of H₂ on Pd₃Pb (100) surface is endothermic by 0.43 eV.

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It indicates that the dissociation of H_2 on this surface is a little energetically unfavorable, which may not be beneficial for catalytic activity of hydrogenation reactions. In contrast, H_2 dissociation is energetically favorable on Pd₃Pb (111) and the (110) surface comes second.



Figure 6. Step-by-step hydrogenation mechanism of phenylacetylene to phenylethane on the Pd₃Pb (111) surface. Numbers in the parentheses indicate the barriers of elementary steps; Pb, grey; Pd, blue; C, green; H, yellow.

In order to further investigate the reaction mechanisms of hydrogenation of phenylacetylene on these different surfaces, the energy barriers on the (111) (110) (100) surfaces of Pd₃Pb were computed by transition states (TS) search. As shown in **Figure 6**, on the (111) surface, phenylacetylene tends to adsorb on two adjacent Pd atoms with adsorption energy of -1.23 eV, which promotes the hydrogenation of phenylacetylene. The kinetic barriers of the first two-step hydrogenation are calculated to be only 0.25 eV (TS1) and 0.29 eV (TS2) on the (111) surface, suggesting that the (111) surface of Pd₃Pb is highly active for the hydrogenation of phenylacetylene to styrene. The hydrogenation of styrene to the PhCHCH₃ intermediate is found to be the rate-

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determining step in the whole processes of the hydrogenation of phenylacetylene, with a barrier of 0.58 eV. The desorption energy of styrene on the Pd₃Pb (111) catalyst surface is 1.18 eV, which is much higher than its hydrogenation barrier. This result indicates that the Pd₃Pb (111) surface is very active for the hydrogenation of styrene to phenylethane. On the other hand, on (110) surface (see Figure S17), the energy barriers of the first two-step hydrogenation are calculated to be only 0.41 eV (TS1) and 0.22 eV (TS2), which suggests that the (110) surface of Pd₃Pb is also highly active for the hydrogenation of phenylacetylene to styrene. However, the barrier of TS3 is 0.91 eV which is a little larger than the desorption energy of styrene (0.86 eV). It indicates that there is a competition between the desorption of styrene and the hydrogenation to PhCHCH₃. Compared with (111) surface, (110) surface shows a higher hydrogenation selectivity. Lastly, the reaction mechanisms on (100) surface was shown in Figure S18. The energy barriers of TS1 and TS2 were 0.67 eV and 0.75 eV, which are much larger than those on the (111) surface (0.25 eV, 0.29 eV) and (110) surface (0.41eV, 0.22 eV). It suggests that (100) surface shows a lower activity for the hydrogenation of phenylacetylene to styrene, which may result from the unfavorable dissociation of H_2 on (100) surface. Besides, the desorption energy of styrene is 1.22 eV, which almost equals to the barrier of TS3 (1.23 eV), which also shows a competition between the desorption and hydrogenation of styrene. That is to say, the (100) surface shows a higher selectivity than (111) and (110) surface. Therefore, the three different surfaces have different catalytic performances: the (111) surface shows the best catalytic activity but the lowest selectivity; the (100) surface shows the highest selectivity but the lowest catalytic activity; but the (110) surface shows an idealized activity for hydrogenation from phenylacetylene to styrene and an optimum selectivity. This trend is consistent with the general rule that the surface with lower catalytic activity has a higher selectivity.

Furthermore, we found that the activity and selectivity of the catalytic hydrogenation of phenylacetylene are closely related to the distribution of Pd and Pb atom on the surface. As shown in **Figure S19**, the atomic distribution of the (100), (110), and (111) surface of Pd₃Pb were displayed. It

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can be seen that on the (100) surface of Pd₃Pb, there are four Pb atoms around the Pd atom. The Pd atom on the (110) surface is surrounded with two Pd atoms and two Pb atoms. On the (111) surface, the central Pd atom is surrounded with four Pd atoms and two Pb atoms. It is easy to find that the atomic distribution of the surface can greatly affect the catalytic performance and selectivity; for instance, on (100) surface the Pd was surrounded with four Pb atoms which are inert element, and the (100) surface also shows the lowest catalytic performance but has the highest selectivity among the three surfaces. For the (110) and (111) surface, there are more Pd atoms around the central Pd atom in (111) surface than those of (110) surface, indicating higher activity and lower selectivity for (111) surface. Based on this trend, we can speculate that there may be more Pd atoms distributed on the surface of SCNCs and CNCs, than those of NCs, because the conversion of phenylacetylene is higher on the SCNCs and CNCs surface. At the same time, compared with the surface of SCNCs, the surface of CNCs would have higher concentration of Pb, because CNCs show a higher selectivity than SCNCs.

CONCLUSIONS

To summarize, we have demonstrated a wet-chemical strategy to create series of intermetallic Pd₃Pb NCs with different concave degree that can be used as efficient catalysts for semihydrogenation of alkynes with both superior activity and excellent selectivity. The intermetallic Pd₃Pb CNCs exhibited excellent catalytic performance for phenylacetylene semihydrogenation with 99.9% conversion and 94.6% selectivity, better than other Pd₃Pb nanomaterials as well as the commercial Pd/C, making it among the most active catalysts for alkynes semihydrogenation reported to date. Simultaneously, the Pd₃Pb CNCs exhibited high stability with minor decay after five cycles. XPS results show that the higher ratio of metallic state Pd results in the higher conversion for phenylacetylene semihydrogenation and the higher ratios of Pb/Pd and Pb²⁺ contribute to higher

styrene selectivity. The DFT calculations reveal that the excellent activity and high selectivity of the acetylene semihydrogenation are due to the favorable adsorption energy of phenylacetylene and desirable desorption energy of styrene on the Pd₃Pb surface. We expect our study will stimulate the rational design of efficient Pd-based nanomaterials with well-defined size, structure, composition and phase for semihydrogenation reactions.

ASSOCIATED CONTENT

Supporting Information. Figure S1-19&Table S1-3. This material is available free of charge via the Internet at http://pubs.acs.org.

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