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Fu-min Li, Qi Shao, Mancheng Hu, Yu Chen, and Xiaoqing Huang ACS Catal., Just Accepted Manuscript • DOI: 10.1021/acscatal.8b00347 • Publication Date (Web): 19 Mar 2018 Downloaded from http://pubs.acs.org on March 19, 2018

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Hollow Pd-Sn Nanocrystals for Efficient Direct H₂O₂ Synthesis: The Critical Role of Sn on Structure Evolution and Catalytic Performance

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ABSTRACT: The development of efficient catalysts with high activity and selectivity for the direct synthesis of H_2O_2 from H_2 and O_2 is highly desirable yet challenging. Herein, a series of Pd-Sn bimetallic nanocrystals with hollow structure have been successfully created as highly active and selective catalysts for direct H_2O_2 synthesis. We found that the introduction of Sn played an important role on the morphology evolution and composition control of the hollow Pd-Sn nanocrystals. Significantly, after rapid thermal treatment, the obtained hollow Pd-Sn/TiO₂ catalysts can deliver complete inhibition of H_2O_2 decomposition/hydrogenation, resulting in a large activity enhancement for the H_2O_2 production. The H_2 selectivity enhancement of hollow Pd-Sn/TiO₂ catalysts for the direct H_2O_2 synthesis can be attributed to the presence of PdO, the ensemble effect between the Pd and Sn as well as the interface effect of Pd/SnO_x and PdO/SnO_x. **KEYWORDS:** H_2O_2 production, hollow structure, activity, selectivity, interface effect

INTRODUCTION

Hydrogen peroxide (H₂O₂) is an important chemical oxidizing reagent and disinfectant, which is widely used in medicine, military and industry.¹⁻⁷ Currently, the main synthetic methods of H₂O₂ include electrolysis, anthraquinone process, direct hydrogenation of oxygen (O_2) , isopropanol oxidation method and so on. While the anthraquinone process is widely used in industrial production,^{6, 8-9} it requires abundant poisonous organic compounds.¹⁰ Recently, due to the simple process, low energy consumption as well as limited environment pollution, the direct hydrogenation of O₂ to H₂O₂ with hydrogen (H₂) has received increasing research interests.¹¹⁻¹³ While palladium (Pd) is considered to be a superior catalyst for the H₂O₂ production by direct hydrogenation approach, it is also very active towards the H₂O₂ decomposition/hydrogenation and the H. combustion due to the low reaction selectivity, which largely reduces the utilization of H, and the efficiency of the catalysts.¹⁴⁻¹⁵ To this end, a great deal of attentions have been directed to improve the activity and H, selectivity of Pd-based catalysts for the H₂O₂ production. Several conventional strategies, including controlling the Pd oxidation state, adding H⁺ and/or halogen ions to the reaction medium, and forming Pd-based bimetallic catalysts, have been developed to boost the direct H₂O₂ synthesis catalysis.¹⁶⁻¹⁷ Nevertheless, these approaches are still not very efficient, since they can also lead to new problems, such as low catalytic stability, difficult product

purification, as well as high costs (i.e., Pd-Au bimetallic catalyst). Thus, it is still a challenge to achieve effecient Pd-based catalysts for the direct H_2O_2 production.

Recently, Hutchings and co-workers have synthesized a series of Pd-Sn catalysts by the impregnation-reduction method with enhanced activity and H₂ selectivity for the direct H₂O₂ production, promising to replace the expensive Pd-Au catalysts.¹⁸ However, their thermal treatment process are multi-step and time-consuming, and the activity remains to be further improved. Here, we reported the successful creation of hollow Pd-Sn bimetallic alloy nanocrystals supported on TiO₂ with more efficient direct H₂O₂ synthesis. Through a simple rapid thermal treatment process, the degradation of H₂O₂ could be completely inhibited. When water was used as the reaction medium, high H₂ selectivity (80.1%) and excellent activity (120.1 mol kg_{cat}⁻¹ h⁻¹) could be achieved simultaneously.

RESULTS AND DISCUSSION

Hollow Pd-Sn nanocrystals were obtained through a facile solvent-thermal method. Their composition and morphology were readily controlled by tuning the amount of SnCl₂ supplied and the reaction temperature. Specifically, hollow Pd₂Sn, Pd₄Sn, and Pd₅Sn nanocrystals were synthesized at 140 °C by using different amounts of SnCl₂. As a contrast, the solid Pd₆Sn nanocrystals were obtained under the same synthetic condition of hollow Pd₂Sn except for a lower reaction temperature of 120 °C. The ratio of Pd to Sn was determined by the scanning

electron microscope energy-dispersive X-ray spectroscopy (SEM-EDX) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Figure S1 and Table S1). The typical transmission electron microscopy (TEM) images of four Pd-Sn nanocrystals show their particle sizes are about 10~15 nm (Figure 1A-D). It reveals that the Pd₂Sn, Pd₄Sn, and Pd₅Sn nanocrystals have bright center and dark edge, suggesting the presence of hollow structure (yield > 60%), while the Pd₆Sn nanocrystals are solid. The powder X-ray diffraction (PXRD) patterns exhibit that the Pd₄Sn, Pd₅Sn, and Pd₆Sn nanocrystals have four distinct diffraction peaks, which can be readily indexed to the (111), (200), (220), and (311) reflections of face-centered cubic (fcc) crystal (Figure 1E). Compared with standard fcc Pd diffraction data (JCPDS: 87-0643), these diffraction peaks shift towards the lower angle, which can be attributed to the insertion of Sn with the larger atomic radius into the Pd lattice. The lattice expansion indicates the successful formation of Pd-Sn alloy. Meanwhile, the shift of diffraction peaks increases with increasing Sn content, which is evident at the high angle. Moreover, the hollow Pd₂Sn nanocrystals with intermetallic phase (JCPDS: 89-2057) has been obtained, as revealed by the PXRD pattern (Figure 1E).

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Figure 1. TEM images of (A) Pd_2Sn , (B) Pd_4Sn , (C) Pd_5Sn , and (D) Pd_6Sn nanocrystals. (E) PXRD patterns of these four Pd-Sn nanocrystals. HRTEM images of the typical (F) hollow and (G) solid Pd_2Sn nanocrystals. (H) HAADF-STEM image and EDX elemental mappings of Pd_2Sn nanocrystals. Pd: green, Sn: red. (I) EDX line scannings of Pd_2Sn nanocrystals.

The in-depth characterizations and discussions were implemented on hollow Pd₂Sn nanocrystals as a representative sample. High resolution transmission electron microscopy (HRTEM) image shows the hollow nanocrystals have a lattice spacing of 0.229 nm, which corresponds to (013) lattice spacing of intermetallic Pd₂Sn crystal (JCPDS: 89-2057, Figure 1F). In addition, solid products have a lattice spacing of 0.236 nm that matches (210) lattice spacing of intermetallic Pd₂Sn crystal (JCPDS: 89-2057, Figure 1G). High-angle annular dark-field scanning TEM (HAADF-STEM) image and EDX elemental mapping patterns, in consistenting with the PXRD result, demonstrate that the Pd element and the Sn element have even distributions (Figure 1H), which confirms the formation of Pd₂Sn intermetallic nanomaterials. The EDX line scanning of the hollow Pd₂Sn nanocrystals displays the characteristics of the hollow structure (Figure 1I), which can improve the utilization of Pd.¹⁹⁻²³

To explore the formation process of hollow Pd₂Sn intermetallic compound, the intermediate products obtained at different reaction times were investigated. The time-dependent TEM images and PXRD patterns were collected and analyzed (Figure 2A and B). Based on these TEM images, it reveals that hollow nanocrystals appear in the reaction time between 40 and 80 min, and the proportion of these hollow nanocrystals increases during the subsequent reaction. The phase transformation was decoded by the PXRD patterns. In the initial stage of the reaction (20 min), the Pd(II) precursor is reduced to Pd nanocrystals. Then, the Sn(II) precursor is reduced and Pd nanocrystals begin to transform into Pd-Sn nanocrystals at 40 min, which can be evidenced by a significant shift of diffraction peak. In the subsequent reaction time (from 80 to 240 min), Pd-Sn nanocrystals gradually evolve into intermetallic Pd₂Sn nanocrystals. Therefore, it can be found that 40 min is an important reaction time node.

То clarify the formation mechanism, the crystallographic texture of intermediate products obtained at 40 min was further investigated by PXRD (Figure 2C). After deconvolving the strongest (111) diffraction peak, two small diffraction peaks were revealed, indicating two kinds of intermediate Pd-Sn products, including Sn-deficient and Sn-riched Pd-Sn alloys. Previous literatures demonstrated that Pd could be etched by halogen ions and oxygen in reaction system, followed by the formation of corrosion site.²⁴⁻²⁶ Meanwhile, the reduction of Sn²⁺ ions occured at the corrosion site, which would expand into a hole and eventually form a hollow structure.²⁴ In other words, the oxidative etching process of Pd and the reduction of Sn²⁺ ions synergistically led to the formation of hollow structure. Based on the PXRD results, we can conclude that the Sn-deficient Pd-Sn alloy intermediate products eventually transformed into hollow Pd₂Sn intermetallic nanocrystals because of the subsequent reduction of Sn²⁺ ions. In contrast, the Sn-riched Pd-Sn alloy intermediate products will evolve into solid nanocrystals owing to the lack of Sn²⁺ reduction process. In addition, a high temperature (140 °C) and more SnCl₂ feed can provide sufficient energy and raw materials for the oxidative etching process, respectively.25, 27 Therefore, when the lower temperature (120 °C) or less SnCl, feed is applied, only solid products can be obtained (Figure 1D and Figure S2).



Figure 2. Time-dependent morphology and composition evolution of Pd₂Sn nanocrystals based on (A) TEM images and (B) PXRD patterns. (C) Enlarged PXRD pattern obtained at 40 min.

The hollow Pd2Sn nanocrystals supported on TiO2 nanocrystals $(Pd_{3}Sn/TiO_{3})$ were chosen as а representative sample to investigate the activity and selectivity of Pd-Sn nanocrystals for the direct H₂O₂ production (Figure S₃A). Detailed procedures for the direct H₂O₂ production are shown in the experimental section. Herein, a mixed solution of methanol and water was used as the reaction medium. By regulating the ratio of methanol to water, the highest reactivity is achieved at a methanol/water ratio of 8 : 2 (Figure 3A). After that, hollow Pd₂Sn nanocrystals loaded on different supports were also prepared (Figure S4) and invsetiaged for their catalytic activities. The experimential results show that hollow Pd₂Sn/TiO₂ catalyst has the best catalytic activity (Figure 3B), which can be attributed to the promoting effect of TiO₂ for the direct H_2O_2 production,²⁸⁻³² such as the improved charge transport, owing to Ti³⁺ species and Ovacancy defects in bulky TiO2.33 Under this optimized synthesis condition, the performances of a series of Pd-Sn/TiO₂ catalysts (Figure S₃B-D), commercial Pd/C and Pd/TiO₂ catalysts (Figure S5) were also evaluated, where the hollow Pd₅Sn/TiO₂ exhibits the highest activity of 98.4 mol kg_{cat}^{-1} h⁻¹ (Figure 3C). Compared with Pd/TiO₂ catalyst, the enhanced activity of Pd-Sn/TiO₂ indicates that the introduction of Sn improves the activity of Pd for the the direct H_2O_2 production. The rate of H_2O_2 degradation (i.e., the decomposition and hydrogenation of H₂O₂) on various catalysts was further investigated, which showed that all catalysts exhibited high activity for the conversion of H_2O_2 to H_2O (Figure 3C), which is detrimental to the H₂ selectivity. In order to inhibit the

conversion of H_2O_2 to H_2O , a thermal treatment process was applied to these catalysts, and hollow Pd_5Sn/TiO_2 catalyst was selected as the candidate due to its highest activity. Since the long time thermal treatment leads to the particle aggregation (Figure S6), the treatment process was carried out at high temperature (350 °C) for a short time so as to largely maintain the morphology and composition of these nanocrystals (Figure S7). With the increase of treatment time, the reaction of H_2O_2 to H_2O is effectively inhibited, while the rate of H_2O_2 production increases gradually (Figure 3D). When the treatment time is 6 min, the degradation rate of H_2O_2 is decreased to o mol kg_{cat}⁻¹ h⁻¹, and the activity of H_2O_2 production reaches to 160.2 mol kg_{cat}⁻¹ h⁻¹.



Figure 3. (A) H_2O_2 productivity of Pd_2Sn/TiO_2 in different reaction media. (B) H_2O_2 productivity of Pd_2Sn supported on different carriers. (C) H_2O_2 productivity and degradation of different catalysts under optimized conditions. (D) H_2O_2 productivity and degradation of Pd_5Sn/TiO_2 under different processing times.

Although all Pd-Sn/TiO, catalysts can also exhibit similar activity change (i.e., the H₂O₂ production enhancement and H₂O₂ degradation inhibition) after the rapid thermal treatment (Figure 4A), all Pd-Sn/TiO₂ catalysts show low H₂ selectivity of about 15% (Figure S8). Considering the complete inhibition of H₂O₂ degradation on these catalysts, the low H₂ selectivity must be attributed to the combustion of H₂. To improve the H₂ selectivity, the ratio of water to methanol was reconsidered. The results show that the H₂ selectivity can reach to 80.1% in pure water medium with the H₂O₂ production of 120.1 mol kg_{cat}^{-1} h⁻¹ at hollow Pd₅Sn/TiO₂ catalyst (Figure 4B), which is superior to most of the reported values (Table S2).^{12, 18, 34-36} Compared with the mixed medium, the pure water solvent improves the reaction selectivity, but the catalytic activity is also reduced. Previous reports showed that the solubility of H₂ and O₂ in water is far less than that in methanol.³⁷ As a result, the reduced reactant concentration loses some catalytic activity but also changes reactive mode of H₂ and O2 with active sites, resuluting in the selectivity ehancement. Moreover, hollow Pd₅Sn/TiO₂ catalyst can exhibit promising stability in both the methanol/water mixture and pure water (Figure 4C). After 5 reaction

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rounds, the catalytic activity remains more than 80% of the initial activity. Since TEM image and EDX analysis show no obvious changes in the morphology and composition of Pd_5Sn nanocrystals (Figure S9), the deactivation may originate from the mass loss of catalysts due to the multiple centrifugation.



Figure 4. (A) H_2O_2 productivity and degradation of different catalysts after rapid thermal treatment at 350°C for 6 min. (B) H_2 selectivity and H_2O_2 productivity of Pd_5Sn/TiO_2 in different reaction media. (C) Recycling performance of Pd_5Sn/TiO_2 in the methanol/water mixture and pure water.

Since the H_2O_2 generation reaction occurred on the surface of catalyst, the surface-sensitive X-rav photoelectron spectroscopy (XPS) was used to reveal the structure-activity relationship of these Pd-Sn/TiO, catalysts.38-43 Considering Pd atoms were the main active sites for the the direct H₂O₂ production, Pd 3d XPS signal was analyzed firstly. For Pd₅Sn/TiO₂, the proportion of Pd(o) drastically reduces after the thermal treatment (Figure 5A), which has a major contribution for the H_2O_2 degradation inhibition.¹³ The evolution of the Pd chemical state is also observed in other Pd-Sn/TiO₂ (Figure 5B). Since the thermal treatment induces that the bonding of both O and Sn atoms on Pd surface, the electronic structure of Pd will be changed. Considering that the difference between the electronegativity of O (X=3.44) and Pd (X=2.20) is much greater than that of Sn (X=1.96) and Pd (X=2.20),44 the influence of Sn on the Pd electronic structure may be very weak. Combined with previous experimental results, it could be found that the introduction of Sn further strengthens the inhibition, which should be attributed to the ensemble effect of Pd-Sn alloy.¹⁶ Benefiting from this inhibition, the H₂O₂ production rate on all the catalysts is improved after the thermal treatment. The XPS data of Sn element show that Sn exists mainly in the form of SnO_x in the original Pd₅Sn/TiO₂ (Figure 5C). Subsequent thermal treatment results in the increased proportion of SnO_x. This evolution also occurs on other Pd-Sn/TiO₂ (Figure S10). Compared to Pd/TiO_2 , the introduction of SnO_x fundamentally enhances the activity of Pd-based catalysts for the H₂O₂ production. Furthermore, considering that SnO_x is active in adsorbing O₂ but inefficient in O²O bond

scission,⁴⁵⁻⁴⁷ a reasonable interface effect is established to explain the enhanced performance (Figure 5D). Specifically, Pd or PdO can activate both H₂ and O₂, but its high activity often results in O₂ splitting, which is not beneficial for producing H_2O_2 . The SnO_x can achieve weak activation of O_2 without breaking the O-O bond. Therefore, when SnO_x adsorbs an O₂ and Pd or PdO near SnO_x activate a H₂, H₂O₂ will rapidly generate at Pd/SnO_x and PdO/SnO_x interfaces. In this work, CTAB is used in Pd-Sn nanocrystals synthesis, and Br⁻ has been identified to enhance catalytic performance for the H₂O₂ production.³⁷ Therefore, XPS analysis was used to detect the presence of Br⁻. The results show that there is no Br on the surface of Pd₅Sn/TiO₂ (Figure S11), which also proves once again that Sn plays a key role in improving catalytic performance of Pd-Sn/TiO₂ catalysts for the H_2O_2 production.



Figure 5. (A) XPS patterns of Pd ₃d of Pd₅Sn/TiO₂ before and after a thermal treatment within a short time. (B) The proportion of Pd(o) based on XPS results for several Pd-Sn/TiO₂ before and after a thermal treatment within a short time. (C) XPS patterns of Sn ₃d of Pd₅Sn/TiO₂ before and after a thermal treatment within a short time. (D) The illustration of the interface effect in Pd-Sn catalysts.

CONCLUSIONS

To summarize, we have successfully synthesized a series of Pd-Sn bimetallic nanocrystals with hollow or solid structure, which closely related to the amount of $SnCl_2$ supplied and the reaction temperature. Through a facile rapid thermal treatment, the complete inhibition of H_2O_2 degradation has been achieved on these Pd-Sn/TiO₂; among them, hollow Pd₅Sn/TiO₂ exhibited the highest activity for the direct H_2O_2 production. By controlling the reaction medium, 80.1% H_2 selectivity and 120.1 mol kg_{cat}⁻¹ h⁻¹ activity could be obtained for the hollow Pd₅Sn/TiO₂. The enhanced activity of hollow Pd-Sn/TiO₂ can be attributed to the existance of PdO, the ensemble effect of hollow Pd-Sn, as well as the interface effect of Pd/SnO_x and PdO/SnO_x interfaces. Our study presents a promising Pd-based nanostructure for direct

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 H_2O_2 synthesis catalysis with excellent activity and selectivity.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was financially supported by the Ministry of Science and Technology (2016YFA0204100, 2017YFA0208200), the National Natural Science Foundation of China (21571135), Young Thousand Talented Program, the start-up supports from Soochow University, the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), Fundamental Research Funds for the Central Universities (GK201602002 and 2016TS044).

Supporting Information.

This material is available free of charge via the Internet at http://pubs.acs.org. Experimental details, results of TEM, EDX, selectivity, XPS, and ICP-AES, and comparison of performances.

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