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Xinyao Shan,<sup>a,b</sup> Ning Sui,<sup>a,b</sup> Wengang Liu,<sup>a</sup> Manhong Liu,<sup>a</sup> and Jian Liu<sup>a,\*</sup>

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In-Situ Generation of Supported Palladium Nanoparticles from a Pd/Sn/S Chalcogel and Applications in 4-Nitrophenol Reduction and Suzuki Coupling

Abstract: Supported ultrafine palladium nanoparticles with uniform distribution exhibit remarkable catalytic capabilities in various applications. Obtaining size-controlled Pd nanoparticles on a support remains challenging and here we present a one-step *insitu* route to well-defined Pd nanoparticles through reduction of a Pd-containing chalcogel (Pd/Sn/S) with tunable size distribution. The spacings of the Pd nanoparticles on the chalcogel can be controlled by using with antimony containing chalcogels (Pd-Sb/Sn/S). The catalytic performance of Pd nanoparticles supported on the chalcogel surface was assessed in 4-nitrophenol reduction and Suzuki-Miyaura coupling reaction, and found to exhibit good activities and robust stability. This *in-situ* and one-step synthetic method could be further extended to synthesize a series of noble metal nanoparticles for a variety of applications.

Synthesizing ultrafine noble metal nanoparticles (NPs) with controllable size distribution is important to uncover their superior activity and stability in various catalytic applications.<sup>1-7</sup> Host materials are generally employed to support the nanoparticles, inhibit aggregation, simplify separation steps after the reaction and deliver optimized catalytic behavior and stability. Various classical supporting materials have been developed including porous silica, carbon, carbon nitride, graphene, metal oxide, polymers, and non-classical metal organic frameworks, and covalent organic frameworks etc.8-15 However, controllable regulation of NPs size and dispersion is still an outstanding problem which often derives from weak interactions between the supports and metal NPs. Therefore, it is imperative to develop novel chemical routes to prepare ultrafine NPs with high stability and narrow size distribution simultaneously.

The in-situ formation of the supported NPs is highly desirable for catalytic applications.<sup>16-19</sup> Shumaker-Parry and co-workers reported that the noble metal precursors incorporated in a polymer matrix can be reduced to anchor Au, Pt, or Pd NPs at the polymer-diamond surface.<sup>20</sup> Zhang and co-workers reported the synthesis of ultrafine and highly dispersed Pt or Pd NPs on covalent organic framework.<sup>21</sup> Stair and co-workers reported the use of atomic layer deposition technique to deposit the Pt NPs onto a series of oxides for CO oxidation and water-gas-shift reactions.<sup>22</sup> Chalcogels are a new class of aerogels composed of metal chalcogenide frameworks, offering numerous exciting properties relevant to catalysis, adsorption, separations, environmental remediation, etc.23-25 Similar to MOF,<sup>26</sup> a series of metal ions acting as the metal centers and thioanions such as  $[SnS_4]^{4-}$  as the linking building blocks are used to synthesize a broad variety of chalcogels through metathesis reactions.<sup>27</sup> We previously reported a synthesis strategy that can simultaneously address both the dispersion and nanointerface by in-situ partly reducing the metal species in the chalcogel backbone to obtain the supported Pt NPs.<sup>28</sup> Because Pd NPs are useful for promoting and catalyzing C-C coupling reactions, including Heck, Suzuki and Stille couplings, 29-32 it is therefore of great significance to develop active and stable Pd NPs catalysts.33

Herein, we report the facile synthesis of ultrafine and welldispersed Pd NPs supported on a chalcogel matrix, motivated by our previous work.<sup>28</sup> Due to the flexibility of the chalcogel synthesis, the Pd content could be tailored by varying the amount of antimony dopant. The particle size distribution and loading density of the Pd NPs could be adjusted accordingly. The dispersed Pd NPs supported in partly reduced chalcogel were

<sup>&</sup>lt;sup>a.</sup> College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P.R. China, E-mail: <u>liujian@qust.edu.cn</u>

b. These authors contributed equally.

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confirmed by high-resolution transition electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and elemental mapping. The catalytic behavior of the chalcogelsupported Pd NPs were investigated in Suzuki-Miyaura coupling reaction and 4-nitrophenol reduction.



Scheme 1. Schematic illustration of growing Pd NPs from chalcogels.



Figure 1. (a) HAADF-STEM image and (b-e) STEM-EDS mapping of composition elements in reduced chalcogel.

The Pd based chalcogel was synthesized through the metathesis reaction between  $Pd(CH_3COO)_2$  and  $Na_4SnS_4\cdot 14H_2O$  in formamide.<sup>28</sup> Since  $K_2(SbC_4H_2O_6)_2 \cdot 0.5H_2O$  could also react with  $Na_4SnS_4$ ·14H<sub>2</sub>O to form  $Sb_4Sn_3S_{12}$  chalcogel,<sup>34</sup> diluting with Sb could control the content and dispersion of Pd in the hybrid chalcogel matrix.<sup>35, 36</sup> The initial raw ratios of Pd versus Pd+Sb for forming chalcogels were set at 1, 0.4, 0.2 and 0.05, respectively. After left standing for certain time in organic solvent, the gelated chalcogel monolith were ready for washing and for further characterizations. Area-averaged compositions of the pristine chalcogels from EDS analysis indicate an empirical formula close to "PdSn<sub>1.2</sub>S<sub>3.5</sub>", "PdSb<sub>2.9</sub>Sn<sub>0.7</sub>S<sub>5.8</sub>", "PdSb\_{5.8}Sn\_{0.85}S\_{10.69}" and "PdSb\_{32.7}Sn\_{4.7}S\_{52.2}", respectively (See Figure S1 of Supporting Information, abbreviated as SI in the following context). The elemental compositions agree well with the expected values. For simplicity, the pristine chalcogels are abbreviated according to the initial ratios as  $Pd_xSb_{1-x}$ -SnS (x=1, 0.4, 0.2, 0.05) in the following context.



Figure 2. TEM images and corresponding size distribution profiles of Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub> (x=1, 0.4, 0.2 and 0.05) chalcogel: a-c, Pd-SnS<sub>reduced</sub>; d-f, Pd<sub>0.4</sub>Sb<sub>0.6</sub>-SnS<sub>reduced</sub>; g-i, Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub>; j-l, Pd<sub>0.05</sub>Sb<sub>0.95</sub>-SnS<sub>reduced</sub>.

The Pd NPs supported on reduced chalcogel were prepared by reducing the pristine  $Pd_xSb_{1-x}$ -SnS (x=1, 0.4, 0.2, and 0.05) chalcogel with NaBH<sub>4</sub>, as illustrated in Scheme 1.<sup>28</sup> As seen from Figure 1a, the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) analysis of the reduced chalcogel shows uniform Z-contrast (proportional to atomic number), indicating Pd well distributed in the chalcogel. The energy dispersive X-ray spectroscopy (EDS) elemental mapping further reveals that all the elements (i.e., Pd, Sb, S, and Sn) distribute uniformly within reduced chalcogels. (See Figure 1 and Figure S2-3 of SI). Scanning electron microscopy energydispersive X-ray spectroscopy (SEM-EDS) mapping images (Figure S4-5 of SI) further confirm the homogeneous distribution of composed elements in Pd-SnS<sub>reduced</sub> and Pd<sub>0.05</sub>Sb<sub>0.95</sub>-SnS<sub>reduced</sub> chalcogel in large area. The inductively coupled plasma (ICP) analysis shows that the Pd content in Pdand Pd<sub>0.4</sub>Sb<sub>0.6</sub>-SnS<sub>reduced</sub>,  $Pd_{0.2}Sb_{0.8}$ - $SnS_{reduced}$ SnS<sub>reduced</sub>,  $Pd_{0.05}Sb_{0.95}$ -SnS<sub>reduced</sub> is 28.33, 9.51, 5.15 and 0.98 wt%, respectively. The obtained Pd ratio among four reduced chalcogels are comparable with the raw ratio (1:0.4:0.2:0.05), indicating the negligible leaching of Pd species during reduction process.

By adjusting the ratio of Sb and Pd in the precursor chalcogel, a series of Pd NPs with tunable sizes in a range of 1.8-4.5 nm were synthesized (See the gelation process in Figure S6-7 of SI). Transmission electron microscope (TEM) images of Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub> (x=1, 0.4, 0.2, 0.05) confirm the presence of uniformly distributed Pd NPs on the chalcogel surface (see Figure 2 and Figure S8 of SI). Across the Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub> (x=1, 0.4, 0.2, 0.05) chalcogel series, the size and loading density of the as-obtained Pd NPs decreases as a function of x. The HR-TEM images are shown in Figure 2b, e, h and k, respectively. The lattice spacings of nanoparticles on the four kinds of reduced chalcogels are 0.23 nm, which correspond to the (111) spacings of metallic Pd. These TEM results confirm that the Pd<sup>2+</sup> species in the chalcogel network are directly reduced by the NaBH<sub>4</sub> to NPs which are then directly deposited on the remaining chalcogel surface. X-ray diffraction (XRD) patterns of pristine Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS

chalcogel and Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub> (x=1, 0.4, 0.2, 0.05) chalcogels (Figure S9 of SI) indicate the amorphous nature, consistent with

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the previous report.<sup>23</sup> As there is no discernible NPs in the pristine  $Pd_{0.2}Sb_{0.8}$ -SnS chalcogel (Figure S10 of SI), the observed Pd NPs in chalcogel skeleton result from the *in-situ* reduction of Pd<sup>2+</sup> from the Pd-chalcogel. As seen from Figure 2c, f, i and I, the NPs supported in Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub> (*x*=1, 0.4, 0.2, 0.05) chalcogel have an average size of 4.5, 4.0, 2.7 and 1.8 nm in diameter with narrow size distributions.



X-ray photoelectron spectroscopy (XPS) is used to investigate the oxidation states of the elements in both the pristine chalcogels and the reduced counterparts (Figure 3). As shown in Figure 3a, Pd 3d spectra of pristine  $Pd_{0.2}Sb_{0.8}$ -SnS chalcogel present the doublet peaks corresponding to Pd  $3d_{5/2}$  and Pd  $3d_{3/2}$ , respectively.<sup>37, 38</sup> No metallic Pd  $3d_{5/2}$  peak at around 335 eV is observed, suggesting the absence of Pd NPs in the pristine chalcogel. The spectrum of Pd 3d region for the pristine Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS chalcogel (Figure 3a) shows a doublet containing  $3d_{5/2}$  peak and  $3d_{3/2}$  at 336.8 and 342.11 eV, respectively.

From Plot (i) in Figure 3b, the Pd 3d<sub>5/2</sub> levels of Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> exhibit binding energies of 335.69 eV and 336.38eV, respectively, indicating that part of Pd<sup>2+</sup> was reduced into Pd<sup>0</sup>. Apart from the existence of Pd<sup>0</sup> species supported on the surface, a good fraction of Pd<sup>2+</sup> ions remain as linking metal ions with chalcogenide-based clusters ([SnS<sub>4</sub>]<sup>4-</sup>) for keeping chalcogel skeleton intact. In addition, the fitting analysis of Sn 3d spectra shows the coexistence of Sn<sup>0</sup>, Sn<sup>2+</sup> and Sn<sup>4+</sup> (Figure S11 of SI). The peaks at 485.6 eV, 486.2 eV and 486.8 eV are assigned to Sn<sup>0</sup>, Sn<sup>2+</sup> and Sn<sup>4+</sup>, respectively. The result suggests that the Sn<sup>4+</sup> in pristine chalcogel was partially reduced to Sn<sup>2+</sup> and Sn<sup>0</sup>. The oxidation state of Sb in the reduced chalcogel remains unchanged (Figure S12 of SI). The results of Pd and Sn binding energies of  $Pd_xSb_{1-x}$ -SnS<sub>reduced</sub> (x=1, 0.4, 0.2, 0.05) and pristine  $Pd_{0.2}Sb_{0.8}$ -SnS<sub>reduced</sub> are shown in Table S1 of SI, suggesting that the Pd NPs are successfully prepared.



**Figure 4.** (a) UV-vis spectra of 4-nitrophenol aqueous solution before (i) and after catalysis with (ii) Pd-SnS<sub>reduced</sub>, (iii) Pd<sub>0.4</sub>Sb<sub>0.6</sub>-SnS<sub>reduced</sub>, (iv) Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub>, (v) Pd<sub>0.05</sub>Sb<sub>0.95</sub>-SnS<sub>reduced</sub>, respectively; (b) typical optical images of reaction mixtures with Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> catalyst at 0 and 10 min; (c) recyclability of the Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> catalyst; (d) TEM image of recycled Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> chalcogel after reduction reaction of 4nitrophenol.

The Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub> is readily dispersed in water and other organic solvents for catalytic applications. The reduction of 4nitrophenol to 4-aminophenol with NaBH<sub>4</sub> is used to evaluate the catalytic activity of Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub> (x=1, 0.4, 0.2, 0.05), which serves an important role in industry.<sup>39</sup> This reaction is easily monitored by UV-vis spectroscopy. The blank experiment without chalcogel catalyst does not show any activity for 4nitrophenol reduction (Figure S13 of SI). With 15 mg of Pd<sub>x</sub>Sb<sub>1</sub>x-SnS<sub>reduced</sub> (x=1, 0.4, 0.2, 0.05) loaded into reaction system, the absorption peak at 400 nm diminishes after 10 min (as shown in Figure 4a). The complete discoloration of the solution from bright yellow to colorless is observed (as seen in Figure 4b). Sb<sub>4</sub>Sn<sub>3</sub>S<sub>12</sub> chalcogels (Pd-free), whose compositions are close to SbSn<sub>0.32</sub>S<sub>1.7</sub>, show negligible catalytic activity for such reaction, as illustrated in Figure S14-16 of SI. This indicates that the Pd NPs supported in Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub> is capable of catalyzing 4nitrophenol to 4-aminophenol in the presence of NaBH<sub>4</sub>. Consecutive experiments are performed to study the stability and reusability of Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub>, which are important parameters to evaluate a heterogeneous catalyst for practical applications.<sup>40</sup> The  $Pd_{0.2}Sb_{0.8}$ -SnS<sub>reduced</sub> catalyst toward 4nitrophenol reduction was investigated in consecutive 20 cycles, with no obvious variation in the conversion ratio. To show the advantage of Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> over some other catalysts, the catalytic role of the Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> in reduction reaction of 4-nitrophenol to 4-aminophenol with NaBH<sub>4</sub> was compared with reported catalyst in the literature (Table S2 of SI). With an overall look at Table S2, we can see that Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> is comparable with other reported catalyst in term of recycled stability. From the HR-TEM image of recycled Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> chalcogel in Figure 4d, no apparent agglomeration of Pd-based NPs could be observed. The above

results indicate that the Pd NPs supported on  $Pd_xSb_{1-x}$ -SnS<sub>reduced</sub> have a good stability and catalytic activity.

**Table 1.** Catalytic performance of Pd-SnS<br/>reduced and  $Pd_{0.2}Sb_{0.8}$ -<br/>SnS<br/>reduced in the Suzuki-Miyaura couplings reaction.



Entry <sup>a</sup>	Aryl halide	Arylboronic acid	Yield (%) <sup>b</sup>
1	4-Me–C <sub>6</sub> H <sub>4</sub> –I	C <sub>6</sub> H <sub>5</sub> –B(OH) <sub>2</sub>	93.6
2	3-Me–C <sub>6</sub> H <sub>4</sub> –I	C <sub>6</sub> H <sub>5</sub> –B(OH) <sub>2</sub>	99.6
3	4-OH–C <sub>6</sub> H <sub>4</sub> –I	C <sub>6</sub> H <sub>5</sub> –B(OH) <sub>2</sub>	93.0
4	C <sub>6</sub> H <sub>5</sub> –I	C <sub>6</sub> H₅−B(OH)₂	97.4
5	C <sub>6</sub> H <sub>5</sub> –I	4-Me-C <sub>6</sub> H₅− B(OH)₂	99.1
6 <sup>c</sup>	4-Me–C <sub>6</sub> H <sub>4</sub> –I	C <sub>6</sub> H₅−B(OH)₂	0

<sup>a</sup>Reaction condition: aryl haide (1 mmol), arylboronic acid (1.1 mmol), NaOH (1.5 mmol), Pd-SnS<sub>reduced</sub> (28.33 wt% Pd loading, 10 mg), ethanol (12 mL), 70 °C, 24 h. <sup>b</sup>Determined by GC analysis using an internal standard method. The yield was averaged over five independent runs. <sup>c</sup>The catalysis is Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> (5.15 wt% Pd loading, 15mg).

The Suzuki-Miyaura reaction is a widely investigated synthetic tool in fundamental research and industrial applications.<sup>41, 42</sup> The catalytic activity of Pd NPs catalysts was further studied in the Suzuki-Miyaura coupling reaction between aryl halide and arylboronic acid. A mixture of aryl halide, arylboronic acid, NaOH, and Pd-based catalysts in ethanol was stirred with heating, and the product was analyzed by gas chromatograph (GC). The 4-phenyltoluene yield was 93.6% after 24 h reaction (Table1, Entry 1). The yield of 3-phenyltoluene was 99.6% (Entry 2) and the yield of 4-phenylphenol was 93.0% (Entry 3), respectively. Iodobenzene was used for further tests; 97.4% yield for diphenyl and 99.1% yield for 4-phenyltoluene were obtained, respectively (Entry 4, 5). The Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> catalyst was tested for comparison (Entry 6). Unfortunately, the Sb doping completely inhibited the activity towards Suzuki-Miyaura coupling reaction. As mentioned above, Pd<sup>0</sup> species as catalytic active sites for Suzuki-Miyaura reaction will become inactive due to stronger coordination with the chalcogel skeleton via electron transfer from Pd<sup>0</sup> species to Sb. From XPS spectra shown in Figure 3b, the  $3d_{5/2}$  peak position of Pd<sup>0</sup> species for Pd-SnS<sub>reduced</sub> chalcogel which is before catalytic reaction distinctly shifted to higher binding energy with the doping content of Sb species, which implied the electron transfer from Pd<sup>0</sup> species to Sb via chalcogenide-based cluster links ([SnS<sub>4</sub>]<sup>4-</sup>). Consequently, the Sb species in Pd<sub>0.2</sub>Sb<sub>0.8</sub>-SnS<sub>reduced</sub> catalyst poisoned the reactivity of Suzuki-Miyaura reaction. As a contrast, the  $\mathsf{Pd}\text{-}\mathsf{SnS}_{\mathsf{reduced}}$  catalyst exhibited satisfying yield of coupling product (Entry 1-5). In order to verify the absence of leaching for Pd-SnS<sub>reduced</sub> catalyst, the Pd content in reactant solution without catalysts was tested by ICP-MS, which shows lower than 100 ppb of Pd, thus suggesting the low

leaching of Pd during catalysis reaction. The  $\sqrt{Pd}_{A}NPs_{O}still$  maintained the pristine particle size and  $\sqrt{Pd}_{A}NPs_{O}still$  chalcogel, as evidenced by the TEM image of the recollected Pd-SnS<sub>reduced</sub> (see Figure S17 of SI).

## Conclusions

In conclusion, we developed a one-step and *in-situ* strategy of size tunable Pd NPs by direct reduction of Pd-based chalcogel. The obtained Pd<sub>x</sub>Sb<sub>1-x</sub>-SnS<sub>reduced</sub> (x=1, 0.4, 0.2, 0.05) chalcogels have variable noble metal loading by adjusting the ratio of Pd and Sb. The catalysts show high catalytic activity, good stability and easy recyclability for the reduction of 4-nitrophenol to 4aminophenol with NaBH<sub>4</sub>. Pd-SnS<sub>reduced</sub> is further used to catalyze Suzuki-Miyaura coupling and shows high catalytic activity and stability. Further diversifying the size of the Pd NPs would provide more versatility to synthesize composite nanomaterials supported on reduced chalcogels for different catalytic applications. The present work shows the superiority of chalcogel as a starting platform for in-situ formation of transition-metal NPs. Nevertheless, for a profound understanding of the structure-activity relationship of reduced chalcogel, further work is needed. We believe that chalcogels offer new opportunities for designing highly active catalysts with hierarchic architectures and tailored compositions.

## **Conflicts of interest**

There are no conflicts to declare.

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## *In-Situ* Generation of Supported Palladium Nanoparticles from a Pod/Son/Servaticle Online Chalcogel and Applications in 4-Nitrophenol Reduction and Suzuki Coupling

ToC figure



A one-step in-situ route to obtain well-defined and controllable Pd nanoparticles was reported and employed for catalytic applications.