

# Enhancement in Aerobic Alcohol Oxidation Catalysis of Au<sub>25</sub> Clusters by Single Pd Atom Doping

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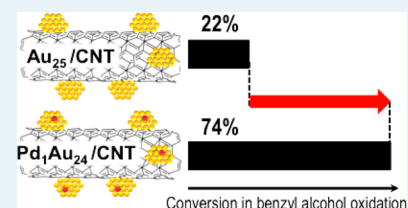
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## S Supporting Information

**ABSTRACT:** Au<sub>25</sub> and Pd<sub>1</sub>Au<sub>24</sub> clusters on multiwalled carbon nanotubes were developed via adsorption of Au<sub>25</sub>(SC<sub>12</sub>H<sub>25</sub>)<sub>18</sub> and Pd<sub>1</sub>Au<sub>24</sub>(SC<sub>12</sub>H<sub>25</sub>)<sub>18</sub>, respectively, on the nanotubes, followed by calcination. Comparison of their catalysis for the aerobic oxidation of benzyl alcohol showed that single Pd atom doping significantly improved the catalytic performance of Au<sub>25</sub> for the first time.



**KEYWORDS:** Au<sub>25</sub> clusters, single Pd atom doping, aerobic oxidation, multiwalled carbon nanotubes

Bimetallic nanoparticles (NPs) are attracting great interest because they exhibit excellent catalytic properties as a result of synergy between their constituent elements, in addition to size effects.<sup>1</sup> For example, gold–palladium NPs exhibit better catalytic performance than their monometallic counterparts in the oxidation of alcohol, oxidation of CO, oxidation of C–H bonds, and synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub>.<sup>2–4</sup> However, the origin of this alloying effect has not been clarified, mainly because bimetallic NPs prepared by conventional methods show distributions in their structural parameters, such as compositions, sizes, and mixing modes.<sup>5</sup> Several efforts have been made to establish the relation between structures and catalysis by reducing the distributions of these structural parameters. Prati and co-workers uniformized the compositions of Au–Pd NPs supported on carbon by depositing Pd onto preformed Au NPs.<sup>6</sup> Han's group succeeded in controlling the atomic distributions (alloy vs core–shell) in Au–Pd NPs by optimizing reduction rates of the precursor metals while retaining other parameters, such as morphology and surfactants.<sup>7</sup> Recently, Toshima reported the preparation of “crown-jewel-structured” Au–Pd NPs via galvanic replacement of Pd atoms at the vertex or corner of Pd NPs (1.8 ± 0.6 nm) with Au atoms.<sup>8</sup> However, a higher-level of precision in the structural parameters is required to tailor the catalysis of bimetallic clusters composed of less than ~100 atoms.

Previous studies on model systems, such as bimetallic clusters isolated in the gas phase or supported on a clean surface, have demonstrated that the chemical properties of the entire system can be changed dramatically by doping even a single atom. For example, Walter and Häkkinen theoretically predicted that Au<sub>16</sub><sup>−</sup> will become reactive toward O<sub>2</sub> by endohedral doping of a Si atom.<sup>9</sup> Heiz and Landman demonstrated that the catalysis for CO oxidation by small Au clusters on an MgO surface was

significantly improved by doping a single Sr atom.<sup>10</sup> Atomic-level control of these parameters of bimetallic clusters in the real-world is a technical challenge.

We recently synthesized Au clusters with well-defined sizes, such as Au<sub>10</sub>, Au<sub>11</sub>, Au<sub>18</sub>, Au<sub>25</sub>, and Au<sub>39</sub> on solid supports, such as mesoporous silica and hydroxyapatite, using ligand-protected, size-selected Au clusters as precursors.<sup>11–14</sup> In the present study, we extend this approach to precisely control the size and composition of bimetallic clusters using Pd<sub>1</sub>Au<sub>24</sub>(SR)<sub>18</sub>.<sup>15,16</sup> This bimetallic cluster has a structure similar to that of the well-known magic cluster Au<sub>25</sub>(SR)<sub>18</sub>, except the central Au atom is replaced by a Pd atom<sup>17–19</sup> and provides an ideal opportunity to investigate the effect of a single Pd atom doping on the catalysis. We immobilized Au<sub>25</sub> and Pd<sub>1</sub>Au<sub>24</sub> on multiwalled carbon nanotubes (CNTs) and observed that replacement of a single Au atom in Au<sub>25</sub> by a Pd atom significantly enhances the aerobic oxidation catalysis of benzyl alcohol.

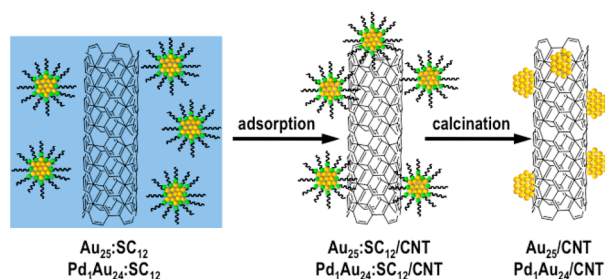
Au<sub>25</sub> and Pd<sub>1</sub>Au<sub>24</sub> on CNTs were obtained according to the procedure shown in Scheme 1. We first prepared Au<sub>25</sub>(SC<sub>12</sub>H<sub>25</sub>)<sub>18</sub> and Pd<sub>1</sub>Au<sub>24</sub>(SC<sub>12</sub>H<sub>25</sub>)<sub>18</sub> using the procedures reported by Negishi et al.<sup>15,20</sup> These compounds are hereafter referred to as Au<sub>25</sub>:SC<sub>12</sub> and Pd<sub>1</sub>Au<sub>24</sub>:SC<sub>12</sub>, respectively. The purity of these compounds was confirmed by matrix-assisted laser desorption ionization (MALDI) mass spectrometry (Supporting Information Figure S1) and transmission electron microscopy (TEM) (Supporting Information Figure S2).<sup>20</sup> The Au<sub>25</sub>:SC<sub>12</sub> and Pd<sub>1</sub>Au<sub>24</sub>:SC<sub>12</sub> clusters (0.05–1.0 wt % of metal) were then mixed with CNTs dispersed in toluene, and the

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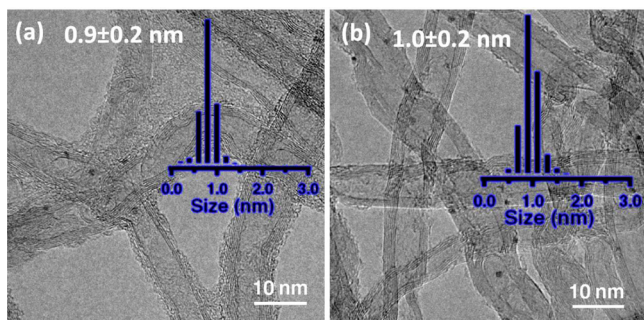
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### Scheme 1. Synthetic Scheme of Au<sub>25</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/CNT



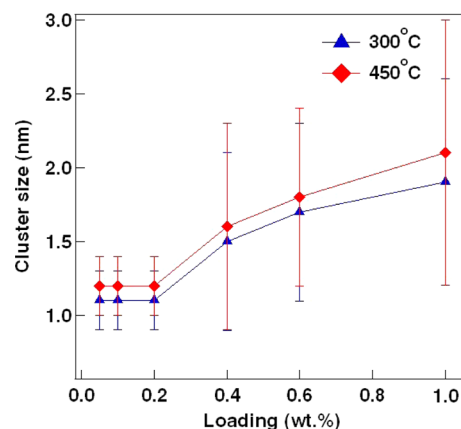
Au<sub>25</sub>:SC<sub>12</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>:SC<sub>12</sub>/CNT composites were collected by filtration. Comparison of UV–vis spectra of the initial dispersion and the colorless filtrate shows that the clusters were completely adsorbed on the CNTs (Supporting Information Figure S3).<sup>20</sup> TEM observation of Au<sub>25</sub>:SC<sub>12</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>:SC<sub>12</sub>/CNT (Figure 1) revealed that the cluster



**Figure 1.** Typical TEM Images and Cluster Size Distributions of (a) Au<sub>25</sub>:SC<sub>12</sub>/CNT and (b) Pd<sub>1</sub>Au<sub>24</sub>:SC<sub>12</sub>/CNT.

sizes were very similar to those of the precursor clusters (Supporting Information Figure S2). This result indicates that Au<sub>25</sub>:SC<sub>12</sub> and Pd<sub>1</sub>Au<sub>24</sub>:SC<sub>12</sub> were efficiently adsorbed on the CNTs in intact form through the weak hydrophobic interaction.<sup>21</sup>

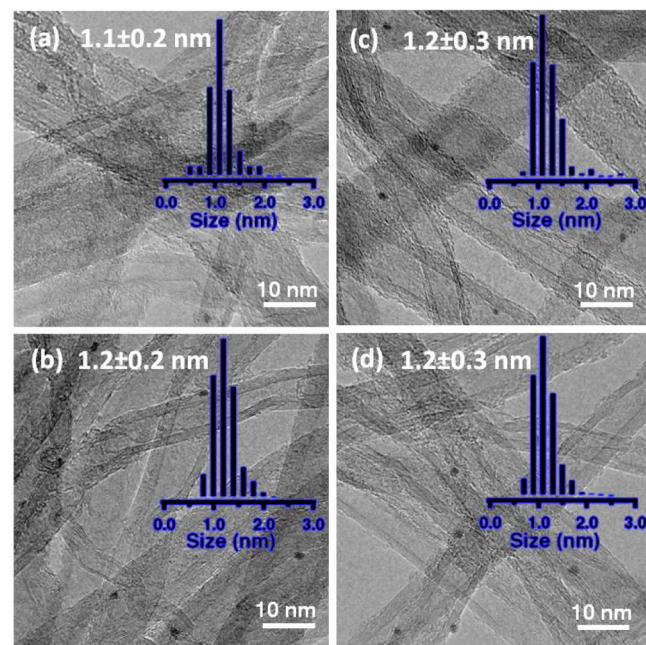
Finally, Au<sub>25</sub>:SC<sub>12</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>:SC<sub>12</sub>/CNT were calcined in vacuo to remove thiolate ligands, and Au<sub>25</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/CNT were obtained. Thermogravimetric analysis of Au<sub>25</sub>:SC<sub>12</sub>/CNT showed that all the ligands were removed by heat treatment at 300 °C for 2 h in vacuum (Supporting Information Figure S4).<sup>20</sup> Mass spectrometric analysis revealed that major species desorbed from Au<sub>25</sub>:SC<sub>12</sub>/CNT during calcination at 300–450 °C were didodecyl disulfide and dodecanethiol; sulfur-free species such as dodecane and 1-tetradecene were produced as the minor species (Supporting Information Figure S5).<sup>20</sup> These results indicate that the organic ligands were removed via breakage of the Au–S bonds without the loss of Au atoms. Considering that the interaction between gold and CNTs is rather weak,<sup>22,23</sup> a major concern is a possibility for aggregation of the Au clusters due to heat-induced diffusion. Such possibility can be minimized by reducing the initial populations of the precursors on CNTs. To determine the optimal loading, the size distributions of the clusters were determined from TEM images obtained after calcining Au<sub>25</sub>:SC<sub>12</sub> with various loadings in the range 0.05–1.0 Au wt % at 300 °C for 2 h. The results shown in Figure 2 indicate that the average cluster size is nearly constant when the loading is <0.2 wt % and increases monotonically when the



**Figure 2.** Dependence of Au<sub>25</sub>:SC<sub>12</sub> loading on Au<sub>25</sub>/CNT cluster size. Error bars indicate the size distribution determined by TEM.

loading is >0.2 wt %. This behavior suggests that aggregation of the clusters is negligible when the loading is smaller than 0.2 wt %, whereas the cluster aggregation is obvious at a higher loading.

Similar behavior was also observed at the calcination temperature of 450 °C (Figure 2). On the basis of these results, Au<sub>25</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/CNT used for the catalytic test were prepared by calcinating the precursors (0.2 wt %) at 300 and 450 °C. TEM images and size distributions of the prepared Au<sub>25</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/CNT (Figure 3) show both clusters



**Figure 3.** Typical TEM images of Au<sub>25</sub>/CNT calcined at (a) 300 and (b) 450 °C and Pd<sub>1</sub>Au<sub>24</sub>/CNT calcined at (c) 300 and (d) 450 °C. Insets show the cluster size distributions obtained for more than 300 particles.

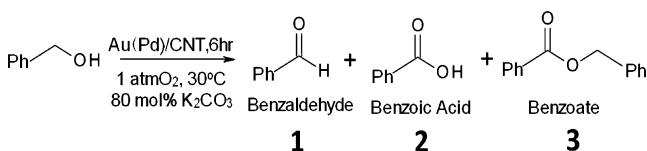
having average sizes in the range 1.1–1.2 nm, which are slightly larger than those of the precursors on the CNTs (Supporting Information Figure S2). The slight increase in diameter is probably associated with the intrinsic preference of small Au clusters to form 2-dimensional or low-density structures<sup>24</sup> or the flattening induced by strong interactions with defects of the



CNTs.<sup>25,26</sup> Inductively coupled plasma analysis confirmed that total amounts of metal (Au and Pd) loaded were similar for these catalysts. The presence of Pd was confirmed by energy-dispersive spectroscopy of Pd<sub>1</sub>Au<sub>24</sub>/CNT calcined at 450 °C (Au/Pd ≈ 22:1) (Supporting Information Figure S6).<sup>20</sup> These results indicate that individual clusters in Au<sub>25</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/CNT have identical sizes and compositions.

The catalytic performances of Au<sub>25</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/CNT prepared at 300 and 450 °C were compared in a test reaction involving the aerobic oxidation of benzyl alcohol. Table 1

**Table 1. Catalytic Performances of Au<sub>25</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/CNT for Benzyl Alcohol Oxidation<sup>a</sup>**



entry	catalyst <sup>b</sup>	conversion (%)	yield (%) <sup>g</sup>		
			1	2	3
1	CNT	0	0	0	0
2	Au <sub>25</sub> :SC <sub>12</sub> /CNT	0	0	0	0
3	Pd <sub>1</sub> Au <sub>24</sub> :SC <sub>12</sub> /CNT	0	0	0	0
4	Au <sub>25</sub> /CNT (300)	11	57	14	29
5	Pd <sub>1</sub> Au <sub>24</sub> /CNT (300)	35	36	29	35
6	Au <sub>25</sub> /CNT (450)	22	37	29	34
7	Au <sub>25</sub> /CNT (450) <sup>c</sup>	20	42	16	42
8	Au <sub>25</sub> /CNT (450) <sup>d</sup>	16	50	10	40
9	Pd <sub>1</sub> Au <sub>24</sub> /CNT (450)	74	24	53	23
10	Pd <sub>1</sub> Au <sub>24</sub> /CNT (450) <sup>e</sup>	68	20	57	23
11	Pd <sub>1</sub> Au <sub>24</sub> /CNT (450) <sup>f</sup>	59	30	47	23

<sup>a</sup>Reaction conditions: amount of catalyst, 50 mg ( $2.5 \times 10^{-4}$  mmol of metal); amount of PhCH<sub>2</sub>OH, 12.5 mg (substrate-to-metal molar ratio = 463:1); amount of K<sub>2</sub>CO<sub>3</sub>, 10 mg; volume of water, 10 mL; temperature, 30 °C; O<sub>2</sub> pressure, 1 atm. <sup>b</sup>The numbers in the parentheses indicate the calcination temperature in degrees Celsius. <sup>c</sup>Recovered from entry 6. <sup>d</sup>Recovered from entry 7. <sup>e</sup>Recovered from entry 9. <sup>f</sup>Recovered from entry 10. <sup>g</sup>Determined by gas chromatography.

summarizes the results obtained from the test reaction. Both catalysts produced benzaldehyde (1), benzoic acid (2), and benzyl benzoate (3) as the major products (entries 4–11). Pristine CNTs did not exhibit any catalytic activity, which indicates that CNTs are not involved in the catalysis (entry 1). The uncalcined composites Au<sub>25</sub>:SC<sub>12</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>:SC<sub>12</sub>/CNT also did not show any activity (entries 2 and 3), indicating that a thiolate layer poisons the catalyst, as expected. In contrast, both Au<sub>25</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/CNT prepared at 300 °C catalyzed the reaction (entries 4 and 5), whereas the catalysts prepared at 450 °C showed much higher activities. Since similar cluster sizes were obtained at all calcination temperatures (Figures 2 and 3), this result suggests that clusters prepared at 300 °C are poisoned by trace amounts of organic residues, whereas such contamination was completely removed by calcination at 450 °C.

Most notably, Au<sub>25</sub>/CNT (450) and Pd<sub>1</sub>Au<sub>24</sub>/CNT (450) exhibited a significant difference in the catalysis: the conversion of the latter (74%) is nearly three times higher than that of the former (22%) (entries 6 and 9). The reproducibility of this enhancement was confirmed by performing measurements on five samples that had been independently prepared. On the

basis of these results, we conclude that Pd atom doping is the main cause of the enhanced activities.<sup>27</sup> To the best of our knowledge, this is the first demonstration of the effect of single atom doping on the catalytic properties of “real-world” cluster catalysts. These catalysts were found to be robust and durable. The activities of both catalysts decreased only slightly when they were reused (entries 6–11, Table 1). The Au concentration in the reaction solutions after the first usage was below the detection limit (1–10 ppb), which indicates that metal leaching was negligible.<sup>20</sup> TEM analysis of the catalysts before and after the first usage showed similar size distributions (Supporting Information Figure S7).<sup>20</sup>

There are two possible mechanisms by which the Pd atom can enhance the catalysis. One possible mechanism is that it directly creates a highly active reaction site on the surface of Au<sub>24</sub> (the so-called “ensemble” effect).<sup>28</sup> Schiffrin reported that individual Pd atoms dispersed onto a Au NP host that acts as an electrocatalytic center for the oxygen reduction.<sup>29</sup> The other possible mechanism is that the Pd atom activates the Au sites by modulating the electronic structure (the so-called “ligand” effect).<sup>28</sup> Toshima proposed that Au atoms located at the vertex or corner of Pd NPs ( $1.8 \pm 0.6$  nm) act as a highly reactive site for aerobic glucose oxidation due to electron transfer from Pd.<sup>8</sup>

Although the structure of Pd<sub>1</sub>Au<sub>24</sub> clusters on CNTs is not understood, we believe that the latter mechanism is more plausible on the basis of the following considerations: First, recent theoretical studies on Au–Pd clusters revealed that it is thermodynamically favorable for a Pd atom to be located inside an Au sheath, since this increases the number of Pd–Au bonds, which are stronger than Au–Au bonds.<sup>30</sup> Density functional theory calculations on Pd<sub>1</sub>Au<sub>n</sub> ( $n = 54, 78, 91,$  and  $97$ ) predict that electron transfer occurs from Pd to Au<sup>31</sup> and that the Pd–Au bond becomes more ionic with decreasing size.<sup>32</sup> Within the framework of this structural model, Au sites in Pd<sub>1</sub>Au<sub>24</sub>/CNT, which are more negative than those in Au<sub>25</sub>/CNT due to electron transfer from Pd, may activate O<sub>2</sub> more effectively, and as a result, Pd<sub>1</sub>Au<sub>24</sub>/CNT shows higher catalytic activity than Au<sub>25</sub>/CNT for aerobic alcohol oxidation.<sup>8,33</sup> However, to answer the effect of Pd doping, the structures of Au<sub>25</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/CNT must be investigated in more detail using spectroscopic and microscopic tools, such as extended X-ray absorption fine structure analysis, X-ray photoelectron spectroscopy using synchrotron-based light source,<sup>34</sup> and an aberration-corrected scanning transmission electron microscope.<sup>4,35–39</sup>

In summary, we successfully synthesized Au<sub>25</sub> and Pd<sub>1</sub>Au<sub>24</sub> on CNTs using the corresponding clusters protected by dodecanethiolates. Single Pd atom replacement was demonstrated for the first time to have a significant effect on oxidation catalysis. This doping effect is proposed to be due to modulation of the electronic structures by intracuster electron transfer from Pd to Au. The synthetic method reported here will provide a unique way to control the size and composition of alloy clusters with atomic precision; the scope of application will be expanded as a result of the increasing variation of the precursors.<sup>40–43</sup>

## EXPERIMENTAL METHODS

**Preparation of Catalysts.** Dodecanthiolate-protected clusters Au<sub>25</sub>:SC<sub>12</sub> and Pd<sub>1</sub>Au<sub>24</sub>:SC<sub>12</sub> were prepared according to a protocol previously reported.<sup>15,44</sup> CNT is commercial available and obtained from Nanocyl (Belgium, NC-7000). A toluene solution containing the calculated amount (0.05–1.0

wt %) of clusters was injected into a suspension of CNT under vigorous magnetic stirring. After 1 h, the composites were filtered and dried in vacuum (<20 Pa) for 12 h. Calcination of the Au<sub>25</sub>/SC<sub>12</sub>/CNT and Pd<sub>1</sub>Au<sub>24</sub>/SC<sub>12</sub>/CNT composites was performed in a quartz-tube oven under vacuum conditions (<0.003 Torr): the oven temperature was raised to 50 °C at a rate of 2 °C/min and then maintained for 0.5 h. Subsequently, the oven temperature was elevated to 300 or 450 °C at a heating rate of 2 °C/min, and kept at 300 or 450 °C for 2 h.

**Catalytic Test.** Aerobic oxidation of benzyl alcohol was studied under conditions similar to those in ref 11. Oxidation of benzyl alcohols was performed in an organic synthesizer (EYELA, PPS-2510, Japan). Benzyl alcohol (12.5 mg), K<sub>2</sub>CO<sub>3</sub> (10 mg), and H<sub>2</sub>O (10 mL) were added to a test tube. After sonication for 2 min, the Au(Pd)/CNT catalyst (50 mg) was added and stirred vigorously at 1000 rpm. The temperature was maintained at 30 °C. An oxygen balloon was used to supply molecular oxygen to the sealed test tube. After 6 h, the reaction was quenched with 2 M HCl. The products were extracted three times with AcOEt (10 mL). The extracted organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, diluted to 100 mL, and analyzed by gas chromatography (Shimadzu, GC-2014, Japan). Quantitative analysis was performed using the external standard method.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Details of experimental procedures and characterization results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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