Controlling Au–Pd Surface on Au Nanocubes for Selective Catalytic Alkyne Semihydrogenation

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The heterogeneous nanocatalyst based on palladium (Pd) is one of the most preferable choices for catalytic hydrogenation reactions as the adsorption and dissociation of hydrogen molecules (H₂) are almost spontaneous on Pd surface to form the adsorbed H atoms (H_{ad}). However, in terms of alkyne semihydrogenation, it remains a grand challenge to optimize both the activity and selectivity of reactions using bare Pd catalysts as the case is largely complicated by the excessive H_{ad} produced from rapid H₂ dissociation and the strong Pd–H binding. In this communication, a well-designed model is developed for seeking a selective semihydrogenation catalyst based on surface lattice engineering. In the proposed model, the ultrathin atomic layer of AuPd shell is grown on the Au nanocubes. The Au nanocubes provide specific facets as substrates for hosting catalytic sites, which can also provide information for further lattice engineering design. While Pd atoms are the active centers for hydrogenation reactions in the nanostructures, alloying Pd atoms with Au in the shells can significantly alter the binding of H_{ad} to metals. As such, the activity and selectivity in catalytic alkyne semihydrogenation can be substantially maneuvered by tailoring the atomic arrangement of Pd and Au on surface. As a proof of concept, the Au@AuPd nanocatalyst with a surface Pd/Au ratio of 1:4 achieves a 98.9% semihydrogenation selectivity with a conversion of 98.2% in the 2-methyl-3-butyln-2-ol (MBY) hydrogenation reaction.

Catalytic semihydrogenation of alkenes has attracted widespread interest owing to its industrial and commercial applications.[1,2] To improve the activity and selectivity of reactions, various types of catalytic nanostructures have been investigated for the semihydrogenation of alkenes.[3,4] Ideally well-designed nanostructures may offer numerous benefits including lower energy consumption requirements, higher atomic economy, and more controllable reaction pathways in catalysis. To this end, it is strongly demanded to design nanostructures toward highly active and selective catalysts.[5,6] Among various catalysts, the heterogeneous nanocatalyst based on palladium (Pd) is one of the most preferable choices for catalytic hydrogenation reactions. This widespread application mainly takes advantage of the basic physical phenomenon that the adsorption and dissociation of hydrogen molecules (H₂) are almost spontaneous on Pd surface to form the adsorbed H atoms (H_{ad}).[7–10] As a result, the Pd-based catalysts have extensively shown excellent performance in H₂-related reactions.[11] However, in terms of alkyne semihydrogenation, it remains a grand challenge to optimize both the activity and selectivity of reactions using bare Pd catalysts as the case is largely complicated by the excessive H_{ad} produced from rapid H₂ dissociation and the strong Pd–H binding.[10,11]

Most recently, bimetallic nanocatalysts have been designed for catalytic hydrogenation reactions by manipulating the interactions of metals and H₂/H_{ad}.[4,10–15] For example, the interstitial modification of Pd in PdAu alloy would alter the desorption of H_{ad} and the hydrogenation barrier of alkene.[16] The progress highlights the opportunity that the interstitial control of Pd may maneuver the interactions between Pd and H₂/H_{ad} for efficient and selective semihydrogenation. The previous investigations have been mainly focused on the Pd-based alloy or intermetallic compound nanoparticles which allow lattice engineering on Pd sites; however, the presence of Pd atoms in bulk phase brings about the concern that the dissociated H atoms may diffuse into the bulk lattice, dramatically complicating the case. For this reason, it would be a more straightforward strategy to regulate the atomic arrangement of Pd sites within the surface regime nanocatalysts (i.e., surface lattice engineering) while using the inactive metal for H diffusion in the bulk phase. We thus specifically select the Au nanocubes covered with (100) facets as a model system on which AuPd alloys with various compositions are supported. Such surface lattice engineering on Pd sites can effectively manipulate the metal–H_{ad} interaction, thereby enabling the semihydrogenation selectivity of Pd-based nanocatalysts.

In this communication, a well-designed model is developed for seeking a selective semihydrogenation catalyst based on surface lattice engineering. In the proposed model, the ultrathin atomic layer of AuPd shell is grown on the Au nanocubes (covered with (100) facets). The Au nanocubes provide specific facets as substrates for hosting catalytic sites, which can also provide information for further lattice engineering design.
While Pd atoms are the active centers for hydrogenation reactions in the nanostructures, alloying Pd atoms with Au in the shells can significantly alter the binding of $H_2$ to metals.\textsuperscript{[16]} As such, the activity and selectivity in catalytic alkyne semihydrogenation can be substantially maneuvered by tailoring the atomic arrangement of Pd and Au on surface. During the material synthesis process, the surface composition of Au and Pd atoms can be facilely regulated by changing the added Pd/Au molar ratios. As a proof of concept, the Au@AuPd nanocatalyst with a surface Pd/Au ratio of 1:4 achieves 98.9\% semihydrogenation selectivity with conversion of 98.2\% in 2-methyl-3-butyn-2-ol (MBY) hydrogenation reaction.

The synthetic approach to Au@AuPd nanocrystals is shown in Figure 1a. In the synthetic process of Au@AuPd nanostructures, Au nanocrystals with a cubic profile and an average edge length of 48.2 nm are prepared using a previously developed procedure (Figure S1a, Supporting Information),\textsuperscript{[17]} and are chosen as the substrates for the growth of AuPd alloy shells. The growth of AuPd shells is achieved by co-reducing Pd$^{2+}$ and Au$^{3+}$ by ascorbic acid (AA) on the surface of Au nanocubes, in the presence of cetyltrimethylammonium bromide (CTAB), at 303 K for 11 h. Inductively-coupled plasma mass spectrometry (ICP-MS) measurement shows that the Au and Pd precursors added into the synthetic solution are reduced and converted to metal atoms on Au nanocubes completely. By tightly controlling the amounts of metal precursors, only a few atomic layers of AuPd alloys are loaded onto the Au nanocubes. According to the ICP-MS characterization, the AuPd alloy shell of an Au@AuPd

![Figure 1.](image-url) a) Schematic illustration for the proposed co-reduction approach to the ultrathin AuPd alloy shells on Au nanocubes (cross-section view in the middle). TEM images of b) Au@Au$_4$Pd$_1$ and c) Au@Au$_1$Pd$_4$ nanocubes. d) High-resolution TEM image of the Au@Au$_4$Pd$_1$ nanocube. e) EDS mapping profiles (red, Pd; yellow, Au) of an Au@Au$_4$Pd$_1$ nanocube.
nanocrystal contains about 4–6 atomic layers (see Supporting Note 1 in the Supporting Information).

By simply adjusting the molar ratio of H$_2$PdCl$_4$ to HAuCl$_4$·4H$_2$O precursors, the surface compositions of Au and Pd atoms can be regulated. As the Au and Pd precursors have been completely converted to the metal atoms on Au nanocubes (Table S1, Supporting Information), we can name the obtained nanostructures according to the ratios of Au to Pd precursors: Au@Au$_6$Pd$_1$ (Figure S1b, Supporting Information), Au@Au$_4$Pd$_1$ (Figure 1b; Figure S1c, Supporting Information), Au@Au$_2$Pd$_1$ (Figure S1d, Supporting Information), Au@Au$_3$Pd$_1$ (Figure S1e, Supporting Information), Au@Au$_1$Pd$_1$ (Figure 1c; Figure S1f, Supporting Information), Au@Au$_2$Pd$_4$ (Figure 1d; Figure S1g, Supporting Information), and Au@Au$_0$Pd$_5$ (Figure S1h, Supporting Information), respectively. Representative transmission electron microscopy (TEM) images of the Au@Au$_n$Pd$_m$ nanocrystals clearly show that the shape of original Au nanocubes remains unchanged after the coating of AuPd atomic layers. The average edge length of produced Au@Au$_n$Pd$_m$ nanocubes is 49.8–50.2 nm (see the histograms of size distributions in Figure S2 in the Supporting Information), and the limited size increase as compared to Au nanocubes (48.2 nm) agrees with our estimation from ICP-MS measurement (4–6 atomic layers). Moreover, the high-resolution TEM (HRTEM) image of Au@Au$_4$Pd$_1$ nanocrystal (Figure 1d) suggests that the Au matrix lattice has been slightly altered upon the deposition of AuPd shells. The strain in the shell, indicated by the atomic arrangement at the edge of nanocrystal, should result from the lattice constant difference between Au (4.07 Å) and Pd (3.89 Å). The spatial elemental distribution of Pd and Au atoms is further confirmed by energy-dispersive spectroscopy (EDS) mapping (Figure 1e). The HRTEM characterization together with EDS mapping unambiguously demonstrates that AuPd alloy shells have been deposited on the surface of Au nanocubes, forming Au@AuPd core-shell nanocubes.

To further prove the core-shell structures, depth-dependent X-ray photoelectron spectra (XPS) also has been performed on the Au@Au$_4$Pd$_1$ nanocubes using a synchrotron radiation technique at incident photon energies of 450, 500, 550, and 600 eV, respectively, which can provide qualitative information about vertical elemental distribution. As estimated by the depth-dependent XPS data (Figure 2a), the average Pd atomic fraction of our Au@Au$_4$Pd$_1$ nanocubes decreases from 10.6% to 8.1% as the depths are extended from ~0.8 nm ($h\nu = 450$ eV) to ~1.0 nm ($h\nu = 600$ eV). This qualitative result confirms that the obtained nanostructures are the core-shell nanocubes with AuPd alloy layers outside and Au cores inside.

Upon resolving the core-shell structures of Au@AuPd nanocubes, we have employed high-resolution XPS to examine the distribution of Pd atoms in typical samples—Au@Au$_4$Pd$_1$, Au@Au$_2$Pd$_3$, and Au@Au$_1$Pd$_4$ nanocubes in reference to pure Au and pure Pd (Figure 2b–d). The two characteristic peaks at 83.6 and 87.3 eV are in correspondence with the Au 4f7/2 and Au 4f5/2, respectively (Figure 2b). Since the peaks of Au 4d5/2 and Pd 3d5/2 are overlapped at 334.7 eV, the other two characteristic peaks at 340 and 353 eV that can be assigned to Pd

![Figure 2. a) Dependence of Pd and Au atomic fractions of the obtained Au@Au$_4$Pd$_1$ nanocrystals measured by XPS as a function of photon energy. b) Au 4f, c) Pd 3d, and d) high-resolution Pd 3d5/2 XPS spectra of Au@Au$_4$Pd$_1$, Au@Au$_2$Pd$_3$, and Au@Au$_1$Pd$_4$ nanocrystals for comparison, in reference to those of pure Au and pure Pd.](image-url)
3d\textsubscript{3/2} and Au 4d\textsubscript{3/2}, respectively, provide more detailed information (Figure 2c). The high-resolution Pd 3d\textsubscript{3/2} spectrum shows a slight shift toward higher binding energy for Au@Au\textsubscript{1}Pd\textsubscript{1} (Figure 2d). This slight shift in the peak of Pd 3d\textsubscript{3/2} is mainly caused by the electron transfer from Pd atoms to Au atoms due to the smaller electronegativity of Pd (2.2) than Au (2.4).\cite{19} When a Pd atom is surrounded by more Au atoms, more distinct Pd 3d\textsubscript{3/2} peak shift should be observed. This thus suggests that the Pd atoms are well distributed in the Au lattice in the sample of Au@Au\textsubscript{1}Pd\textsubscript{1}.

We are now in a position to evaluate the catalytic hydrogenation performance of Au@AuPd nanocubes. To assess the catalytic activity of each Pd site, the hydrogenation reactions are performed on various catalysts including Au@Au\textsubscript{6}Pd\textsubscript{1}, Au@Au\textsubscript{4}Pd\textsubscript{1}, Au@Au\textsubscript{3}Pd\textsubscript{1}, Au@Au\textsubscript{2}Pd\textsubscript{1}, Au@Au\textsubscript{2}Pd\textsubscript{3}, Au@Au\textsubscript{1}Pd\textsubscript{4}, and Au@Au\textsubscript{0}Pd\textsubscript{5} with the same Pd molar amount (0.4 nmol). As a proof of concept, MBY is employed as a typical alkyne example which can be semihydrogenated into 2-methyl-3-butene-2-ol (MBE) or over-hydrogenated into 2-methyl-3-butan-2-ol (MBA). Figure 3a shows the activity of various Au@AuPd nanocubes in catalytic MBY hydrogenation, in which the same reaction time is maintained with several replicates. The volcano-shaped curve shows the maximum activity at Au@Au\textsubscript{2}Pd\textsubscript{1} for MBY hydrogenation.

Such a volcano-shaped trend can be well explained by the interactions of Pd sites and H\textsubscript{2}/H\textsubscript{ad}. During the hydrogenation reactions, three key steps are generally involved: (1) the formation of H\textsubscript{ad} through the adsorption of molecular H\textsubscript{2} on metal surface and its dissociation into two adsorbed H atoms, (2) the spillover of H\textsubscript{ad}, and (3) the breakage of metal–H\textsubscript{ad} bond or/and the reaction between H\textsubscript{ad} and reactive molecule. Since Au surface is incapable of spontaneously activating and dissociating H\textsubscript{2}, the formation of H\textsubscript{ad} can be regarded as the major contribution from Pd atoms. After the first step, the dissociated H\textsubscript{ad} atoms would randomly spillover on the Au\textsubscript{n}Pd\textsubscript{m} surface with different H\textsubscript{ad} coverage. This H\textsubscript{ad} coverage should depend on the distribution state of Pd sites in Au lattice. In order to confirm this hypothesis, the electrochemical H adsorption experiment is performed on various Au@Au\textsubscript{n}Pd\textsubscript{m} nanocubes (Figure S3, Supporting Information). The experiment results show that the

![Figure 3](image-url)
surface coverage of $H_{ad}$ increases nearly as a cubic function of Pd composition. As the number of surface Pd sites should increase linearly as a function of Pd composition, the surface amount of $H_{ad}$ would be insufficient for efficient hydrogenation reactions at low Pd compositions, which can be responsible for the left side of volcano-shaped curve.

On the other hand, the samples with sufficient $H_{ad}$ surface coverage exhibit the reduced reaction activity when the Pd content is increased too high in the right side of volcano-shaped curve. This feature should be associated with the third step—the cleavage of Pd–$H_{ad}$ bonds. It has been reported that too high Pd composition would result in strong Pd–$H_{ad}$ binding, which disfavors the reaction between $H_{ad}$ and reactive molecule and limits the reaction activity of catalysts. In this case, the designed nanostructures with optimal Pd distribution can offer both sufficient $H_{ad}$ coverage and suitable metal–$H_{ad}$ binding, located at the volcano center for the highest catalytic hydrogenation activity. Based on this mechanism, the catalytic hydrogenation activity is mainly tuned by maneuvering the interactions of Pd sites and $H_{ad}/H_{2}$, regardless of the substrate molecule. To support this argument, we have also collected the activity of various Au@Au$_{n}$Pd$_{m}$ nanocatalysts in catalytic MBE hydrogenation (Figure 3a). Similarly, it exhibits a volcano-shaped trend with the maximum activity at Au@Au$_{2}$Pd$_{1}$.

In addition to catalytic activity, semihydrogenation selectivity is another key parameter to the assessment. To look into the role of surface structure in reaction selectivity, we evaluate the semi-hydrogenation selectivity to MBE with about 95% conversion of MBE by Au@Au$_{5}$Pd$_{1}$, Au@Au$_{4}$Pd$_{1}$, Au@Au$_{3}$Pd$_{1}$, Au@Au$_{2}$Pd$_{3}$, Au@Au$_{4}$Pd$_{4}$, and Au@Au$_{6}$Pd$_{4}$ (Figure 3b). The evaluation shows that Au@Au$_{6}$Pd$_{1}$, Au@Au$_{5}$Pd$_{1}$, and Au@Au$_{4}$Pd$_{1}$ remain high selectivity even when the conversion of MBE reaches 95–99%. In comparison, the reaction selectivity decreases with higher Pd compositions. As the usage of catalysts is determined by the amount of Pd atoms (0.4 nmol Pd), this indicates that the well-separated Pd sites in Au lattice can offer the high selectivity in the semihydrogenation of MBE.

To better appreciate the effect of catalyst surface structures on reaction selectivity, the time-dependent conversion and selectivity of MBE hydrogenation are evaluated on Au@Au$_{6}$Pd$_{1}$, Au@Au$_{5}$Pd$_{1}$, Au@Au$_{4}$Pd$_{1}$, Au@Au$_{3}$Pd$_{1}$, Au@Au$_{2}$Pd$_{3}$, and Au@Au$_{4}$Pd$_{3}$ nanocubes, respectively (Figure 3c–e; Figure S4, Supporting Information). The Au@Au$_{6}$Pd$_{1}$ and Au@Au$_{4}$Pd$_{1}$ nanocrystals exhibit excellent semihydrogenation selectivity, which can be well maintained for several hours after the total conversion of MBE. In sharp contrast, the catalysts with high percentages of Pd (e.g., Au@Au$_{4}$Pd$_{1}$, Au@Au$_{3}$Pd$_{1}$, and Au@Au$_{6}$Pd$_{3}$) possess relatively low semihydrogenation selectivity through the whole reaction process, and the semihydrogenation selectivity keeps decaying as the reaction continues after the full conversion of MBE. This clearly demonstrates that the high semihydrogenation selectivity can be ensured by the separation of Pd sites in Au lattice. To achieve both high activity and selectivity, the catalyst of Au@Au$_{6}$Pd$_{1}$ nanocubes appears to be an ideal candidate.

Such Au@AuPd nanocatalysts can be easily separated from the catalytic reaction system and reused in subsequent reactions almost without the loss of catalytic activity or selectivity. Figure 3f shows the cycling tests for Au@Au$_{6}$Pd$_{1}$ nanocubes—the best catalyst in our investigation. The catalyst shows negligible decay for the selectivity and activity after four cycles of hydrogenation reactions, indicating an excellent catalytic stability of Au@Au$_{6}$Pd$_{1}$ catalysts. The high stability of catalyst is further confirmed by TEM (Figure S5, Supporting Information), in which the Au@Au$_{6}$Pd$_{1}$ nanocubes well maintain their morphology after the catalytic hydrogenation reactions.

Upon identifying the excellent performance of Au@Au$_{6}$Pd$_{1}$ nanocubes, a question naturally arises: what factor enables the high selectivity in catalytic semihydrogenation? Figure 3a shows that both MBE and MBE hydrogenation activities have a volcano-shaped relationship with surface compositions owing to the tunable $H_{ad}$ surface coverage and metal–$H_{ad}$ binding, which should not make a major contribution to the high selectivity at low Pd contents. To further investigate the origin for the high catalytic selectivity by Au@Au$_{6}$Pd$_{1}$, the in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) has been employed to examine the chemisorption of MBE on Au@Au$_{6}$Pd$_{1}$ and Au@Au$_{5}$Pd$_{1}$ nanocatalysts (Figure 4a). In the characterization, quantitative MBE is added into the suspensions of Au@Au$_{6}$Pd$_{1}$ and Au@Au$_{5}$Pd$_{1}$ nanocubes that contain the same amount of Pd atoms. The suspension is then treated at 353 K in vacuum to remove the physically adsorbed molecules after reaching the adsorption equilibrium. The adsorption peaks located at 1670–1620 and 1000–1120 cm$^{-1}$ result from C=C stretching vibration and C–O stretching vibration, respectively, and the adsorption peaks located at 1350–1500 cm$^{-1}$ correspond to C–H in-plane bending vibration, which can
be assigned to the surface adsorption of MBE on Au@AuPd nanocubes.\textsuperscript{[22]} The comparison clearly shows that Au@Au\textsubscript{4}Pd\textsubscript{1} offers the stronger adsorption of MBE than Au@Au\textsubscript{1}Pd\textsubscript{4} according to the stronger peaks at 1000–1120, 1350–1500, and 1670–1620 cm\textsuperscript{-1}. Owing to the weak chemisorption to Au@Au\textsubscript{4}Pd\textsubscript{1} surface, the product of MBY semihydrogenation—MBE can more readily desorb from the surface instead of performing the overhydrogenation to MBA.

The weak chemisorption of MBE to the surface with low Pd contents is also evidenced by the isothermal adsorption comparison for Au@Au\textsubscript{4}Pd\textsubscript{4} and Au@Au\textsubscript{1}Pd\textsubscript{4} nanocubes (Figure 4b). Similarly to the DRIFTS measurement for MBE chemisorption, the isothermal adsorption curves show that Au@Au\textsubscript{4}Pd\textsubscript{1} offers a lower capability of adsorbing MBE than Au@Au\textsubscript{1}Pd\textsubscript{4}. It can be thus concluded that the facile desorption of MBE from Au@Au\textsubscript{4}Pd\textsubscript{1} nanocubes may contribute to the high semihydrogenation selectivity. This opens up an opportunity for maneuvering H\textsubscript{ad} surface coverage, metal–H\textsubscript{ad} bonding and alkene desorption by tailoring surface AuPd alloy compositions, promoting the activity and selectivity of semihydrogenation. As a matter of fact, this strategy has been proven universal to the semihydrogenation of various alkynes, as demonstrated by the comparison between Au@Au\textsubscript{4}Pd\textsubscript{1} and Au@Au\textsubscript{1}Pd\textsubscript{4} (Table 1).

In summary, core-shell Au@AuPd nanocubes have been developed through a coreduction process on the surface of Au nanocubes. This method can control the surface Au/Pd atomic ratios simply by altering the amounts of metal precursors in the synthesis system, which offers the capability of regulating the surface state of Pd sites in Au lattice. Enabled by the control over Pd sites, the H\textsubscript{ad} surface coverage, metal–H\textsubscript{ad} binding, and reactive molecule desorption can be balanced to dramatically enhance the activity and selectivity of semihydrogenation reactions. As a result, an optimal nanocatalyst with both high activity and selectivity for semihydrogenation has been identified by manipulating metal–hydrogen and metal–alkene interactions. The concept demonstrated here calls for future efforts on rationally designing bimetallic catalysts for semihydrogenation reactions.

**Experimental Section**

**Synthesis of Au@AuPd**: In a typical synthesis of Au@Au\textsubscript{4}Pd\textsubscript{1} nanocrystals, L-ascorbic acid (50 μL, 100 × 10\textsuperscript{-3} M, Sinopharm Chemical Reagent Co. Ltd, 10004014, ≥99.7%), CTAB (2.5 mL, 100 × 10\textsuperscript{-3} M, Sinopharm Chemical Reagent Co. Ltd, 30037416, ≥99%), and deionized water (9 mL) were added into a conical flask, followed by the addition of 4.5 μmol Au nanocubes and aqueous solution of H\textsubscript{2}PdCl\textsubscript{4} (50 μL, 2 × 10\textsuperscript{-3} M, prepared according to the reaction: 2HCl + PdCl\textsubscript{2} = H\textsubscript{2}PdCl\textsubscript{4}, Sinopharm Chemical Reagent Co. Ltd, 51018011, Pd% ≥ 59%) and HAuCl\textsubscript{4}·4H\textsubscript{2}O (200 μL, 2 × 10\textsuperscript{-3} M, Sinopharm Chemical Reagent Co. Ltd, 10010711, Au% ≥ 47.8%) under stirring. The mixture was stirred for water at 5000 rpm for 20 min. For the Au@AuPd nanocubes with other Pd/Au ratios, the volumes of H\textsubscript{2}PdCl\textsubscript{4} (2 × 10\textsuperscript{-3} M) and HAuCl\textsubscript{4}·4H\textsubscript{2}O (2 × 10\textsuperscript{-3} M) aqueous solution were adjusted while the whole volume was constantly controlled at 250 μL.

**Measurements of Catalytic Hydrogenation**: The hydrogenation of MBY (Macklin, M813339-100 mL, 98%) or MBE (Aladdin, M106453-100 mL, 98%) was carried out in a quartz tube. A certain amount of Au@AuPd nanocubes with different Pd/Au ratios was added into the tube to maintain the same amount Pd (0.4 nmol based on ICP-MS measurements), followed by the addition of 0.1 mmol MBY. Deionized water was added into the solution until the total volume of mixture reached 1 mL. A balloon filled with 100% H\textsubscript{2} was used to enclose the system and to provide reaction gas H\textsubscript{2}. After exhausting air with H\textsubscript{2} for four times, the catalytic reactions were carried out at 303 K under mild stirring for several hours. The resultant solution was analyzed by a gas chromatography (GC, 7890B, flame ionization detector, FID, Ar carrier, Agilent).

**DRIFTS Spectroscopic Characterizations**: The DRIFTS measurement for MBE chemisorption was performed using a Bruker IFS 66v Fourier transformation spectrometer with a Harrick diffuse reflectance accessory at the Infrared Spectroscopy and Microspectroscopy Endstation (BL01B) in National Synchrotron Radiation Laboratory (NSRL), Hefei. The samples were mixed with 20 μL of MBE, and then treated at 353 K for 4 h under vacuum to remove the physically adsorbed organic molecules. The usage of Au@Au\textsubscript{1}Pd\textsubscript{4} nanocubes was determined by the molar content of Pd atoms (2 μmol). Based on the identical experiment condition, the intensity difference between samples can be quasi-quantitatively analyzed for the MBE chemisorption.

**Isothermal Adsorption Measurements**: Isothermal adsorption measurements of MBE were carried out in a thermostat at 303 K. In a

<table>
<thead>
<tr>
<th>Substrate\textsuperscript{a)}</th>
<th>Catalyst</th>
<th>Conversion [%]</th>
<th>alkene selectivity [%]</th>
<th>alkane selectivity [%]</th>
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</thead>
<tbody>
<tr>
<td>Au@Au\textsubscript{4}Pd\textsubscript{1}</td>
<td>97.0</td>
<td>81.9</td>
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<tr>
<td>Au@Au\textsubscript{1}Pd\textsubscript{4}</td>
<td>96.3</td>
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<td>30.1</td>
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<tr>
<td>Au@Au\textsubscript{4}Pd\textsubscript{1}</td>
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<td>90.2</td>
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</tr>
<tr>
<td>Au@Au\textsubscript{1}Pd\textsubscript{4}</td>
<td>99.3</td>
<td>68.6</td>
<td>31.4</td>
<td></td>
</tr>
<tr>
<td>Au@Au\textsubscript{4}Pd\textsubscript{1}</td>
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<td>9.50</td>
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<tr>
<td>Au@Au\textsubscript{1}Pd\textsubscript{4}</td>
<td>97.5</td>
<td>65.1</td>
<td>34.9</td>
<td></td>
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\textsuperscript{a)} Reaction conditions: Au@Au\textsubscript{4}Pd\textsubscript{1} and Au@Au\textsubscript{1}Pd\textsubscript{4} (Pd: 0.4 nmol), substrate (0.1 mmol), temperature (303 K), reaction time (4–12 h). The conversion and selectivity were determined by GC or GC-MS.

Table 1. Semihydrogenation of various alkynes by Au@Au\textsubscript{4}Pd\textsubscript{1} and Au@Au\textsubscript{1}Pd\textsubscript{4} nanocubes.
typical process, 1 mg of sample was dispersed in 2 mL of H$_2$O solution containing various amounts of MBE, which was then stirred for 4 h to achieve fully adsorption. The samples were separated by centrifugation subsequently. The remaining amounts of MBE in supernatant liquid were analyzed by a GC (7890B, FID, Ar carrier, Agilent) with ethanol as the internal standard.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was financially supported in part by National Key R&D Program of China (2017YFA0207301), NSFC (No. 21471141, U1532135, 21601173, 11404095), CAS Key Research Program of Frontier Sciences (QYZDB-SSW-SLH018), CAS Interdisciplinary Innovation Team, Innovative Program of Development Foundation of Hefei Center for Physical Science and Technology (2016FXCX003), Anhui Provincial Natural Science Foundation (1608085QB24), and Chinese Universities Scientific Fund (No. WK2310000067). DRIFTS and XPS measurements were performed at the Infrared Spectroscopy and Microspectroscopy Endstation (BL01B) and the Catalysis and Surface Science Endstation (BL11U) in the National Synchrotron Radiation Laboratory (NSRL) in Hefei, China.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
catalysis, palladium, selectivity, semihydrogenation

Received: October 11, 2017
Revised: November 1, 2017
Published online: December 27, 2017