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# Tuning chemical compositions of bimetallic AuPd catalysts for selective catalytic hydrogenation of halogenated quinolines

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Catalytic hydrogenation of halogenated quinolines is a longstanding challenge due to the harsh reaction conditions and disillusionary chemoselectivity owing to dehalogenation. Exploration of novel catalytic materials is still a big challenge. Herein, density functional theory calculations indicate that halogenated quinolines are selectively adsorbed on Au surface *via* nitrogen atom in the tilted orientation and on Pd *via* quinoline ring in the flat orientation, respectively. In the tilted orientation, the C-Cl bond is away from the surface of catalysts, which can avoid the hydrogenation of C-Cl bond by the surface activated hydrogen species. Then, a series of Au<sub>1-x</sub>Pd<sub>x</sub> bimetallic catalysts were deposited on CeO<sub>2</sub> nanorods by a facile electroless chemical deposition method. The Au<sub>1-x</sub>Pd<sub>x</sub> catalysts with low Pd entities delivered enhanced activity and improved chemoselectivity for hydrogenation of halogenated quinolines. Highly dispersed Pd in Au matrix of bimetallic catalysts with low Pd entities triggers hydrogen activation on Pd sites and leads to the selective adsorption of halogenated quinolines on Au sites in the tilted orientation. The generated active hydrogen species can diffuse from Pd to Au sites for hydrogenation of the tilted halogenated quinolines, resulting in the suppressed dehalogenation and a high chemoselectivity to the expected products.

#### Introduction

Catalytic hydrogenation of quinoline and their derivatives represents a promising and challenging approach with the practical simplicity and high atom economy for the production of 1,2,3,4thetrahydroquinoline, which is an important building block of many biologically active natural products and organic intermediates.<sup>1-4</sup> Transition metal and/or metal-free catalysts have been reported to catalyze the hydrogenation of N-heteroarenes, which require high reaction temperature ( > 120  $^{\circ}$ C) and long reaction time ( > 24 h) due to their low capability for  $H_2$  activation.<sup>5-8</sup> Noble metal (*e.g.* Ir, Ru, Rh, Pd, Pt) catalytic systems exhibit high catalytic activity for hydrogenation of quinolines.<sup>9-20</sup> However, either heterogeneous or homogeneous catalysts generally show a poor substrate scope in the presence of other reducible functional groups (-Cl. -OH. -CHO ect.), leading to a low catalytic chemoselectivity.<sup>21-23</sup> Moreover, the strong adsorption of quinolines and hydrogenated quinolines on the surface of noble metals may cause the poison of catalysts.<sup>24</sup>

Among various functionalized derivatives, halogenated

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quinolines are useful reagents in metal-catalyzed cross-coupling reactions for formation of C-C, C-N or C-S bonds.<sup>25-28</sup> However, only a few heterogeneous cases with low selectivity have been reported due to dehalogenation under the reductive environment (Table S1).<sup>7, 8, 14, 24, 29</sup> Recently, Au-based catalysts have been reported to realize the hydrogenation of N-heteroarenes.<sup>18, 24</sup> Especially, Au/TiO<sub>2</sub> catalysts featured with very small Au nanoparticles ( < 2 nm) and large surface area of support ( > 120  $m^2/g$ ) can deliver a high chemoselectivity hydrogenation of 6-chloroquinoline into 6-chloro-1,2,3,4-tetrahydroquinolin.<sup>24</sup> Heterolytic H<sub>2</sub> cleavage was proposed at the interface of Au nanoparticles and TiO<sub>2</sub> support. However, the catalytic mechanism is still unclear. Compared to Pd catalysts, the capability of Au for hydrogen activation is generally 1 ~ 2 orders of magnitude lower than that of Pd.<sup>30, 31</sup> Pd catalysts delivered high catalytic activity for hydrogenation of quinolines and their derivatives but very poor chemoselectivity.<sup>8, 24</sup>

Generally, halogenated quinolines can be adsorbed on the surface of metal catalysts with a tilted configuration *via* nitrogen atom in *N*-heteroarene or with a flat configuration *via* quinoline ring. The tilted orientation of halogenated quinolines can effectively avoid dehalogenation due to a long distance between the C-X (X=CI, Br and I) bond and surface of catalysts. A feasible approach to enhance the chemoselectivity is to control adsorption configuration of quinoline molecules in the tilted configuration on the surface of catalysts. While, hydrogen also can be effectively activated on the surface of catalysts. For this part, bimetallic catalysts with controllable surface chemical compositions and electronic structures may provide a potential solution to improve

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Electronic Supplementary Information (ESI) available: summary of the adsorption configuration of 6-chloroquinoline molecule on Pd(111) and Au(111) crystal face, structural characterization, UV-vis adsorption spectra and TEM image of original CeO<sub>2</sub> and reduced CeO<sub>2</sub>, characterization of Au/CNR and Pd/CNR catalysts, TEM image of Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR catalyst after 4 times recycling, summary of CeO<sub>2</sub> nanorods catalysts and optimization of the reaction conditions. See DOI: 10.1039/X0xX00000x

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the chemoselectivity of the hydrogenation of halogenated quinolines.  $^{\rm 32,\,33}$ 

Initially, density functional theory (DFT) calculations were employed to investigate the adsorption configurations of 6chloroquinoline on Pd(111) and Au(111) surfaces. Results show that 6-chloroquinoline is selectively adsorbed on Au(111) with a tilted configuration and on the Pd(111) with a flat configuration. When small amount of Pd is alloying with the second metal, hydrogen activation on surface Pd species and the selective adsorption of quinolines on the second metal with the tilted configuration may realize a high chemoselectivity for hydrogenation of halogenated guinolines. Guided by theoretical predictions, a series of alloyed AuPd catalysts supported on CeO2 nanorods (Au1-<sub>x</sub>Pd<sub>x</sub>/NR-CeO<sub>2</sub>) were synthesized through a facile electroless chemical deposition (ECD) process. To our delight, the AuPd catalysts with the decreased Pd entities can significantly enhanced both catalytic activity and chemoselectivity for hydrogenation of 6chloroquinoline into 6-chloro-1,2,3,4-tetrahydroquinoline. The improved catalytic activity and chemoselectivity can be attributed to the selectively adsorbed quinolines on Au via a tilted configuration and efficiently activated hydrogen by surface Pd species, respectively.

#### **Results and discussion**

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Bimetallic AuPd catalysts have been widely explored for many reactions in both theoretically and experimentally.<sup>34-38</sup> Adsorption of 6-chloroquinoline molecule on Pd(111) and Au(111) as a model system were investigated by DFT calculations. As shown in Fig. 1 and Fig. S1, 6-chloroquinoline molecule preferentially adsorbs on Pd via flat orientation with high adsorption energy of -0.44 eV. While, the adsorption energy of +0.23 eV suggests that the tilted orientation is energetically and thermodynamically unstable configuration. In the flat orientation, the reductive hydrogen species activated by Pd can attack both N-heteroarene and C-Cl bond simultaneously, implying the concurrent hydrogenation and dehalogenation. Moreover, the bond length of C-Cl in the adsorbed 6-chloroquinoline on Pd via the flat orientation is extended from the intrinsic 1.73 Å to 1.75 Å, indicating the activated C-Cl bond on Pd for dehalogenation. Thus, the flat orientation of 6chloroguinoline on Pd leads to a poor chemoselectivity. In contrast, the tilted orientation of 6-chloroguinoline can effectively avoid dehalogenation due to a long distance between the C-Cl bond and activated hydrogen species. Thus, the strategy to control the adsorption of halogenated quinolines shows the potential to improve the chemoselectivity of catalytic hydrogenation.

Despite very low capability of Au for  $H_2$  activation, the selective hydrogenation of halogenated quinolines by Au was reported.<sup>24</sup> Heterolytic  $H_2$  cleavage was proposed at the interface of very small Au nanoparticles and TiO<sub>2</sub> support with a very large surface area. However, the catalytic mechanism is still unclear. This unusual catalytic activity and selectivity of Au for hydrogenation of halogenated quinolines may indicate their alternated adsorption structures on Au. DFT results show 6-chloroquinoline molecule tends to bind with Au(111) *via* nitrogen atom in the tilted orientation with an adsorption energy of -0.54 eV (Fig. 1 and Fig. S2).



Figure 1. Adsorption configurations and energy of 6-chloroquinoline on Pd (111) and Au (111) surfaces.

This value is much higher than that of 6-chloroquinoline on Au(111) (-0.11 eV) and larger than that on Pd(111) (-0.44 eV) both in the flat orientation. Motivated by DFT calculations and native capability of metals for  $H_2$  activation, we envision that the bimetallic AuPd catalysts with tunable chemical compositions have potential to present the satisfactory catalytic activity and improve chemoselectivity of hydrogenation of halogenated quinolines. In this strategy, the activated hydrogen species on Pd can diffuse to Au for hydrogenation of the selective adsorbed halogenated quinolines in the tilted orientation.

Bimetallic AuPd catalysts with controllable atomic ratios were obtained by a three-step wet chemical approach: (1) synthesis of CeO<sub>2</sub> nanorods (CNR) as supports;<sup>39</sup> (2) chemical reduction of CNR by ascorbic acid  $(AA)^{40}$  and (3) metal ECD in the presence of the desired amount of metal precursors. CNR was selected as the functional support due to their excellent catalytic performance in various hydrogenation or oxidation reactions.<sup>41-45</sup> X-ray diffraction (XRD) pattern and dark field transmission electron microscope (TEM) image demonstrated that as-synthesized CeO<sub>2</sub> was cubic fluorite phase and rod-like morphology with a length of ~ 90 nm and diameter of ~ 6.1 nm (Fig. S3). The apparent blue-shift of the ultraviolet-visible (UV-vis) absorption spectra induced by AA treatments indicated the successful surface reduction with a decreased surface Ce<sup>4+</sup> fraction (Fig. S4). The reduced CNR preserved their structural features as that of the freshly synthesized nanorods (Fig. S5).

A series of Au<sub>1-x</sub>Pd<sub>x</sub>/CNR with a similar metal weight loading (0.9%~1%) were synthesized by ECD process between the reduced CNR and aqueous Na<sub>2</sub>PdCl<sub>4</sub> and/or HAuCl<sub>4</sub> precursors in the absence of any reductant and additives. Typical TEM images of Au<sub>1-</sub> <sub>x</sub>Pd<sub>x</sub>/CNR catalysts showed the rod-like morphology of assynthesized catalysts decorated with uniform metal particles (Fig. 2a and Fig. S6). The actual Au and Pd loadings were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Table 1). The ICP-OES characterization is capable of bulk elemental analysis but is not able to distinguish the surface elemental

catalyst fringes (nm) diameter (nm) (wt %) (wt %)	PSª
Au/CNR 0.238 6.7 ± 2.1 0.92 0 0	0
Au <sub>0.93</sub> Pd <sub>0.07</sub> /CNR 0.235 4.1 ± 0.9 0.96 0.039 0.075 0.	091
Au <sub>0.9</sub> Pd <sub>0.1</sub> /CNR 0.231 4.5 ± 0.8 0.85 0.047 0.11 0.	099
Au <sub>0.75</sub> /Pd <sub>0.25</sub> /CNR 0.23 4.2 ± 1.2 0.81 0.146 0.33 0	.24
Au <sub>0.4</sub> Pd <sub>0.6</sub> /CNR 0.228 5.0 ± 1.5 0.55 0.43 1.5 1	.98
Au <sub>0.25</sub> Pd <sub>0.75</sub> /CNR 0.227 4.7 ± 1.3 0.35 0.56 3	3.4
Pd/CNR 0.223 4.7 ± 0.8 0 0.96 ∞	∞

Table 1. Summary of various Au<sub>1-x</sub>Pd<sub>x</sub>/CNR catalysts

<sup>a</sup> The atomic ratios of Pd:Au were calculated from the area ratios of Pd:Au in XPS spectrum (Fig. S8).

compositions. X-ray photoelectron spectroscopy (XPS) was performed to track the surface chemical compositions of the alloyed AuPd catalysts. The ratio of integral area of Au peak to integral area of Pd peak was calculated as a descriptor to reveal the surface atomic ratios of Au:Pd for various Au<sub>1-x</sub>Pd<sub>x</sub>/CNR catalysts, as shown in Fig. S8. With the increase of bulk Pd, the surface Pd fractions were also increased (Table 1). Fig. 2 showed the TEM images of AuPd bimetallic catalysts with a chemical composition of Au<sub>0.9</sub>Pd<sub>0.1</sub>, in which the weight loadings of Au and Pd were 0.85% and 0.047%, respectively. The Au/CNR and Pd/CNR catalysts were also synthesized with a similar total weight loading (Table 1 and Fig. S7). Derived from TEM images, the average sizes of Au<sub>0.9</sub>Pd<sub>0.1</sub>, Au and Pd particles were 4.5  $\pm$  0.8, 6.7  $\pm$  2.1 and 4.7  $\pm$  0.8 nm, respectively. Compared with the Au/CNR, the characteristic absorption peak of Au nanoparticles at 540 nm was absent in the UV-vis spectrum of the Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR (Fig. 2c), indicating their bimetallic structure. The measured planar spacing of 0.231 nm of Au<sub>0.9</sub>Pd<sub>0.1</sub> in the aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image was slightly smaller than 0.238 nm of the Au(111) crystalline plane but larger than 0.223 nm of Pd(111) plane (Fig. 2d and Fig. S7), which can be attributed to the large Au atoms replaced by the small Pd atoms.<sup>46</sup> Energy dispersive X-ray (EDX) elemental mapping of metal particles further confirmed the alloyed structure of  $Au_{0.9}Pd_{0.1}$ 

Figure 2. Structural characterizations of the  $Au_{0.9}Pd_{0.1}/CNR$  catalysts. (a) TEM image, (b) size distribution (c) UV-vis

absorption spectra of various catalysts, (d) High resolution HAADF-STEM image. EDX elemental mapping of (e) Au and (f) Pd, respectively.

on CNR support (Fig. 2e and 2f).

Initially, the catalytic performance of various catalysts was evaluated using a model hydrogenation of 6-chloroquinoline (1). The optimized reaction conditions were under 100 °C and 2.0 MPa H<sub>2</sub> in toluene (Table S2). The Au/CNR catalysts delivered no hydrogenation activity under the optimized conditions (Fig. S9). Introduction of small amount of Pd (x=0.07) in Au particles triggered the hydrogenation of 1 with a conversion of 26.4% for the initial 1 h (Fig. 3a). Increase of x to 0.1, 0.25 and 0.6 resulted in improved conversions of 1 to 34.6%, 65.9% and 94.7% in the same duration (1 h), respectively. However, the conversions of 1 inversely decreased to 88.5% and 30.5% on the further increase of Pd contents at x = 0.75 and 1.0, respectively. Introduction of Pd in Au can lower the activation barrier to H<sub>2</sub> dissociation and the bound activated hydrogen is weakly enough to allow hydrogen spillover onto Au surface.<sup>47, 48</sup> Thus, high catalytic activity of the Au<sub>1</sub>- $_xPd_x/CNR$  over the Au/CNR or Pd/CNR can be understood by this synergistic effect, similar to previous reports.  $^{30,\;31,\;49,\;50}$  Compared to the Pd/CNR, the relative low activity of the Au<sub>0.93</sub>Pd<sub>0.07</sub>/CNR can be attributed to the limited amount of the surface Pd species for H<sub>2</sub> activation.

In addition to the evolution of the catalytic activity of bimetallic AuPd as a function of chemical compositions, the chemoselectivity into 6-chloro-1,2,3,4-thetrahydroquinoline (2) was found to be significantly affected by the Pd entities within the initial 1 h (Fig. 3a). The Pd/CNR catalysts delivered a very poor selectivity of 51.7% to the desired product 2. Decreasing the Pd percentage in the bimetallic catalysts, the chemoselectivity to 2 was significantly

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Figure 3. Catalytic activity and chemoselectivity of hydrogenation of 6-chloroquinoline over a series of Au<sub>1-x</sub>Pd<sub>x</sub>/CNR catalysts. Reaction conditions: 0.2 mmol of 6-chloroquinoline, 5 mg of catalysts, 2 mL of toluene, 100 °C and 2.0 MPa  $H_2$ . (a) Catalytic activity and selectivity of 2 for 1 h. (b) Product distributions when the conversions of 6-chloroquinoline were over 90% for all catalysts.



Schematic 1. Proposed catalytic process for hydrogenation of 6chloroquinoline catalyzed by the Au<sub>1-x</sub>Pd<sub>x</sub>/CNR at low Pd entity.

improved to 56.3%, 64.9%, 75.7%, 89.7% and 92.3% for the  $Au_{1-}$ <sub>x</sub>Pd<sub>x</sub>/CNR catalysts with x=0.75, 0.6, 0.25, 0.1 and 0.07, respectively. The similar trend was also observed in the final yields of product 2. As shown in Fig. 3b, the yield of 2 reached 91.6% for the  $Au_{0.93}Pd_{0.07}$ /CNR catalysts with low yields of by-product **3** (5.4%) and 4 (1.4%), respectively. With the increase of the surface Pd fractions in the bimetallic catalysts, the yields of 2 decreased to 86.8%, 73.6%, 61.7%, 51.9% for the Au<sub>1-x</sub>Pd<sub>x</sub>/CNR catalysts with x=0.1, 0.25, 0.6 and 0.75, respectively and only 47.9% for the Pd/CNR catalysts.

The similar sizes of bimetallic  $Au_{1-x}Pd_x$  and monometallic Au and Pd particles suggest that their difference in catalytic hydrogenation is originated from the alloying effect. At low Pd entities, Pd metal is highly dispersed in the Au host matrix. As shown in Schematic 1, one Pd metal atom can be supported on or sandwiched between the Au host atoms, as well as the formation of very small Pd clusters on the surface of bimetallic catalysts. In this situation, 6chloroquinoline molecules tend to be selectively adsorbed on the surface abundant Au sites via the tilted orientation (Schematic 1), according to DFT calculations (Fig.1). It has been well documented experimentally and theoretically that these highly dispersed Pd can dissociate H<sub>2</sub> more readily and bind it more weakly than that on the surface of pure metals.<sup>47, 48, 51</sup> The generated active hydrogen

species (H<sub>a</sub>) on Pd can spill over onto the surface Au sites for hydrogenation. The selective adsorbed halogenated quinolines on Au sites via tilted orientation allow the selective hydrogenation of N-heteroarenes and block the dehalogenation, resulting in the improved chemoselectivity to the desired products. High percentages of Pd in the bimetallic particles result in more surface Pd atoms and formation of the large Pd clusters on the surface of the bimetallic catalyst. It induces a primary change in the adsorption configurations of reactants from the selective tilted orientation on Au at low Pd entity to both the tilted orientation on Au and flat orientation on Pd at high Pd entity. Thus, the dehalogenation and poor chemoselectivity were indeed observed when more Pd was introduced into the bimetallic catalysts.

Among various bimetallic catalysts, the Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR exhibited much better selectivity and higher catalytic activity over the Pd/CNR. As shown in Fig. 4a, the yield of 86.5% for product 2 was obtained with the 96.4% conversion of 1 after 5 h reaction. In contrast, the Pd/CNR catalysts led to a much lower yield (47.3%) of product 2 under the same reaction conditions, where the conversion of 1 was



Figure 4. (a) Time course of conversion and (c) catalytic stability of Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR for hydrogenation of 6-chloroquinoline. (b) Time course of conversion and (d) catalytic stability of Pd/CNR for hydrogenation of 6-chloroquinoline. Reaction conditions: 6chloroquinoline (0.2 mmol), Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR or Pd/CNR catalyst (5 mg) (15 mg for stability test), toluene (2 mL), 100 °C and 2 MPa H<sub>2</sub>.

91.6% (Fig. 4b). Also, large amount of the undesired dehalogenated by-products 3 (8.6%) and 4 (39.7%) were yielded. The commercial Lindlar catalysts (5 wt% Pd) only delivered a 24.1% conversion of 1 and 64.8% selectivity of 2 under the identical reaction conditions (Fig. S10). Thus, the  $Au_{0.9}Pd_{0.1}$ /CNR catalysts exhibited a satisfactory activity as well as the significantly improved chemoselectivity.

Catalytic stability is also a very important criterion to evaluate the performance of catalysts. As shown in Fig. 4c, the Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR catalysts delivered stabilized activity with slight deactivation during the cyclic hydrogenation. Importantly, the chemoselectivity to 2 was well maintained at the level of 89% for the initial consecutive four cycles. The unchanged morphology of the Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR also indicated their structural robustness for

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a 100

Conversion (%)

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hydrogenation (Fig. S11). Very low metal bleaching of the Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR with concentrations of 1.45 ppm (Au) and 0.35 ppm (Pd) in the reaction solution after 4 cycles suggested the stability of the catalysts. While, for the Pd/CNR, the conversion of **1** decreased continuously from initial 85.6% to 31.5% after four cycles (Fig. 4d). Very high Pd concentration of 30.5 ppm in the liquid reaction solution was 87 times higher than that of the Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR catalysts, suggesting a serious metal bleaching of the Pd/CNR catalysts during the hydrogenation process.

Next, the scope of Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR was extended to various substituted quinolines containing halogen and reducible groups. As shown in Table 2, the >99.9% chemoselectivity of 1,2,3,4-tetrahydroquinlone was obtained at both 5 h (46.9% conversion, Entry 1) and 10 h (92.6% conversion, Entry 2). For 6-bromo- and 6-iodo-quinoline, the high selectivity (>93.2%) of 6-halo-1,2,3,4-tetrahydroquinoline was yielded under either low or high conversions of substrates (Entries 3, 4, 5 and 6). Introducing the reducible groups, the hydrogenation selectivity of 6-methoxy-quinoline to 6-methoxy-1,2,3,4-tetrahydroquinolin reached 98.3%

#### Table 2. Hydrogenation of various substituted quinolines by the Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR\*

Entry	Substrate	Product	Time (h)	Con. (%)	Sel. (%)
1		$\square$	5	46.9	>99.9
2		N N	10	92.6	>99.9
3	Br	Br	5	36.2	98.5
4		N N	8	98.2	96.4
5	I CONT		5	10.2	95.1
6		N N	20	76.5	93.2
7	H <sub>3</sub> CO	H <sub>3</sub> CO	3	33.6	98.3
8		N N	10	96.3	95.6
9	OHC	OHC	3	35.6	98.1
10		N N	10	86.3	96.1
11		CI	3	30.1	94.1
12			10	89.6	92.3

\* **Reaction conditions:** 5 mg of Au<sub>0.9</sub>Pd<sub>0.1</sub>/CNR, 0.2 mmol of substrate, 2.0 mL of toluene, 100 °C and 2.0 MPa H<sub>2</sub>.

and 95.6% at the conversions of 33.6% and 96.3%, respectively (Entries 7 and 8). In the presence of the reducible –CHO group, the high chemoselectivity to 6-formyl-1,2,3,4-tetrahydroquinolin (>96.1%) was also obtained (Entries 9 and 10). When chlorine located at 4-positions of quinoline ring, the chemoselectivity to the desired products was higher than 92.3% (Entries 11 and 12).

#### Conclusions

In summary, we have designed and synthesized the  $Au_{1-x}Pd_x$ bimetallic catalysts with tunable chemical compositions on  $CeO_2$ nanorods synthesized by a facile ECD method, which deliver high activity and chemoselectivity for hydrogenation of halogenated quinolines. Improved chemoselectivity could be attributed to the selective adsorption configurations of halogenated quinolines on Au *via* tilted orientation rather than on Pd *via* flat orientation, when the Pd entities were low. The reductive hydrogen species activated by surface Pd can spill over from Pd to Au sites and selectively hydrogenate the halogenated quinolines to the expected products. Such cooperative effects between two different metals associated with different adsorption configurations of reactants on each metal may benefit the design of novel catalysts with improved chemoselectivity for many important reactions.

#### Experimental

All chemicals (AR grade) were used as received. Water with a resistivity of 18.2 M $\Omega$  · cm was used for all experiments. All glassware were thoroughly washed by aqua regia (a volume ratio of 1: 3 of concentrated nitric acid and hydrochloric acid) to avoid any possible contamination. (*Caution: Aqua regia is highly corrosive and extremely dangerous and must be handled with the proper protective equipments*)

4.1 Theoretical calculation. The density functional calculation (DFT) was carried out by Vienna Ab-initio Simulation Package (VASP).<sup>52-57</sup> Frozen-core all-electron projector augmented wave (PAW) method and plane wave basis were set. The generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof functional (PBE)<sup>55</sup> was chosen for electron exchange and correlation. The energy cut off is 400 eV. The lattice parameters of bulk metals were 0.4173 nm (for Au), and 0.3949 nm (for Pd), which are approach to the experiment data (0.408 nm and 0.389 nm). A p(3x3) supercell with 4 atom layers of Pd (111) was choose as the slab model, including a relaxation of the top two layers. A vacuum thickness of 20 Å was used to avoid the interaction from the top supercells. The Brillouin-zone integration has been performed with a 2 x 2 x 1 Monkhorst-Pack grid. For the 6-chloroquinoline molecular, a supercell of 20 Å x 20 Å x 20 Å is selected, and the Brillouin-zone integration has been performed with a 1 x 1 x 1 Monkhorst-Pack grid. For the geometry relaxation, a criterion of 0.02 eV/Å on forces is used. And the convergence criterion for the energy was 10-5 eV.

The adsorption energy was defined as the follow equation:

Eadsorption=Etot-Emetal- Emolecule

 $(E_{tot}:$  The total Energy of the metal surface and an absorbed molecule,  $E_{metal}:$  the energy of metal surface model,  $E_{molecule}:$  the energy of molecule.)

**4.2** Synthesis of CeO<sub>2</sub> nanorods (CNR). Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (1.736 g) and NaOH (19.2 g) were dissolved in 10 and 70 mL of MQ water, respectively. After aging for 30 min, the mixture was transferred into a stainless steel autoclave for hydrothermal treatment at 100 °C for 24 h. The solid products were collected by centrifugation, washed with ethanol and water, and dried at 60 °C overnight.

**4.3 Synthesis of Au<sub>1-x</sub>Pd<sub>x</sub>/CNR catalyst.** Firstly, 100 mg of CNR support was dispersed in 50 mL of ascorbic acid (0.1 mmol) solution. The mixture was stirred at room temperature for 1 h. The solid was obtained by centrifugation and washed immediately with water for 3 times. Then, the solid was re-dispersed in another 100 mL water and desired amount of HAuCl<sub>4</sub> and/or NaPdCl<sub>4</sub> was added subsequently. The mixture was stirred for another 12 h. After centrifugation, the products were reduced by 5% H<sub>2</sub>/Ar at 200 °C to obtain the metallic catalysts.

**4.4 Catalytic hydrogenation of quinolines.** Hydrogenation of quinolines was carried out in a stainless steel autoclave equipped

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with pressure control system. For a typical catalytic reaction, 0.2 mmol of quinolines and 5 mg of catalysts were mixed in 2 mL of toluene. The reactions were performed in the autoclave charged with 2.0 MPa of  $H_2$  at 100 °C. The products were analyzed by gas chromatography-mass spectrometer (GC-MS) and GC with m-xylene as internal standard.

#### Acknowledgements

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