



# Oxide-supported atomically precise gold nanocluster for catalyzing Sonogashira cross-coupling



Gao Li<sup>a</sup>, De-en Jiang<sup>b</sup>, Chao Liu<sup>a</sup>, Changlin Yu<sup>a</sup>, Rongchao Jin<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, United States

<sup>b</sup> Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States

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## ABSTRACT

We report that thiolate-protected Au<sub>25</sub>(SR)<sub>18</sub> (R = CH<sub>2</sub>CH<sub>2</sub>Ph) nanoclusters supported on oxides (such as CeO<sub>2</sub>, TiO<sub>2</sub>, MgO, and SiO<sub>2</sub>) can catalyze Sonogashira cross-coupling reaction between phenylacetylene and *p*-iodoanisole with high conversion of *p*-iodoanisole (up to 96.1%) and excellent selectivity (up to 88.1%). The well-defined structure of Au<sub>25</sub>(SR)<sub>18</sub> provides an important clue as to the catalytically active sites: the sterically unhindered facets on the cluster surface allow easy reactant access; each facet comprises three surface gold atoms from three separate “staple”-like –S(R)–Au–S(R)–Au–S(R)– surface-protecting motifs. Density functional theory modeling of the reactant adsorption shows that both reactants prefer to adsorb on the open facet with the phenyl ring facing a surface gold atom. Each reactant has an adsorption energy of –0.40 to –0.48 eV. When they co-adsorb on the catalyst, the total adsorption energy reaches –0.90 eV (a relatively strong adsorption state); more interestingly, at this state the two reactants are well positioned to couple with their Ph–C≡CH and Ph–I groups pointing toward the third gold atom of the open facet. The combined experimental and DFT results suggest a great potential to correlate the atomic configuration of the active sites to the catalytic performance of an atomically precise nanocluster.

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## 1. Introduction

Metals in the forms of nanoparticles and complexes have played an important role in industrial catalysis, including oil refinery, petrochemical, fine chemical, and pharmaceutical industries. With respect to fundamental catalysis, a major thrust is to create catalysts with well-defined structures (especially for nanoparticle-based catalysts) in the hope of understanding the correlation between the catalyst structure and catalytic properties. This thrust led to the development of bulk single crystal model catalysts in the 1970–1980s and the recent shape-controlled nanocrystal catalysts [1–3]. Using these model catalysts, experiment and theory have revealed a wealth of information on molecular adsorption and catalytic reaction pathways, especially on well-defined metal surfaces [2]. Applying this approach to colloidal metal nanoparticle-derived nanocatalysts is, however, difficult from a theoretical perspective, mainly due to their less well-defined surface structures (i.e., the precise surface atom arrangement).

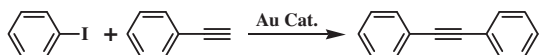
In very recent research, atomically precise metal nanoclusters with total structures determined by X-ray crystallography have emerged as a new class of nanomaterial [4] and may offer an

opportunity to achieve atomic level understanding of the relationship between the active-site structure and the catalytic selectivity and activity. We are interested in applying such nanoclusters to important reactions in organic chemistry such as carbon–carbon coupling reactions which are traditionally catalyzed by metal complexes, but recyclability and removal of homogenous metal catalysts in the end-products have long been major concerns in fine chemical and pharmaceutical industry, while supported metal nanoparticles readily circumvent these issues.

Among the metal-catalyzed coupling reactions [5–7], Sonogashira cross-coupling reaction, which gives rise to new carbon–carbon bonds between a terminal alkyne and an aryl or vinyl halide, is strategically important in organic synthesis. Recently, much attention has been focused on the use of Au<sup>I</sup> and Au<sup>III</sup> complexes [8–11], and metallic Au<sup>0</sup> nanoparticle [12–14] as catalysts for the Sonogashira cross-coupling reaction of phenylacetylene and iodobenzene (Scheme 1). Two side-products (i.e., the two homocoupling products – diphenyldiacetylene and biphenyl) would be yielded in the cross-coupling process when catalyzed by gold nanoparticles [12]. Lambert et al. have reported that the lanthana-supported metallic Au<sup>0</sup> nanoparticles (~20 nm) as a heterogeneous catalyst show a good conversion of iodobenzene and selectivity for the target cross-coupling product, diphenylacetylene [14]. In contrast to the metallic gold nanoparticle catalysts, ultrasmall non-metallic gold nanoclusters (<2 nm, with a sizable electronic energy gap)

\* Corresponding author. Fax: +1 412 268 1061.

E-mail address: [rongchao@andrew.cmu.edu](mailto:rongchao@andrew.cmu.edu) (R. Jin).



**Scheme 1.** Nanogold-catalyzed Sonogashira coupling between iodobenzene and phenylacetylene.

have shown promise as catalysts for reactions such as oxidation and hydrogenation [15–17]. Herein, we are motivated to investigate the catalytic activity of ultrasmall gold nanoclusters of well-defined composition and structure in Sonogashira cross-coupling reaction.

Among the reported gold nanoclusters protected by thiolate ligands [4,18–20] (referred to as  $Au_n(SR)_m$ , where  $n$  and  $m$  represent the number of gold atoms and  $-SR$  ligands, respectively), the smallest one with structure solved is the  $Au_{25}(SR)_{18}$  nanocluster. Thus, we chose  $Au_{25}(SR)_{18}$  as a model system in this work. The  $Au_{25}(SR)_{18}$  nanocluster exhibits a core-shell type structure [20], which consists of a  $Au_{13}$  icosahedral core and a non-closed gold shell comprised of the remaining 12 gold atoms. According to previous theoretical work [21] that phenylacetylene could be adsorbed on the surface of large gold nanoparticles, we rationalize that phenylacetylene could also be adsorbed by non-metallic nanocluster catalysts; phenylacetylene-capped gold nanocluster have indeed been reported [22]. On the other hand,  $Au \cdots I$  interaction between nanocluster and iodobenzene (i.e., the other reactant for the Sonogashira cross-coupling reaction) may lead to activation of iodobenzene [17,23–25]. These works indicate that Sonogashira cross-coupling would occur on the nanocluster catalyst. The unique core-shell structure and non-metallic electronic properties of the  $Au_{25}(SR)_{18}$  nanocluster may give rise to high activity and selectivity in the Sonogashira cross-coupling.

In this work, we intend to investigate the catalytic activity/selectivity of the  $Au_{25}(SR)_{18}$  nanocluster for the Sonogashira cross-coupling and to correlate the catalytic properties with its structure. Such insight would benefit future catalyst design for achieving high selectivity of nanocluster catalysts for specific reaction processes.

## 2. Materials and methods

### 2.1. Size-focussing method

We briefly describe the principle of the size-focusing methodology (see Ref. [26] for details). First, a proper distribution of size-mixed nanoclusters is obtained by kinetically controlling the reduction of gold precursor (e.g.,  $Au(I)-SR$  polymer) with  $NaBH_4$ . Then, the as-prepared nanoclusters are subjected to size-focusing process under harsh conditions (e.g., at 80 °C and/or in the presence of excess thiol). During the size-focusing process, the unstable nanoclusters decompose or convert to the stable nanoclusters, and eventually, only the most stable nanoclusters survive the size-focusing process. Of note, the initial size range of the size-mixed nanoclusters is very important for obtaining one-sized nanoclusters eventually [26].

### 2.2. Preparation of $Au_{25}(SR)_{18}$ and 2–3 nm $Au:SC_6H_{13}$ nanoclusters

The atomically precise  $Au_{25}(SR)_{18}$  nanoclusters were synthesized as reported previously [18]. For comparison, we also synthesized thiolate-protected 2–3 nm Au nanoclusters (note: these are not atomically precise). Briefly,  $HAuCl_4 \cdot 3H_2O$  (0.2 mmol, dissolved in 5 ml nanopure water) and tetraethylammonium bromide (TOAB, 0.24 mmol, dissolved in 10 ml toluene) were combined in a 25-ml tri-neck round-bottom flask. The solution was vigorously stirred for 15 min, and the aqueous phase was then removed.  $n-C_6H_{13}SH$

(0.4 ml) was added to the flask. After the solution turned to clear (30 min),  $NaBH_4$  (2 mmol, 5 ml cold aqueous solution) was rapidly added all at once. After aging overnight, methanol was added to separate gold nanoclusters from TOAB and other side-products. The small amount of  $Au_{25}(SR)_{18}$  nanoclusters was removed from the crude nanocluster product by extracting the precipitates with acetone. The 2–3 nm  $Au:SC_6H_{13}$  nanoclusters (abbreviated as AuNC) were then extracted with dichloromethane from the black precipitates.

### 2.3. Preparation of the $Au_{25}(SR)_{18}/oxide$ and $AuNC/CeO_2$ catalyst

To prepare the oxide-supported catalyst, 1 mg  $Au_{25}(SR)_{18}$  or 2–3 nm AuNC was dissolved in 5 ml  $CH_2Cl_2$ , and 100 mg oxides ( $TiO_2$ ,  $CeO_2$ ,  $MgO$ , or  $SiO_2$ ) were added. After stirring for 12 h at r.t., the clusters were adsorbed onto the oxide support surfaces. The  $Au_{25}(SR)_{18}/oxide$  catalysts were collected by centrifugation and dried in vacuum. The catalyst was then heated to 150 °C in vacuum for 1 h.

### 2.4. General procedure for the Sonogashira cross-coupling reaction

In a typical Sonogashira cross-coupling reaction, *p*-iodoanisole (0.1 mmol), phenylacetylene (see specific notes in Tables 1–4), base (0.3 mmol),  $Au_{25}(SR)_{18}/oxide$  or 2–3 nm AuNC/ $CeO_2$  (100 mg), and 1 ml solvent were added to a 5-ml one-neck round-bottom flask. The mixture was stirred under  $N_2$  atmosphere at 160 °C for 40 h as indicated in Tables 1–4. After the reaction, 5 ml water was added to the flask, followed by extraction with EtOAc (2 ml  $\times$  3). The products were obtained after removal of EtOAc. The products were characterized by gas chromatography-mass spectrometry (GC-MS) and proton nuclear magnetic resonance ( $^1H$  NMR, 300 MHz) spectroscopy. The conversion of *p*-iodoanisole and selectivity for 4,4'-dimethoxy-1,1'-biphenyl and 1-methoxy-4-(2-phenylethynyl)benzene were determined by nuclear magnetic resonance (NMR) analysis. The products can be purified by silica chromatography using hexane as the eluent. For the recyclability tests, the gold cluster catalyst was separated by centrifugation, washed with water to remove the base and then further washed with EtOAc, and dried in vacuum at room temperature prior to its reuse in the next round of reaction.

### 2.5. Computational details

The Vienna *ab initio* simulation package (VASP) [27] was used to perform density functional theory calculations of the adsorption of phenylacetylene and iodobenzene on the surface of the  $Au_{25}(SCH_2CH_2Ph)_{18}$  cluster in its anionic state. The projector augmented wave (PAW) method was used to describe the interaction between electrons and the nuclei [28]; the Perdew–Burke–Ernzerhof form of the generalized gradient approximation was used for electron exchange and correlation [29]. The DFT-D2 method of Grimme was used to include the van der Waals (vdW) interactions into the system [30]; default vdW parameters in VASP were used for S, C, H, and I, while the parameters for Au were taken from a previous study [31]; a cutoff of 12 Å was applied when evaluating the vdW interactions. The  $Au_{25}(SCH_3)_{18}$  cluster together with the adsorbates was placed at the center of a cubic box of 3.0 nm  $\times$  3.0 nm  $\times$  3.0 nm;  $\Gamma$ -point only was used for the k-point sampling; standard VASP-PAW potentials were used for Au, S, H, and I, while the soft version was used for C, so a lower kinetic energy cutoff (274 eV) could be used to reduce the computational cost. A force convergence criterion of 0.025 eV/Å was used for structural relaxation. We define the adsorption energy as the energy difference between the adsorbed system and the sum of the bare cluster and the isolated adsorbate molecule, so a negative value indicates a favorable interaction.

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