Progress in Natural Science: Materials International 26 (2016) 483–486

HOSTED BY

Contents lists available at ScienceDirect

Progress in Natural Science: Materials International

journal homepage: www.elsevier.com/locate/pnsmi

Original Research

Mechanistic insights from atomically precise gold nanocluster-catalyzed reduction of 4-nitrophenol

Shuo Zhao, Anindita Das, Hui Zhang, Renxi Jin, Yongbo Song, Rongchao Jin*

Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States

ARTICLE INFO

Keywords:
Metal nanoclusters
Gold
4-nitrophenol reduction
Atomic packing modes
Electronic structures

ABSTRACT

A trio of thiolate-protected atomically precise gold nanoclusters, $[Au_{23}(S\text{-}c\text{-}C_6H_{11})_{16}]^-$, $Au_{24}(SCH_2pH^tBu)_{20}$ and $[Au_{25}(SCH_2CH_2pH)_{18}]^-$, are utilized as catalysts for 4-nitrophenol (4-NP) reduction to 4-aminophenol (4-AP). Despite nearly identical sizes (~1 nm), the three nanoclusters possess distinctly different atomic packing structures and surface ligand binding modes, which contribute to different catalytic performance. The $[Au_{23}(S\text{-}c\text{-}C_6H_{11})_{16}]^-$ nanocluster shows the highest activity with a kinetic rate constant of 0.0370 s^{-1}, which is higher than those of $Au_{24}(SCH_2pH^tBu)_{20}$ (0.0090 s^{-1}) and $[Au_{25}(SCH_2CH_2pH)_{18}]^-$ (0.0242 s^{-1}). Such a trio of gold nanoclusters indicate that the atomic packing mode and electronic structure play a crucial role in determining their catalytic performance.

1. Introduction

With advances in chemical synthesis, ultrasmall metal nanoclusters are emerging as a new type of nanomaterials with distinct optical, electronic and catalytic properties [1–7]. Atomically precise gold nanoclusters containing tens of gold atoms protected by thiolate ligands, denoted as $Au_n(SR)_m$ (where n and m represent the numbers of gold atoms and thiolate ligands, respectively), have attracted intense interest due to their unique electronic structures and molecular properties [8]. These ultrasmall gold nanoclusters have exhibited extraordinary catalytic reactivity and sensing performance, as well as the promise in energy conversion [9–14]. Zhu et al. investigated the cluster size effect in partial oxidation of styrene [15]. The general order of observed activity was found to be $Au_{25}(SR)_{18} > Au_{38}(SR)_{24} > Au_{144}(SR)_{60}$, indicating the higher efficiency of smaller nanoclusters than larger ones. Kauffman et al. reported the utilization of $Au_{25}(SR)_{18}$ nanoclusters as effective catalysts for electrochemical reduction of CO_2 to CO, showing a ~200 to 300 mV smaller overpotential as compared to larger gold nanoparticles and bulk gold [16]. The $Au_{25}(SR)_{18}$ nanoclusters were also explored as stable and recyclable catalysts for the reduction of 4-nitrophenol (4-NP) [17].

Besides designing catalysts with enhanced activity and selectivity, it is highly desirable to gain a deep understanding of catalytic process, especially at the atomic scale. Conventional nanoparticles are ploydispersed in size distribution, making it difficult to correlate the observed catalytic activity and selectivity to the structure of nanocatalyst since no two nanoparticles are the same. The observed performance has been averaged out by non-uniform nanoparticles and only nominal parameters such as size and morphology can account for the activity. In contrast, the monodispersity and structures of ultrasmall gold nanoclusters make it possible to achieve a precise structure-activity correlation, which is of great significance to fundamental understanding of catalysis as well as the future design of practical catalysts.

Since the properties of gold nanoclusters are extremely sensitive to the number of Au atoms, addition or removal of a single gold atom is expected to induce significant changes in its structure and properties [18–25]. Investigating such nanoclusters in catalytic reactions is expected to achieve atomic level tuning of catalytic properties.

Herein, we report a trio of gold nanoclusters (Au_{23}, Au_{24} and Au_{25}) as catalysts for the reduction of 4-NP, all of which exhibit similar numbers of gold atoms but very different atom packing modes. $[Au_{23}(S\text{-}c\text{-}C_6H_{11})_{16}]^-$ nanoclusters exhibit the highest kinetic rate constant of 0.0370 s^{-1} for 4-NP reduction, which is higher than the rate constants of $Au_{24}(SCH_2pH^tBu)_{20}$ (0.0090 s^{-1}) and $[Au_{25}(SCH_2CH_2pH)_{18}]^-$ (0.0242 s^{-1}). The observed difference in catalytic performance is attributed to distinct atomic packing modes and electronic structures instead of nominal size or number of gold atoms. Such insights are not possible to be revealed with conventional polydisperse nanocatalysts since their structures are unknown. Thus, atomically precise gold nanoclusters hold great promise in unraveling the catalytic mechanisms [1].

Peer review under responsibility of Chinese Materials Research Society.
* Corresponding author.
E-mail address: rongchao@andrew.cmu.edu (R. Jin).

http://dx.doi.org/10.1016/j.pnsc.2016.08.009
Received 31 July 2016; Accepted 16 August 2016
Available online 08 October 2016

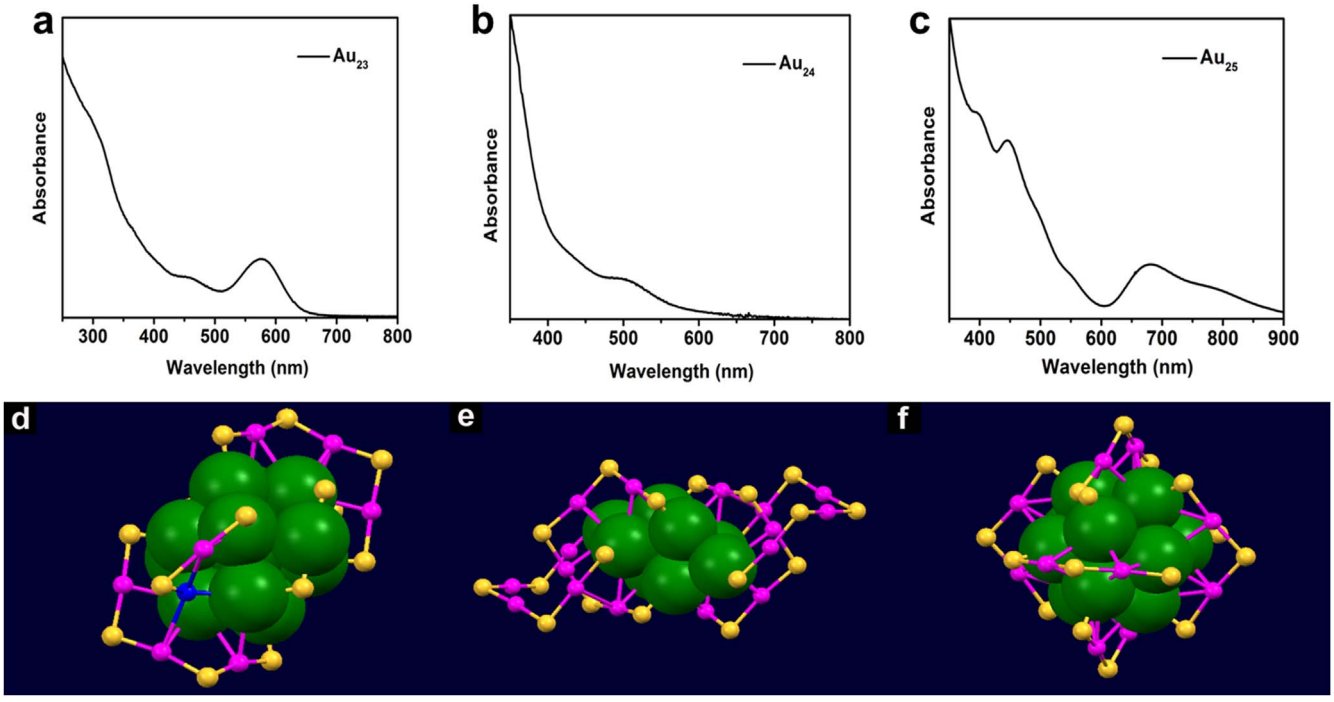

Fig. 1. UV–vis absorption spectra of $[Au_{23}(S\text{-}c\text{-}C_6H_{11})_{16}]^-$ (a), $Au_{24}(SCH_2pH^tBu)_{20}$ (b), and $[Au_{25}(SCH_2CH_2pH)_{18}]^-$ (c). Crystal structure of $Au_{23}S_{16}$ (d), $Au_{24}S_{20}$ (e), and $Au_{25}S_{18}$ framework (f) with the gold kernels highlighted in green, surface gold and sulfur motifs in pink and yellow, and the two extra gold atoms in blue for the case of Au_{23}. All the carbon tails are omitted for clarity.

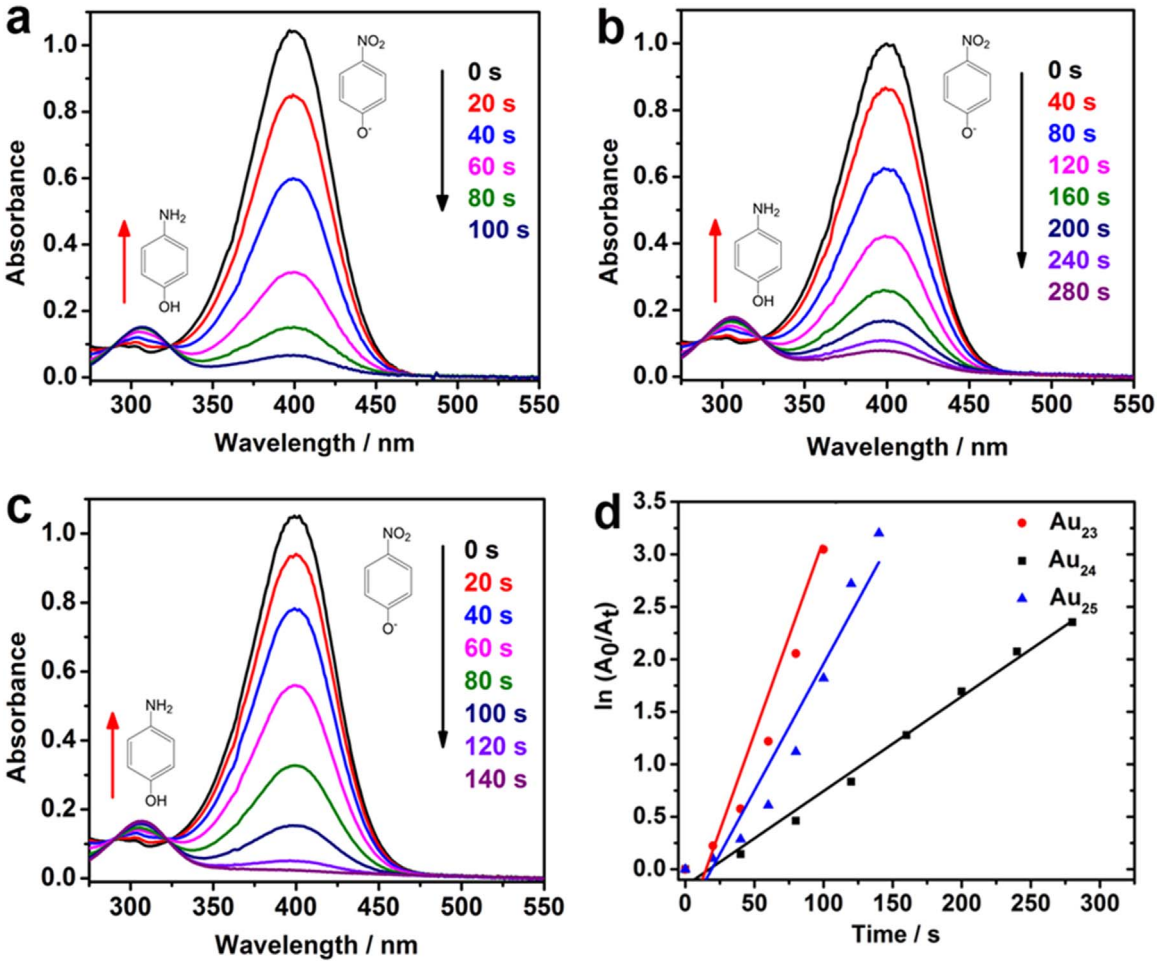

Fig. 2. UV–vis absorption spectra during the catalytic reduction of 4-NP over $[Au_{23}(S\text{-}c\text{-}C_6H_{11})_{16}]^-$ (a), $Au_{24}(SCH_2pH^tBu)_{20}$ (b) and $[Au_{25}(SCH_2CH_2pH)_{18}]^-$ (c). (d) Plots of $\ln(A_t/A_0)$ and the reaction time for 4-NP reduction by thiolate-protected Au_{23}, Au_{24} and Au_{25} nanoclusters, where A_0 and A_t are the absorption peaks at 400 nm initially and at time t, respectively.