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Review

Non-metallic gold nanoclusters for oxygen activation and aerobic oxidation

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ABSTRACT

In recent decade, Au nanoclusters of atomic precision (Au_nL_m , where L=organic ligand: thiolate and phosphine) have been shown as a new promising nanogold catalyst. The well-defined Au_nL_m catalysts possess unique electronic properties and frameworks, providing an excellent opportunity to correlate the intrinsic catalytic behavior with the cluster's framework as well as to study the catalytic mechanisms over gold nanoclusters. In this review, we only demonstrate the important roles of the gold nanoclusters in the oxygen activation (e.g., 3O_2 to 1O_2) and their selective oxidations in the presence of oxygen (e.g., CO to CO_2 , sulfides to sulfoxides, alcohol to aldehyde, styrene to styrene epoxide, amines to imines, and glucose to gluconic acid). The size-specificity (Au_{25} (1.3 nm), Au_{38} (1.5 nm), Au_{144} (1.9 nm), etc.), ligand engineering (e.g., aromatic vs aliphatic), and doping effects (e.g., copper, silver, palladium, and platinum) are discussed in details. Finally, the proposed reactions' mechanism and the relationships of clusters' structure and activity at the atomic level also are presented.

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1. Introduction

Non-metallic gold nanoclusters (Au NCs, 1–2 nm) have attracted considerable attention as new promising nanomaterials in the nanoscience and nanotechnology [1]. These well-defined Au NCs are ligated by organic ligands, e.g., thiolate, phosphine, alkyne, and a few to name. The Au NCs are widely exploited for a serial of catalytic reactions in organic transformations [2–5], which is highly valuable and desirable due to their monodispersity fully determined crystal frameworks. And it enables efficient and accurate simulations for better understanding of homogeneous/heterogeneous catalysis over Au NCs [6–10].

In recent years, remarkable developments have been achieved in wet synthesis of Au NCs by “size-focusing” and “ligand-exchange” methodologies [11]. Specific-size ligand-capped Au NCs (i.e., $Au_n(L)_m$, “L” represents organic ligands) is composed of a precise number of gold atoms, n , and organic ligands, m , (n can vary from ten to a few hundred atoms, equivalent Au core size range of 0.7–2 nm). For example, the size of the $Au_{25}(SR)_{18}$ cluster is 1.3 nm and these for the $Au_{102}(SR)_{44}$ and $Au_{144}(SR)_{60}$ are 1.7 nm and 1.9 nm, respectively. Au NCs with atomic precision can be ligated

by different functional ligands (e.g., thiolate, phosphine, and alkyne) to tune their electronic properties and structures and further tailor their catalytic performance. Of note, the electronic property of the Au NCs also can be slightly turned by the type of the capping ligands (e.g., aliphatic vs aromatic ligands) [6,12].

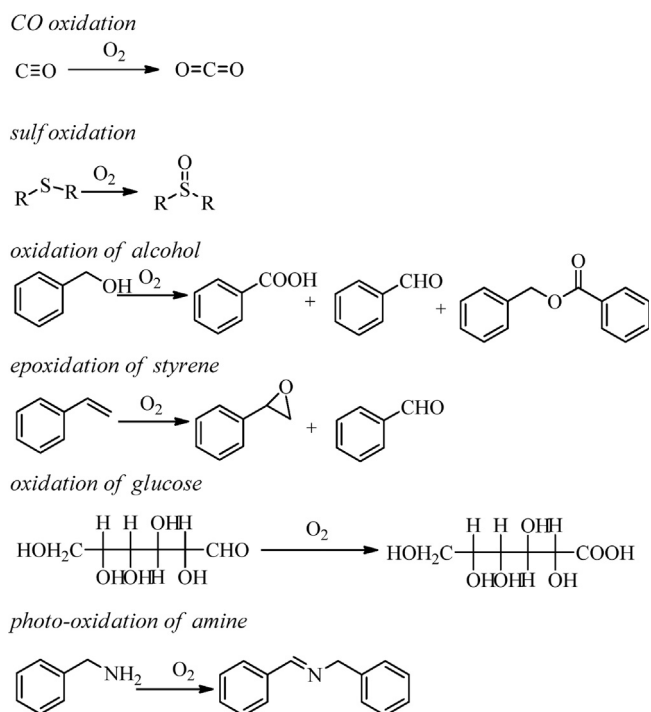
Au NCs are of particular interests in catalysis, as the ultrasmall size of the Au NCs originates strong electron-energy quantization effects [13], in contrast with the continuous conduction band of the metallic Au NPs or bulk gold. In addition, some foreign atoms (e.g., palladium, platinum, silver, copper, etc.) can dope into the core of the Au_nL_m clusters to form bimetallic alloy clusters, i.e., $Au_{n-x}M_xL_m$, which can largely turn the cluster's electronic property and give rise to new or superior catalytic activity [14–17].

In this paper, we mainly summarize Au NCs as a novel promising nanogold catalyst for oxygen activation (normal O_2 to singlet O_2 via a photocatalytic process) and aerobic oxidation, including CO transfers to CO_2 , sulfides to sulfoxides, alcohol to aldehyde, styrene to styrene epoxide as a major product (benzaldehyde and acetophenone as the minor products), amines to imines, and glucose to gluconic acid, as shown in Scheme 1. Of note, the oxygen activation and oxidation using oxygen as oxidant is an important application in the industry. The correlation of catalytic behaviors with intrinsic frameworks of Au NCs is discussed in details. And then the size-specificity, ligand engineering, and the metal doping effects of the clusters also are included.

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Scheme 1. Aerobic oxidation over Au NCs discussed in this Review, including CO to CO₂, sulfides to sulfoxides, alcohol to aldehyde, styrene to styrene epoxide, amines to imines, and glucose to gluconic acid.

Finally, the proposal catalytic active sites on the gold clusters and the tentative catalytic mechanisms simulated *via* DFT (based on the Au clusters' frameworks) are well presented.

2. Optical property, synthesis, and framework of gold nanoclusters

2.1. Optical property

The optical property of gold nanoclusters have greatly attracted scientist interests due to the strong quantum confinement effect, and it is related to their photo-catalysis, in which the Au cluster can absorb specific wavelength [18–22]. For example, the absorption spectrum of Au₂₅(SR)₁₈ shows three bands at 400 (3.10 eV), 450 (2.76 eV), and 670 nm (1.85 eV), which are all due to single-electron transitions between quantized electronic energy levels [23]. The HOMO-LUMO gap of Au₂₅(SR)₁₈ clusters is *ca.* 1.3 eV (Fig. 1). And the behavior of the gold cluster as molecular species is different from the optical absorption of larger gold nanocrystals, which exhibit a distinct SPR band at 520 nm due to collective excitation of

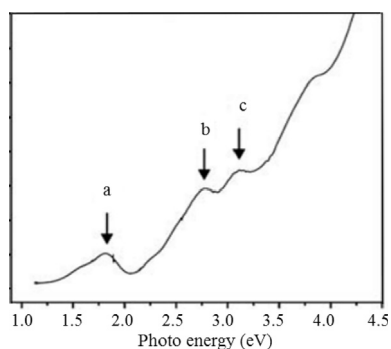


Fig. 1. The UV–vis spectrum of Au₂₅(SR)₁₈ clusters. Copied with permission [25]. Copyright 2008, American Chemical Society.

conduction electrons [24]. It is worthy to note that the UV–vis property of the atomically precise gold nanocluster is unique and characteristic “fingerprint”. Thus, gold cluster of different gold numbers exhibit diverse UV and optical gaps. Thus, the gold clusters can absorb different light due to their native optical property, and they show distinct activity in the photocatalysis.

2.2. Controlled synthesis of gold nanoclusters

In this review, we only take the controlled preparation of the [Au₂₅(PPh₃)₁₀(SR)₅X₂]²⁺ nanorods (H-SR1: alkyl thiol, H-SC₂H₄Ph and H-S(*n*-C₆H₁₃)) and Au₂₅(SR)₁₈ nanospheres (H-SR2: aromatic thiol, H-SPh and H-SNap) as an example to introduce the ligand effects on the cluster synthesis. These Au₂₅ nanorods and nanospheres are adequately investigated in the catalytic reactions (see Section 3). The two Au₂₅ clusters were obtained through an one-phase thiol etching reaction of the polydisperse 1.3 nm Au_n(PPh₃)_m particles (Fig. 2). It is interesting that the alkyl thiol gave rise to Au₂₅ nanorods and the aromatic thiol led to the Au₂₅ nanospheres during the conversion process. And it is also observed that the Au₂₅ nanorods cannot convert to Au₂₅ nanospheres in the presence of excess thiol (both the alkyl and aromatic thiol) even under thermal conditions [25].

2.3. Framework

Au clusters exhibit distinct crystal structures resolved by X-ray crystallography. The structures of [Au₂₅(PPh₃)₁₀(SR)₅Cl₂]²⁺Cl₂ nanorod and Au₂₅(PET)₁₈ nanosphere are briefly discussed, which are used as model to explore catalytic mechanisms (*vide infra*). The Au₂₅ nanorod are composed of two icosahedral Au₁₃ units by sharing one common vertex (Fig. 2) [14,15]. The two Au₅ pentagonal rings at the end of the rod are ligated by ten phosphine ligands. Two Cl atoms bind to two apical Au atoms, and the thiolate ligands bridge the two Au₁₃ icosahedrons (Fig. 2). Whilst, the Au₂₅ nanosphere comprises a 13-atom Au₁₃ icosahedral core and six Au₂(SR)₃ staples (Fig. 2) [16].

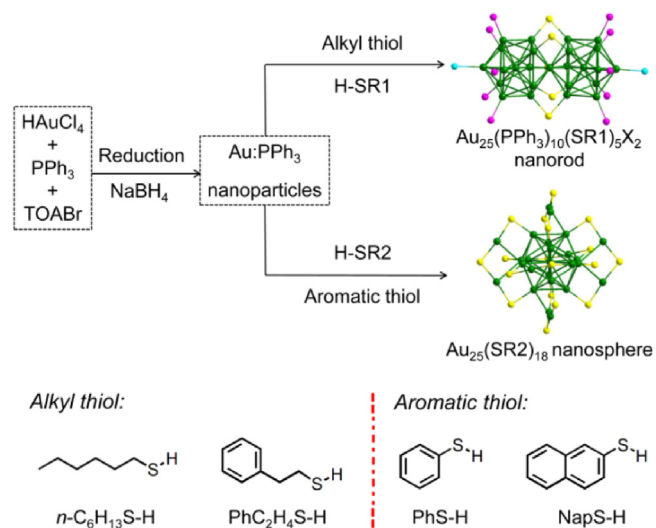


Fig. 2. (Top panel) Synthesis of the four monodisperse Au₂₅(PPh₃)₁₀(SR)₅X₂ (SR1 = SC₂H₄Ph and S(*n*-C₆H₁₃), X = Br/Cl) nanorods and Au₂₅(SR)₁₈ (SR2 = SPh and SNap (2-naphthalenethiolate)) nanospheres *via* the etching of the parent polydisperse Au_n(PPh₃)_m nanoparticles in the presence of excess thiols. (bottom panel) The molecular structures of (*n*-C₆H₁₃)S-H, PhC₂H₄S-H, PhS-H and NapS-H in this work. TOABr = tetraoctylammonium bromide. Of note, all the carbon and hydrogen atoms are omitted for clarity. Color code: Au, green; S, yellow; X, cyan; P, pink. Copied with permission from Ref. [25]. Copyright 2015, Royal Society of Chemistry.

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