



# Gold nanoparticle decorated ceria nanotubes with significantly high catalytic activity for the reduction of nitrophenol and mechanism study

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## ABSTRACT

We report the preparation and catalytic properties of a new nanostructured catalyst, made of small (~5 nm in diameter) and uniform gold nanoparticles (AuNPs) and ceria nanotubes (CeO<sub>2</sub> NTs). “Surfactant-free” AuNPs fabricated by pulsed laser ablation in liquid (PLAL) on a bulk Au target are efficiently assembled onto the surface of CeO<sub>2</sub> NTs without performing any surface functionalization of either component to promote their coupling, thanks to the presence of –OH on the PLAL-AuNPs. The reduction reaction of 4-nitrophenol into 4-aminophenol catalyzed by our PLAL-AuNP/CeO<sub>2</sub>-NT catalyst exhibits remarkably higher reaction rate in comparison to that catalyzed by similar catalysts composed of chemically prepared AuNPs (Chem-AuNPs) as an active phase and/or commercially available CeO<sub>2</sub> powder as support. Their superior catalytic activity is found to be due to the unique, relatively “bare” surface of the PLAL-AuNPs as well as oxidized Au species induced by the strong interaction between the “barrier-free” surface of PLAL-AuNPs and surface defects (oxygen vacancies) of CeO<sub>2</sub> NTs. The important role of unique surface chemistry of PLAL-AuNPs in catalysis was further demonstrated in CO oxidation reaction in gas phase. Our results suggest that the use of PLAL-AuNPs enables easy and efficient attachment of AuNPs onto the surface of the CeO<sub>2</sub> NTs and their unique combination leads to the development of highly efficient catalysts. Our design and fabrication of the nanocatalysts take full advantage of the unique features of the PLAL-AuNPs and potentially constitute a general and efficient route to prepare other metal-NP/metal-oxide-support catalysts, which can therefore largely expand the applications of PLAL-noble metal NPs in catalysis.

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## 1. Introduction

Since the seminal work of Haruta [1], AuNPs have attracted considerable attention because they show specific catalytic properties, which the bulk material does not possess, and hold great potential in many applications, such as selective hydrogenation of nitro-aromatic compounds, carbon monoxide (CO) oxidation, and water–gas shift reaction [2–28]. Nitro-aromatic compounds as toxic organic by-products are generally produced undesirably during the industrial manufacturing process of chemicals, such as agrochemicals, dyes and pharmaceuticals [29,30]. In the presence of AuNP based catalyst, the nitro-aromatic compounds can be efficiently reduced into their corresponding useful aromatic amines [41–49]. Although in principle, smaller NPs show higher catalytic activity, they easily aggregate due to their high surface energy, resulting in a large reduction of their catalytic activity [2,5]. To overcome this problem, appropriate stabilizers, such as surfactants and functional molecules, are required

to control NP nucleation/growth, prevent coalescence and/or link NPs to support materials during wet chemical synthesis [2,5,11–18,27,28]. Nevertheless, it is also noted that the presence of these molecules on NP surface can obstruct the access of reactants to the active sites of NPs and thus decrease their catalytic activity [5]. To remove these stabilizing molecules, extensive washing or extra thermal treatment to NPs has to be conducted. In most cases, unfortunately, these treatments cause a size increase and even agglomeration, which degrade the final catalytic activity of these NPs [5,14,15]. It has been reported that impregnation-incipient wetness, deposition–precipitation (DP) and in situ growth on support materials are other well established approaches to synthesize small AuNPs without using stabilizing molecules [2,10,11,14,15,19–23,44]. Nonetheless, impurities, such as chloride ion (Cl<sup>−</sup>) from HAuCl<sub>4</sub> precursor or sodium carbonate from DP method, remaining in the catalyst must be completely removed by exhaustive washing treatment since these substances exert negative impact on Au catalysts [2]. In particular, the Cl<sup>−</sup> residue not only poisons Au catalysts but also favors NP aggregation at high temperature by promoting mobilization of Au atoms [19–21]. On the other hand, pulse laser ablation on a Au bulk target in gas or liquid phase as an increasingly important “top down” method provides an

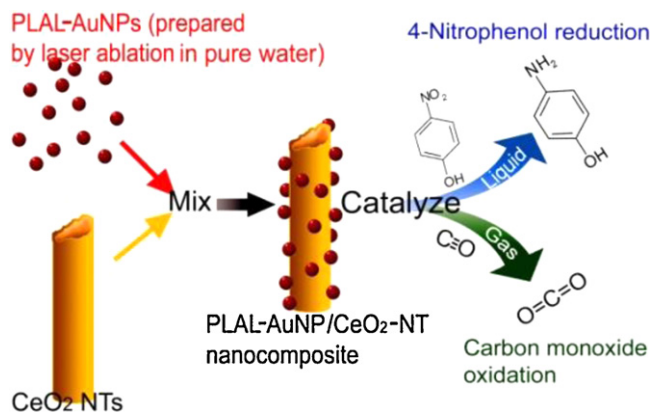
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alternative way to produce relatively “bare and clean” AuNPs [31–39], which are expected to favor catalytic reactions because the reactive sites on the NP surface are mostly exposed and readily accessible for reactants during catalytic reactions. Accordingly, AuNPs prepared by laser ablation technique are anticipated to act as highly promising catalysts.

As far as the laser technique for preparing NPs is concerned, supported AuNP catalysts have successfully been prepared by pulsed laser deposition (PLD) on substrates (such as  $\text{Fe}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{MnO}_2$ ) in a close chamber filled with certain gas [37–39]. And these supported AuNPs exhibit high catalytic efficiency in various gas phase catalytic reactions of oxidizing small organic molecules [37–39]. Although the use of stabilizing chemicals is avoided in this PLD approach, which prevents the contamination of metal NPs, the set-up and operation of PLD system are rather complicated in practice as well as time-consuming. In contrast, pulsed laser ablation in liquid phase (PLAL) offers significant convenience in experimental manipulation. In addition, if appropriately optimized, it is able to yield small, mono-disperse, stable colloidal NPs without intentionally introducing any stabilizing molecules. In particular, this technique can endow unique surface-chemistry features to the AuNPs, due to the high density and temperature of the laser plasma plume in liquid [36], but not available from other synthetic approaches. For example, Luong et al. and our group reported that Au atoms on the surface of freshly prepared AuNPs by laser technique in water are partially oxidized [31,34], Kondow [32], Muniz-Miranda et al. [33] and our group [35] also showed that small  $\text{OH}^-$  groups from aqueous environment adsorb on the PLAL-metal NP surface to form a negatively charged surface to stabilize the NPs. These small  $\text{OH}^-$  groups are expected to impose much less “barrier” effects on catalysis than most stabilizing molecules, which are generally much larger and can block the access of reactant molecules to the catalyst surface. Therefore, it is highly interesting to apply these stable, colloidal PLAL-AuNPs with relatively “bare” surface in catalytic reactions in aqueous phase and compare their catalytic behavior with that of chemically synthesized ones, whose surfaces are always capped by a variety of stabilizing molecules (including bulky polymers). Besides, this  $-\text{OH}$  capped surface is supposed to easily interact with other materials, e.g., metal oxide with rich hydroxyl-group in aqueous solution, to form NP/metal-oxide hybrid structures which are of high relevance to practical applications. However, to date, research on PLAL-AuNPs has been mostly limited to the fabrication and surface chemistry investigations of NPs prepared under different conditions, such as laser parameters, solvents, pH values, and electrolytes [31–33,35]. The evaluation of their catalytic activities in various reactions is still lacking.

Here, we report a new method to prepare a nanostructured catalyst, which is composed of PLAL-AuNPs and  $\text{CeO}_2$  NT support, and its application as highly active catalyst in the reduction of 4-nitrophenol (4-NP) into 4-aminophenol (4-AP), which is very useful for biomedicine and plastic industries [29,30,44]. The catalyst preparation method developed herein involves the fabrication of AuNPs ( $\sim 5$  nm in diameter) by PLAL and their uniform immobilization onto the  $\text{CeO}_2$  NTs by simple mixing in solution, as illustrated in Scheme 1. Such a simple route does not require any additional surface modification processes to either AuNPs or  $\text{CeO}_2$  NTs, while leading to extremely efficient anchorage of the NPs onto the tube surface. The PLAL-AuNPs/ $\text{CeO}_2$ -NTs demonstrate significantly superior catalytic activity in the 4-NP reduction reaction as compared with not only similar catalysts consisting of Chem-AuNPs or commercial  $\text{CeO}_2$  powder, but also other supported Au catalysts reported recently by other groups. Besides, they also show excellent catalytic activity in the CO catalytic oxidation reaction in gas phase. Their remarkable catalytic activity is attributed to the relatively “bare” surface of the PLAL-AuNPs as well as to the strong



**Scheme 1.** Schematic diagram of the simple route for preparation of PLAL-AuNP/ $\text{CeO}_2$ -NT catalyst and its application in 4-NP reduction and CO oxidation.

Au-support interaction associated with the unique surface feature of both PLAL-AuNPs and  $\text{CeO}_2$  NTs. Our novel PLAL-AuNPs/ $\text{CeO}_2$ -NTs are expected to be applicable as a highly efficient catalyst in many other catalytic reactions where AuNPs are involved. It should be possible to extend this simple strategy for the preparation of metal oxide supported nanocatalysts containing AuNPs to the preparation of other nano-heterostructures containing PLAL-metal NPs. This will open the door for PLAL-NPs to a wide variety of applications in catalysis.

## 2. Experimental

### 2.1. Materials

Gold plate target (99.99%), hydrogen tetrachloroaurate hydrate (auric acid,  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), sodium citrate, sodium borohydride ( $\text{NaBH}_4$ ), cerium (III) nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), urea ( $\text{NH}_2\text{CONH}_2$ ), sodium hydroxyl ( $\text{NaOH}$ ), nitric acid ( $\text{HNO}_3$ ), 4-nitrophenol, cerium (IV) oxide powder (mean size  $\sim 500$  nm) were purchased from Sigma–Aldrich and used without further purification. Pressure syringe filter composed of celluloid membrane filters ( $0.2 \mu\text{m}$ ) and pressure filter-holder, and centrifuge filters (Amicon Ultra-4 Ultracel-50K) made by EMD Millipore Cooperation were obtained from Fisher Scientific. Water was purified by a Millipore Ultrapure water system and has a resistivity of  $18.2 \text{ M}\Omega \text{ cm}$  at  $25^\circ\text{C}$ .

### 2.2. Preparation of PLAL-AuNPs

Laser ablation was carried out with a KrF excimer laser (GSI Lumonics PM-846, wavelength: 248 nm, repetition rate 20 Hz). The beam was focused by an objective lens, with a focal length of 7.5 cm, onto a gold plate with a diameter of 8 mm and 1.5 mm in thickness. The gold target was placed at the bottom of a 6 mL glass vessel filled with pure water ( $\text{pH} \approx 6.5$ ). The depth of the water layer above the target was  $\sim 10$  mm. Laser fluence on the target was set at  $\sim 40.0 \text{ J/cm}^2$  during all ablation process.

### 2.3. Synthesis of $\text{CeO}_2$ NTs [54,55]

In a typical experiment, 1.736 g of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 1.44 g of urea were added to 80 mL of water under vigorous magnetic stirring. The clear solution was charged into a 100 mL wide-mouthed jar which was closed and baked at  $80^\circ\text{C}$  for 24 h. The solution was then air-cooled to room temperature. The obtained white powder was then centrifuged, washed with distilled water, and dried at  $60^\circ\text{C}$ . It (0.087 g) was subsequently re-dispersed into 20 mL of distilled water. Upon addition of 2.4 g of  $\text{NaOH}$ , the mixture solution

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