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

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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 (CeO2 NTs). “Surfactant-free” AuNPs fabricated by pulsed laser ablation in liquid (PLAL) on a bulk Au target are efficiently assembled onto the surface of CeO2 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/CeO2-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 CeO2 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 CeO2 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 CeO2 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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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 Fe2O3, SiO2 and MnO2) in a closed 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 OH− groups from aqueous environment adsorb on the PLAL-metal NP surface to form a negatively charged surface to stabilize the NPs. These small 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 –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 CeO2 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 (∼ 5 nm in diameter) by PLAL and their uniform immobilization onto the CeO2 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 CeO2 NTs, while leading to extremely efficient anchorage of the NPs onto the tube surface. The PLAL-AuNPs/CeO2-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 CeO2 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 Au-support interaction associated with the unique surface feature of both PLAL-AuNPs and CeO2 NTs. Our novel PLAL-AuNPs/CeO2-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 tetrachloraurate hydrate (auric acid, HAUcl4·3H2O), sodium citrate, sodium borohydride (NaBH4), cerium (III) nitrate hexahydrate (Ce(NO3)3·6H2O), urea (NH2CONH2), sodium hydroxyl (NaOH), nitric acid (HNO3), 4-nitrophenol, cerium (IV) oxide powder (mean size ∼ 500 nm) were purchased from Sigma–Aldrich and used without further purification. Pressure syringe filter composed of celluloid membrane filters (0.2 μm) 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 MΩ cm at 25 °C.

2.2. Preparation of PLAL-AuNPs

Laser ablation was carried out with a Kr 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 (pH ≈ 6.5). The depth of the water layer above the target was ∼10 mm. Laser fluence on the target was set at ∼40.0 J/cm2 during all ablation process.

2.3. Synthesis of CeO2 NTs [54,55]

In a typical experiment, 1.736 g of Ce(NO3)3·6H2O 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 °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 °C. It (0.087 g) was subsequently re-dispersed into 20 ml of distilled water. Upon addition of 2.4 g of NaOH, the mixture solution
was stirred for 30 min and then kept at room temperature. After 4 days of aging, the light yellow precipitation was washed with 1 M of HNO₃ solution, distilled water, and absolute ethanol sequentially, and then it was dried in a vacuum at 60 °C for 24 h for the following catalyst preparation.

2.4. Synthesis [56] and purification of Chem-AuNPs

One milliliter of 1 wt% HAuCl₄·3H₂O aqueous solution was added into 90 mL of deionized water, followed by injection of 2 mL of 38.8 mM sodium citrate solution. The reaction mixture was then stirred for 1 min. Subsequently, 1 mL of 0.075 wt% freshly prepared NaBH₄ solution (in 38.8 mM sodium citrate solution) was added and then the reaction mixture was stirred overnight at room temperature. After that, all as-synthesized Au colloidal solution was purified to remove any un-attached or un-reacted chemical species, and then 93 mL of 1.25 mM sodium citrate solution was loaded and sonicated to have AuNPs well re-dispersed for the following operation. Consequently, a delicate purification process was performed to the as-prepared Chem-AuNPs solution by using ultra-centrifuge filters. In a typical operation, 12 mL of as-prepared Au colloidal solution was centrifuged at ~4500 rpm with ultra-centrifuge filters into ~4 mL concentrated solution (8 mL of filtrate was discarded). And then ~8 mL of pure water was introduced to re-disperse the 4 mL highly concentrated AuNPs. After this pre-purification, additional washing operation was repeated gently twice in the same way. Final AuNPs were re-dispersed in pure water and used immediately for hybridization and characterization.

2.5. Fabrication of AuNP/CeO₂ catalysts

To 20 mg of CeO₂ NTs (or powder), 2 mL of freshly prepared PLAL-AuNPs solution (or purified Chem-AuNPs) was added and mixed by shaking. The mixture solution was incubated at room temperature for 30 min. After this, the pink precipitate was recovered by centrifugation, followed by washing with distilled water twice. Thus, the AuNP/CeO₂ catalyst was obtained.

2.6. Catalytic reduction of 4-NP

The aqueous solutions of 4-NP (0.12 mM) and NaBH₄ (5 mM) were freshly prepared. Typically, in a 50 mL flask, 10 mg of AuNP/CeO₂ catalyst (containing 0.031 mg of Au) was added to 15 mL of 4-NP aqueous solution. Subsequently, 15 mL of NaBH₄ solution was mixed with the 4-NP solution containing AuNP/CeO₂ nanocomposite under continuous stirring. The molar ratio of Au:4-NP:NaBH₄ in this catalytic reaction was about 1:11:462. All catalytic reactions were carried out at room temperature. In order to monitor the reaction, 1.5 mL of the reaction solution was taken out using a syringe every 60 s, and injected into a quartz cuvette immediately through a pressure syringe filter, which can separate catalyst from the reaction solution and terminate the reaction. The filtrate solution was then measured with the UV-vis absorption spectrometer.

2.7. Catalytic oxidation of CO

Catalytic activity was measured using a continuous flow fixed-bed micro-reactor at atmospheric pressure. In a typical experiment, the system was first purged with high purity N₂ gas and then a gas mixture of CO/O₂/N₂ (1:10:89) was introduced into the reactor containing 50 mg of AuNPs/CeO₂-NTs (1 wt% Au loading) at a flow rate of 33.6 mL/min (corresponding to a space velocity of 40,000 mLh⁻¹g⁻¹ of catalyst), which were pre-annealed at 200 °C for 2 h. Gas samples were analyzed with an online infrared gas analyzer, which simultaneously detects CO and CO₂ with a resolution of 10 ppm. The results were further confirmed with a Gas Chromatograph.

2.8. Characterization

A UV–Visible (UV–vis) spectrometer (Varian 5000) was used to measure the absorption spectra of AuNPs and catalytic reaction solution at room temperature. Transmission electron microscopy (TEM) images were taken with a JEOL-2100F TEM (École Polytechnique de Montréal, Montréal, Canada) by drop casting sample dispersions on carbon-coated copper grids. X-ray photoelectron spectroscopy (XPS) spectra were performed using ESCA Escalab 220i XL with a polychromated Al Kα X-ray source (1486.6 eV) [34]. Elemental analysis with neutron activation analysis (NAA) technique was performed using SLOWPOKE nuclear reactor (École Polytechnique de Montréal, Montréal, Canada) to quantify Au component in the AuNPs/CeO₂ nanostructures, and to determine the amount of catalysts used in each reaction. Thermogravimetric analysis (TGA) was performed in air with a TA Instrument TGA Q500 thermogravimetric analyzer. CeO₂ NT surface area was measured with Quantachrome Autosorb System using nitrogen. The pH values of the solutions were measured with a Mettler-Toledo FG2 pH meter. Gas analyzer (Gasboard-3121, China Wuhan Cuba Co.) and Gas Chromatograph (Shimadzu, GC-14C) were employed to determine and confirm the gas composition in CO oxidation reaction, respectively.

3. Results and discussion

3.1. Preparation and structural characterization of PLAL-AuNP/CeO₂–NT nanocatalyst

A simple, functionalization–step-free solution process has been established to fabricate the AuNP/CeO₂ nanocatalyst. First, PLAL-AuNPs with diameter of ~5 nm were fabricated by laser ablation on a bulk Au target in pure water without any additional chemicals. Meanwhile, CeO₂ NTs were synthesized through a solid–liquid interface reaction between Ce(OH)₂CO₃ nanorods, which serve as template, and NaOH solution to first form a CeO₂ shell, and then followed by acid dissolution of residual Ce(OH)₂CO₃ precursor in the core according to our previous reports [54,55]. Second, the as-prepared PLAL-AuNP solution was simply mixed with the CeO₂ NTs and incubated for 30 min to assemble AuNPs onto the tube’s surface. Fig. 1(a) shows the UV–vis absorption spectra of freshly prepared PLAL-AuNP solution before (solid line) and 30 min after the introduction of the CeO₂ NTs (dashed line), respectively. Before the addition of CeO₂ NTs, the UV–vis spectrum of PLAL-AuNP solution presents a strong Surface Plasmon Resonance (SPR) peak at ~513 nm. After mixing with the CeO₂ NTs, the PLAL-AuNPs demonstrate significantly strong affinity to the CeO₂ NTs, reflected from the dramatic decrease of their SPR peak at 513 nm. Nearly all PLAL-AuNPs are adsorbed onto the NT surface and together they precipitate from the solution. Correspondingly, this considerable difference in the optical absorption of the PLAL-AuNPs in the presence of the CeO₂ NTs is visible in its photographs shown in the insets of Fig. 1(a). The percentage of “free” (i.e., un-attached) AuNPs in the supernatant (deduced from the absorbance of the SPR peak at 513 nm) as a function of incubation time is summarized and illustrated in Fig. 1(c) (circles). It is found that most (~90%) of the AuNPs are adsorbed on the surface of the NTs within 10 min. Lengthening the incubation time to 30 min leads to the complete attachment. Consistently, it was found that the amount of Au element in the colloidal solution before mixing with CeO₂ NTs is the same as that in the fabricated nanocomposite (confirmed by NAA), which indicates
that with this technique AuNPs entirely attach onto the support without any loss and thus the Au/CeO₂ ratio can be accurately controlled by simply varying the amount of feeding Au colloidal solution.

Of technical importance is that this preparative method for the AuNP/CeO₂ nanocomposite does not require any additional functionalization pretreatments to either AuNP or CeO₂ to promote their coupling. The effective immobilizing process is associated with the surface chemistry of the PLAL-AuNPs and CeO₂ NTs. Since the pH value of the incubation solution (pure water) is ~6.5 which is lower than the Isoelectric Point (IEP) of CeO₂ (7.0–7.6) [50], the surface of CeO₂ is partially positively charged [50]. On the other hand, the PLAL-AuNPs are negatively charged due to –OH adsorption [31–33]. Thus, the electrostatic interaction and hydrogen bonding between them lead to the formation of the AuNP/CeO₂ hybrid structure [28]. In terms of nanocomposite fabrication, the unique surface chemistry of PLAL-AuNP does appear advantageous.

Fig. 2(a)–(c) shows the TEM images of the PLAL-AuNPs/CeO₂-NTs. The tubular structure of CeO₂ is quite apparent (Fig. 2(a) and (b)) and at a higher magnification (Fig. 2(b)), the attachment of the PLAL-AuNPs on the tube surface can be clearly observed. The NPs are well distributed on the surface, and no unattached, individually dispersed AuNPs are observed, indicating that the PLAL-AuNPs have good affinity with the CeO₂ NTs. The AuNP/CeO₂-NT nanostructures were further characterized by high-resolution TEM (HR-TEM); as shown in Fig. 2(c), the lattice fringes of an attached AuNP with a diameter of ~5 nm and a CeO₂ NT surface are visible, with the spacing of 2.34 Å corresponding to that of the {1 1 1} planes of face-centered cubic Au [51] and the larger lattice spacing of 3.12 Å matching that of the {1 1 1} crystal planes of cubic fluorite-structured CeO₂ [51]. These results regarding crystalline structures are consistent with those obtained from selected area electron diffraction (SAED) pattern shown in the inset of Fig. 2(a). The PLAL-AuNPs/CeO₂-NTs were also characterized by energy dispersive X-ray spectroscopy (EDS), which reveals the coexistence of both Au and Ce in the nanostructure as presented in Fig. 2(d).

3.2. Catalytic activity of PLAL-AuNP/CeO₂-NT nanocatalyst for 4-NP reduction

The catalytic property of the PLAL-AuNPs/CeO₂-NTs was then evaluated by employing the reduction of 4-NP into 4-AP, in which NaBH₄ was used as a reducing agent. During the catalytic reaction, active hydrogen species are firstly transferred to the surface of AuNPs by borohydride, and then the reduction of 4-NP takes place by the reaction of adsorbed 4-NP molecules and surface-hydrogen. In this study, since NaBH₄ was added to the reaction in large excess as compared to 4-NP, the reaction kinetics basically follows a first-order rate law [41–44]. The kinetic process of the reaction was monitored by measuring the absorbance of a peak at 400 nm (Abs₄₀₀ nm), directly associated with the concentration of 4-nitrophenolate ions, as a function of reaction time. Fig. 3(a) shows that after the addition of the catalyst, the Abs₄₀₀ nm value drops gradually as the reaction proceeds, reflecting the steady decrease of the concentration of the 4-nitrophenolate ions in solution. Based on the absorbance data, Fig. 3(b) plots the C/C₀ (square) and –ln(C/C₀) (circle) vs. reaction time, where C₀ and C are the initial concentration of the 4-nitrophenolate ions and the concentration at time t, respectively. The reaction is almost complete within 1200 s in the presence of the PLAL-AuNP/CeO₂-NT catalyst. The linear
Fig. 2. TEM (HR-TEM) images (a-c) and EDS spectrum (d) of PLALAuNPs/CeO₂-NTs. Insets are the SAED pattern and the magnified TEM image.

Fig. 3. (a) UV–vis absorption spectra during the catalytic reduction of 4-NP over PLAL-AuNPs/CeO₂-NTs; (b) C/C₀ and −ln(C/C₀) as a function of reaction time for the reduction of 4-NP over PLAL-AuNPs/CeO₂-NTs.

The correlation between −ln(C/C₀) and reaction time demonstrates that the reaction is of the first-order in 4-NP reduction. Thus, the kinetic equation of this catalytic reaction could be shown as follows

\[
\frac{dC}{dt} = -k_{app}C
\]

where \( k_{app} \) is the apparent reaction rate constant, which can be obtained from the slope of the linear correlation [43,44,49]. Accordingly, the \( k_{app} \) for the PLAL-AuNPs/CeO₂-NTs catalyzed reaction was calculated to be \( 2.25 \times 10^{-3} \) s⁻¹. To exclude the effect of Au loading on reaction efficiency, and also for fair comparison with the results reported by other groups on AuNP based catalysts, an intrinsic reaction rate constant, \( k \), was introduced by further normalizing \( k_{app} \) with Au content [41,49]:

\[
k = \frac{k_{app}}{M}
\]

where \( M \) is the dosage of Au (μmol) in the catalyst. It was found that \( k (1.40 \times 10^{-2} \) s⁻¹ μmol Au⁻¹) of the PLAL-AuNPs/CeO₂-NTs is impressively higher than those reported recently by others on Au-containing nanocatalysts (see Table S1 for summary) [44–49].

3.3. Mechanism for enhanced catalytic activity

In order to understand why the PLAL-AuNPs/CeO₂-NTs show superior catalytic activity, we prepared similar catalysts containing citrate ligand-capped AuNPs synthesized via a common chemical reduction method (Chem-AuNPs) and/or commercial CeO₂ nanopowder support, and then compared their catalytic activity with that of the PLAL-AuNPs/CeO₂-NTs.
3.3.1. Surface chemistry of NPs: PLAL vs. Chem-AuNPs

To guarantee a fair comparison, it is necessary to exclude particle size effect. Therefore, citrate ligand–capped Chem-AuNPs with the same particle size were prepared by reducing H\textsubscript{AuCl\textsubscript{4}} with NaBH\textsubscript{4} in citrate solution (see Section 2) [56]. TEM observation (Fig. S1(a) and (b) in supplementary data) shows that as-prepared PLAL-AuNPs and purified Chem-AuNPs have a very similar size (∼5 nm in diameter) and size distribution. This was further confirmed by their identical SPR peak position and similar full width at half-maximum (Fig. S1(c)).

The Chem-AuNPs and the CeO\textsubscript{2} NTs are then mixed under the same experimental conditions as those applied for preparing the PLAL-AuNPs/CeO\textsubscript{2}–NTs. Fig. 1(b) shows the UV–vis spectra and photographs of the as-prepared Chem-AuNP solution before (solid line) and 30 min after (dashed line) the addition of the CeO\textsubscript{2} NTs. It is clear that unlike the PLAL-AuNPs, the Chem-AuNPs do not attach to the CeO\textsubscript{2} NTs (black square, Fig. 1(c)).

Abundant “free” citrate molecules in solution have been found necessary to stabilize Chem-AuNPs. Therefore, in general, they are kept in solution for the manipulation of the Chem-AuNPs (such as surface functionalization); otherwise rapid aggregation can easily take place [52]. Based on this consideration, the Chem-AuNPs, which were only purified once to remove un-reacted chemical species and then dispersed in 1.25 mM of sodium citrate solution, were used for coupling with the CeO\textsubscript{2} NTs. Unfortunately, this “standard” stable Au colloidal solution seems inappropriate for the current coupling reaction. Quite likely, free citrate ions in solution are easily adsorbed onto the positively charged CeO\textsubscript{2} NT surface, leading to the formation of a negatively charged surface that hinders the adsorption of negatively charged Chem-AuNPs [27].

To promote the coupling yet avoiding rapid NP agglomeration, a delicate purification/washing protocol was developed for as-prepared Chem-AuNPs (see Section 2). Our study shows that the Chem-AuNPs with ∼0.9 wt% of the citrate ligand content (measured by TGA) can rapidly adsorb on the surface of CeO\textsubscript{2} without evident aggregation. Although successful, the manipulation of the Chem-AuNPs for the catalyst preparation is obviously less convenient and more time-consuming, with respect to the PLAL-AuNPs.

The same amount of the Chem-AuNPs as that of the PLAL-AuNPs was coupled with the NTs (examined by NAA) for comparison of catalytic activity. Inset of Fig. 4(b) presents a typical TEM image of the Chem-AuNPs/CeO\textsubscript{2}–NTs, whose structure is similar to that of the PLAL-AuNPs/CeO\textsubscript{2}–NTs. Fig. 4(a) shows the evolution of the UV–vis spectra of the 4-NP reaction solution when the Chem-AuNPs/CeO\textsubscript{2}–NTs are used as a catalyst. It can be seen that the absorbance of 4-nitrophenolate ions only decreases by half after 1800 s in the presence of the Chem-AuNPs/CeO\textsubscript{2}–NTs, while it drops to ∼0 after the same reaction time in the case of the PLAL-AuNPs/CeO\textsubscript{2}–NTs. Fig. 4(b) displays the variation of C/C\textsubscript{0} and −\text{ln}(C/C\textsubscript{0}) with the reaction time as derived from Fig. 4(a). Both values vary less severely than those shown in Fig. 3(b), indicating a lower reaction efficiency. The k value of the Chem-AuNPs/CeO\textsubscript{2}–NTs is 2.86 × 10\textsuperscript{−3} s\textsuperscript{−1} μmol Au\textsuperscript{−1}, about 5 times smaller than that of the PLAL-AuNPs/CeO\textsubscript{2}–NTs. It is noted that, the PLAL-AuNP/CeO\textsubscript{2}–NT catalyst still keeps rather good catalytic activity after four rounds of successive reactions, and its k value for each round is much higher than that of the Chem-AuNP/CeO\textsubscript{2}–NT catalyst as well (Fig. S2).

As described above, after careful purification, most free ligands are removed from the solution. Nonetheless, the Chem-AuNPs are still covered by certain amounts of citrate ligands. They could directly passivate the reactive sites or prohibit the access of reactant molecules to the reactive sites by providing spatial hindrance. As a consequence, more surface sites of the Chem-AuNPs that should be catalytically active are blocked, resulting to the lower catalytic activity as compared with the relatively “bare” PLAL-AuNPs. Nonetheless, the small –OH groups on the latter NP surface leave more surface sites available for reactants. It is clear that the use of the PLAL-AuNPs is not only beneficial for the easy, time-saving, effective conjugation with the NTs, but also contributes to the increase of catalytic activity. The blocking effect of the PLAL-AuNPs in catalysis is much less, if any, than that of citrate, which are commonly used in AuNP preparation and are indeed already small stabilizing agents. The above observations indicate that the surface chemistry of AuNPs is very important for coupling and catalytic performance.

3.3.2. Au-support interaction: CeO\textsubscript{2}–NT vs. commercial ceria powder

NTs have been considered as interesting support materials for catalytic NPs because their geometry provides a relatively high surface area to volume ratio for better dispersion of NPs. In our case, besides the advantage of the high surface area of CeO\textsubscript{2} NTs, it is anticipated that their interaction with Au may also partially contribute to the excellent catalytic activity of the PLAL-AuNPs/CeO\textsubscript{2}–NTs [7,13,54]. To examine that, commercial ceria nanopowder was introduced as support to disperse and stabilize PLAL- and Chem-AuNPs, and the same preparation procedures as those applied for the CeO\textsubscript{2} NTs were adopted to fabricate the nanocomposites. The insets in Fig. 5(a) and (b) displays the TEM
images of the PLAL-AuNPs/CeO2-powder and Chem-AuNPs/CeO2-powder, respectively. No obvious aggregation of AuNPs was observed and both types of AuNPs disperse well on the surface of CeO2 particles. The variation of their C/C0 and \(-\ln(C/C_0)\) with reaction time during the reduction of 4-NP is shown in Fig. 5(a) and (b), respectively. The \(k\) value of the PLAL-AuNPs/CeO2-powder is nearly 10 times higher than that obtained for the Chem-AuNPs/CeO2-powder, again indicating that the PLAL-AuNPs are more active than the Chem-AuNPs. However, both \(k\) values are far below those achieved when the CeO2 NTs are used as support. Specifically, the \(k\) value of \((1.40 \times 10^{-2}) \text{ s}^{-1} \mu\text{mol} \text{ Au}^{-1}\) for the NT supported PLAL-AuNPs is about 6 times higher than that of the CeO2 powder supported PLAL-AuNPs \((2.28 \times 10^{-3}) \text{ s}^{-1} \mu\text{mol} \text{ Au}^{-1}\). These results strongly suggest that the CeO2 NTs, as supports, have positive impact on the catalytic activity; they are at least partially responsible for the significantly higher catalytic activity of the PLAL-AuNPs/CeO2-NTs in the 4-NP reduction reaction as compared with other Au-containing catalysts [44–49], including those investigated herein.

The surface area of the CeO2 NTs is \(\sim 74 \text{ m}^2/\text{g}\) (Fig. S3), which is much higher than that of commercial powders \(\sim 1.58 \text{ m}^2/\text{g}\). The higher reaction rate with the former sample may thus be simply attributed to the better dispersion of NPs and thus more effective contact with the reactants. However, as AuNPs are uniformly distributed without aggregation (insets of Figs. 4 and 5) and are loaded at the same level in both cases, the surface area difference of CeO2 supports should not be the dominant factor for the significant difference in catalytic activity observed herein. Instead, the Au-support interaction may play a critical role herein [2–4,7–25].

To test this hypothesis, XPS was used as an effective surface analysis tool, to analyze the surface chemistry of both CeO2 supports and AuNPs. Fig. 6(a) shows the Ce 3d5/2 XPS spectra of CeO2 NTs and commercial CeO2 powder. The proportion of Ce\(^{3+}\) indicated by the peak at \(\sim 885.8 \text{ eV}\) [54] in the NTs is considerably higher than that in the commercial powder, suggesting that there are more defects (i.e., oxygen vacancy) enriched on the NT surface [7–10,13,26,40]. It is well-known that the surface defects in CeO2 can strongly interact with Au atoms to modify their electronic structure and stabilize the oxidation states of Au [7–10,13]. These oxidized species have been found to play a positive role in the reduction of 4-NP [43]. From this point of view, it is interesting to examine the chemical status of Au in our nanocomposites. The XPS spectra of Au 4f were thus taken on the PLAL-AuNPs/CeO2-NTs, PLAL-AuNPs/CeO2-powder and Chem-AuNPs/CeO2-NTs. As shown in Fig. 6(b), all deconvoluted Au 4f spectra exhibit two main peaks (red doublet) corresponding to metallic Au\(^0\) [53]. For the PLAL-AuNPs/CeO2-NTs (curve 1), in addition to metallic Au\(^0\), broadened shoulders on the high binding energy side are composed of four distinct additional peaks (blue and green doublets), which can be assigned to the oxidation state of Au (Au\(^+\) and Au\(^{3+}\)) [7]. As compared with the Au 4f spectrum of the PLAL-AuNPs/CeO2-NTs, the intensity of oxidized Au species of the PLAL-AuNPs/CeO2-powder (curve 2) and Chem-AuNPs/CeO2-NTs (curve 3) is much lower. Because the Au oxidation states were not observed for unsupported PLAL- and Chem-AuNPs in their XPS spectra (Fig. S4), the relatively high content of oxidized Au species in the PLAL-AuNPs/CeO2-NTs must originate from the strong Au/CeO2-NT interaction [7–10], which is induced by the defect-enriched CeO2 NTs [18] and enabled by the highly intimate contact of “bare” AuNPs and CeO2 [18]. In contrast, this interaction is weaker in the hybrids containing either the Chem-AuNPs or CeO2 powder due to the steric hindrance effect from the citrate ligand on the Chem-AuNPs and less oxygen vacancies in the CeO2 powder, explaining the much lower content of the oxidized Au species in these two samples. The PLAL-AuNPs and CeO2 NTs together contribute to the strong Au–CeO2 interaction. The oxidized Au species arising from this interaction may act as electron relay system, which accelerates the electron transfer from BH\(_4^-\) to 4-NP in the hydrogenation process [43], leading to the superior catalytic performance of the PLAL-AuNPs/CeO2-NTs.

3.4. PLAL-AuNPs/CeO2-NTs toward CO oxidation

To further illustrate the unique, advantageous feature of the PLAL-AuNPs/CeO2-NTs in catalytic reactions, we also studied their
catalytic activity toward CO oxidation, which has attracted extensive research due to its fundamental importance in air purification. Fig. 7 shows the activity curve of the annealed PLAL-AuNPs/CeO2-NTs along with that of Chem-AuNPs/CeO2-NTs for comparison. The PLAL-AuNPs/CeO2-NTs exhibit higher catalytic efficiency at the same temperature. The reaction rate with the presence of these two catalysts was further calculated at low conversions. For example, at ~45 °C the CO conversion reaches ~15% with the use of the PLAL-AuNPs/CeO2-NTs in contrast to ~8% with the Chem-AuNPs/CeO2-NTs. Accordingly, the reaction rate for the CO oxidation at this temperature proceeding over these two catalysts was calculated to be ~0.42 and ~0.22 mmol CO2 min⁻¹ mg⁻¹, respectively. The reaction rate upon PLAL-AuNPs/CeO2-NTs is comparable with those calculated from other reports using solely chemically prepared AuNPs/CeO2 catalysts [22–25]. Since the CeO2 NT support, and the size and morphology of both types of AuNPs are the same, the higher catalytic activity of the former sample can be attributed to the bare surface of the PLAL-AuNPs and the strong Au-support interaction [7–10]. The benefit of the bare surface of catalysts in oxidation is expected in most catalytic reactions. As for the contribution of the Au–CeO2 interaction, it has been well-studied and largely reported for small molecule oxidation reactions [8–11,13–15,18,20–26]. For example, by studying Au–CeO2 and Au–SiO2 multilayer nanostructures in CO oxidation, Zhou et al. experimentally identified that the active sites for this catalytic reaction are located at the interface of Au and CeO2 [8]. They further found that the extremely low activity of a pure Au thin film in CO oxidation can be enhanced remarkably by decorating it with CeO2-rich CeO2 NPs since the strong interaction occurring at the interface of CeO2 NPs and Au surface induces a significant increase of the active sites on Au surface [9]. In our study, as shown in the XPS part, the CeO2 NTs containing higher concentration of Ce3⁺ defect couple directly with the relatively “bare” and “clean” PLAL-AuNPs without suffering from any steric hindrance, resulting in a stronger interaction at the CeO2–Au interface than that in the samples containing either the Chem-AuNPs or CeO2 powder. This strong interaction leads to an increase of catalytically active sites, as reflected in the XPS as a higher concentration of Au in oxidation states. The positive role of oxidized Au species at the interface introduced by the strong interaction in CO oxidation has been widely accepted because they promote CO2 desorption in the CO oxidation process [7,10]. An interesting question arises: will the Ce3⁺ defect concentration change during and after CO oxidation? Lee et al. found that Ce3⁺ (oxygen vacancy) content of Au–CeO2 nanorods catalyst does not change obviously in the presence of O2 during reaction, whereas it decreases without O2 by monitoring the reaction with Raman scattering [26]. In another report, the Ce3⁺ concentration of very small CeO2 NPs (~5 nm) deposited on Au film was found to decrease after CO oxidation [9]. As Ce3⁺ concentration is believed to be directly related to catalytic activity as well as long-term stability of the catalysts reported herein, the investigation on its variation with catalytic reactions is ongoing.

4. Conclusion

In summary, a highly catalytically active AuNP/CeO2-NT nanocomposite was synthesized by simply mixing laser ablated Au colloids with CeO2 NTs. Due to the OH⁻ group on the AuNP surface resulting from laser ablation process, the PLAL-AuNPs show good affinity with CeO2. The PLAL-AuNPs/CeO2-NTs exhibit high catalytic activity in the reduction of 4-NP in liquid phase and CO oxidation in gas phase. Based on the comparative studies on similar catalysts of the Chem-AuNPs/CeO2-NTs, PLAL-AuNPs/CeO₂-powder, and Chem-AuNPs/CeO₂-powder, it was found that besides the relatively “bare” surface of the PLAL-AuNPs, the presence of relatively high content of the oxidized Au species induced by the strong interaction of the bare PLAL-AuNPs and the defects on the surface of the CeO2 NTs additionally contributes to the superior activity of the PLAL-AuNPs/CeO₂-NTs. This catalyst could be applied to other catalytic reactions, such as degradation of organic molecules in waste water and exhaust gas, in which AuNPs are involved. This work represents the first demonstration of the use of PLAL-metal NPs in catalysis and the simple approach of preparing the nanostructured catalysts can potentially be extended to other hetero-nanostructured materials, made of PLAL-metal NPs (such as Pt and PtAu alloys) and metal oxide (such as TiO₂ and Al₂O₃). Such hetero-structured materials can find a wide range of applications including, but not limited to, catalysis.

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Appendix A. Supplementary data

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References
