One-step femtosecond laser ablation synthesis of sub-5 nm gold nanoparticles embedded in silica

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Abstract

We report the synthesis of silica-gold nanoparticles (silica-Au NPs) using a one-step femtosecond-reactive laser ablation in liquid (fs-RLAL) technique by focusing femtosecond laser pulses onto a silicon wafer immersed in an aqueous KAuCl$_4$ solution. Characterization of the silica-Au NPs revealed two populations of Au NPs: (i) larger, isolated Au NPs with diameter 7.3±2.1 nm, and (ii) smaller Au NPs (3.4±0.8 nm) embedded in an amorphous silica matrix, along with new species of silicon observed from XPS analysis. The catalytic activity of the silica-Au NPs towards the reduction of para-nitrophenol by NaBH$_4$ is significantly higher compared to the control Au NPs synthesized in the absence of a silicon wafer and other Au NPs recently reported in literature. The formation of the two populations of silica-Au NPs is ascribed to reaction dynamics occurring on two distinct timescales. First, the dense electron plasma formed within tens of femtoseconds of the laser pulse initiates reduction of the [AuCl$_4$]$^-$ complex, leading to the formation of larger isolated Au NPs. Second, silicon species ejected from the wafer surface hundreds of picoseconds or later after the initial laser pulse reduce the remaining [AuCl$_4$]$^-$ and encapsulate the growing clusters, forming ultrasmall Au NPs embedded in the silica matrix. The morphologies of the silica-Au NPs generated from fs-RLAL are distinct from those reported in recent RLAL experiments with nanosecond lasers, reflecting distinct mechanisms occurring on the different pulse duration timescales.

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1. Introduction

Pulsed laser ablation in liquid (PLAL) has emerged as a rapidly growing field since the initial report of metal nanoparticle (NP) synthesis using this technique in 1993 [1], with many subsequent demonstrations of the versatility and simplicity of the method [2-4]. Growing interest in this field is driven by the ability to produce stable, surfactant- and contamination-free colloidal NP solutions that are suitable for applications in various fields including biomedicine [5-7], catalysis [8-11], and plasmonics [12-14]. The ability to synthesize metal and semiconductor NPs in a single step at room temperature in water gives PLAL a major advantage over conventional wet chemical synthesis approaches [2-4, 15-18]. In addition to the simple procedures and ambient conditions used to synthesize NPs via PLAL, the highly nonequilibrium conditions created in the ablation plasma and at its interface with the liquid environment can result in metastable phases and NPs possessing unique structures, shapes, and compositions such as nanocubes [19, 20], nanodiamonds [21], and thermodynamically metastable crystal structures of TiO$_2$ [22], Si [23], and Ge [24].

A second laser-assisted approach to metal NP synthesis involves photochemical reduction of metal salts by focusing the laser beam into solution [25]. The dense plasma formed at the laser focus in solution generates a high concentration of reactive species such as hydrated electrons and hydroxyl radicals [26], which can reduce metal salts to form isolated metal atoms that coalesce into NPs. Laser-mediated photochemical reduction has been widely used to synthesize Au [27-33], Ag [34-36], and multiple types of metal alloy [37-40] NPs. Like PLAL, laser photochemical reduction can produce sub-5 nm Au NPs at room temperature in aqueous solution without added surfactants or stabilizers [29, 30]. Because plasma formation is required, laser photochemical reduction is typically performed using laser pulses of picosecond [27, 29] or femtosecond
duration.

Recently, the approaches of PLAL and laser photochemical reduction have been combined into a single process through ablation of a solid target either immersed in or subsequently exposed to metal salt solution, in what is termed reactive laser ablation in liquid (RLAL) \[10\] \[41–48\]. RLAL has been widely used to generate metal-silica nanostructures, including Si/M (M = Ag, Au, Pd, Pt) core/shell NPs \[43\], Ag-core/silica-shell NPs \[44\], and large silica particles decorated with Au or Ag NPs \[45\]. While these RLAL reports have demonstrated the generation of hybrid semiconductor-metal nanocomposite materials in a single step, the metal-silica products are too large for catalysis applications such as CO oxidation that typically requires sub-5 nm metal NPs \[49–52\].

The current limited understanding of the exact timescales and locations of the chemical reactions occurring during RLAL poses challenges to further optimize the reaction conditions for tailoring the properties of the NP products for specific applications. Previous reports of RLAL use laser pulses of nanosecond duration, where it has been suggested that chemical reactions leading to NP formation occur during one or more of the following processes after the laser pulse is over \[4\]: plasma cooling on a timescale of $\sim 1 \, \mu\text{s}$ \[53\], plasma mixing and cavitation bubble formation on a timescale of $\sim 0.1 \, \mu\text{s}$ \[54\], and cavitation bubble collapse on a timescale of several hundred microseconds \[55\]. However, the exact reaction mechanisms and timescales in RLAL, along with the effects of parameters such as laser pulse duration on these mechanisms and product properties, remain unknown.

In this work, we report a RLAL approach where a Si wafer immersed in a KAuCl$_4$ solution is ablated using sub-50 femtosecond (fs) laser pulses (fs-RLAL), producing significantly smaller silica-Au nanostructures than in previous reports using nanosecond lasers \[43\] \[45\]. Two populations of silica-Au NPs are formed in the fs-RLAL technique: (i) isolated $\sim 7$ nm Au NPs, and (ii) sub-5 nm Au NPs embedded in an amorphous silica matrix. The silica-Au NPs are highly active catalysts toward the reduction of para-nitrophenol by sodium borohydride. By exploring the physical and chemical mechanisms and corresponding ultrafast
timescales that may lead to the formation of two types of Au NP products, we hope to stimulate further investigation into how changing the pulse duration may enable determination of the reaction mechanisms in RLAL and superior control over the product morphologies.

2. Materials and Methods

2.1. Materials

Potassium tetrachloroaurate (III) (KAuCl₄, Strem Chemicals), potassium hydroxide (KOH, Fisher Scientific), silicon wafers (n-doped, (111)-oriented, single side polished, 300 µm thick, NOVA electronic materials), sodium borohydride (NaBH₄, Acros Organics), and para-nitrophenol (PNP, Acros Organics) were used as received. Water was purified by a Millipore Ultrapure water system and has a resistivity of 18.2 MΩ cm⁻¹ at 25°C.

2.2. Sample Preparation

A working solution containing KAuCl₄ (0.1 mM) and KOH (0.55 mM) was prepared from stock solutions (25 mM KAuCl₄ and 200 mM KOH), using Millipore Ultrapure filtered water. The working solution was prepared 18–24 hr before carrying out experiments and stored at 6°C. For each sample, 3.0 mL of the working solution was transferred to a 10 × 10 × 40 mm quartz fluorimeter cuvette containing a micro-stir bar (Fisher Scientific) and equilibrated to room temperature. The solution pH was measured to confirm it was 10.0±0.4, and a pre-cut silicon wafer was placed inside the cuvette and secured against one side.

2.3. Catalytic reduction of para-nitrophenol by sodium borohydride

Catalytic test runs were carried out in a home-built in situ UV-vis spectrometer (details in section 2.4). In a typical catalytic reaction, a solution containing a final concentration of 0.1 mM PNP and 10 mM of freshly prepared NaBH₄ was prepared. Prior to addition of the catalyst, the UV-vis absorbance of the para-nitrophenolate ion at 400 nm was monitored for about 20 s to confirm no
reaction occurred in the absence of a catalyst. After the 20 s period, 0.50 mL of the silica-Au NP catalyst was added, initiating the reduction of PNP. The reaction was complete when the absorbance at 400 nm (para-nitrophenolate ion) had disappeared.

2.4. Instrumentation

Laser irradiation was performed using a titanium-sapphire-based chirped-pulse amplifier (Astrella, Coherent, Inc.) delivering 7 mJ, 30 fs pulses with bandwidth centered at 800 nm at a 1 kHz repetition rate. The pulse energy was adjusted to 50 µJ with a zero-order λ/2 waveplate (ThorLabs, Inc.) and broadband thin-film polarizer (Altechna), as well as a dispersion compensated 90:10 (R:T) beamsplitter (Newport, Inc.). The silicon wafer in the cuvette was placed approximately 10 mm before the focal point of a \( f = 50 \) mm lens, resulting in an ablation spot size of 85 µm in diameter based on the measurement of an ablated Si wafer with an optical microscope. Under these conditions, the laser fluence was 0.22 J cm\(^{-2}\) and peak intensity was \( 2.9 \times 10^{13} \) W cm\(^{-2}\).

The sample cuvette was placed on a miniature stir plate (Thermo Scientific) mounted to x- and y- motorized translation stages (Thorlabs). The stages were mounted on a manually controlled z-direction stage (Thorlabs), which was adjusted to focus the laser beam onto the Si wafer (Fig. 1). UV-vis measurements were taken to confirm complete conversion of the precursor KAuCl\(_4\) solution to nanoparticles, with an irradiation time of 8 min required for complete conversion. UV-vis spectra of the sample after incremental laser irradiation times are displayed in Fig. S1a of the Supplemental Material.

For control samples containing only KAuCl\(_4\), 3.0 mL of the working solution was transferred to a cuvette containing a micro-stir bar and placed in a home-built in situ UV-vis spectrometer as described in ref. [30]. Laser pulses were focused into the solution through a \( f = 50 \) mm lens, achieving a focal spot with a beam waist of 6.52 µm (measured with a CCD camera, details reported in ref. [30]) yielding a fluence of 37.4 J cm\(^{-2}\) and an intensity of \( 1.25 \times 10^{15} \) W cm\(^{-2}\). In-situ UV-vis measurements were collected to confirm full conversion of
the KAuCl$_4$ to AuNPs in 10 min (Fig. S1b in Supplemental Material).

![Experimental setup of laser pulses focused onto silicon wafer immersed in aqueous working solution.](image)

Figure 1: Experimental setup of laser pulses focused onto silicon wafer immersed in aqueous working solution.

The PNP catalytic reactions were carried out in second a home-built in situ UV-vis spectrometer consisting of a deuterium-tungsten lamp (Ocean Optics, DH2000-DUV), a sample holder for 10×10×40 mm cuvettes placed on a stir plate, and a compact spectrometer (Ocean Optics, USB4000) connected via optical fibers. Spectra were recorded once per 1.2 seconds using LabVIEW software (National Instruments). A figure of absorbance spectra of the PNP reaction over time is displayed in Fig. S2a in the Supplemental Material.

2.5. Characterization

Transmission Electron Microscopy (TEM). Samples were visualized using a JEOL JEM-1230 TEM at 120 kV, while high resolution TEM (HRTEM) imaging was carried out on a FEI Titan 300 kV equipped with a Gatan 794 Multi-Scan Camera, a HAADF-STEM detector, and EDX Spectroscopy capabilities. The colloidal nanoparticles were drop-casted onto a carbon-coated grid (Ted Pella, Inc.) and left to dry for at least 24 hr at room temperature. Average sizes and size distributions of the samples were measured using ImageJ software, which
referenced 300 quasi-spherical particles from images of three separate areas on the TEM grid.

X-ray Diffraction (XRD). XRD patterns were collected on an X’Pert PRO PANanalytical diffractometer with Cu Kα radiation. Samples were prepared by drop casting the colloidal NPs onto a glass slide heated to 60°C.

X-ray Photoelectron Spectroscopy (XPS). XPS spectra were collected on a Thermofisher ESCALab 250 with a AlKα X-ray source. Samples were prepared by centrifuging colloidal NPs (13,000 rpm, 2 hr), and drying the collected pellets under vacuum at 60°C. Powder samples were deposited on indium foil (ACROS Organics). Spectra were analyzed and deconvoluted using the Thermo Scientific Avantage Software; all peaks were referenced to the C1s peak, which was adjusted to center at 284.8 eV.

3. Results

3.1. Characterization

The silica-Au NP and control Au NP samples were visualized using TEM and high-resolution TEM (HRTEM), with representative images displayed in Fig. 2 and Fig. S3 in the Supplemental Material. The silica-Au NPs in Fig. 2a and 2c show two distinct populations of particles- larger, often isolated particles (light blue arrow in Fig. 2a) and small particles within a matrix (dark blue arrow in Fig. 2a). Size analysis of the two populations showed that the mean diameter of the particles within the matrix was approximately half that of the isolated particles (3.4±0.8 nm versus 7.3±2.1 nm). The control Au NPs in Fig. 2b and 2d were larger and more polydisperse, having a mean diameter of 9.3±4.6 nm. Several nanotriangles are also visible in the image. The HRTEM images in Fig. 2c and 2d show polycrystalline particles, with lattice spacings corresponding to fcc-Au. Both populations of the silica-Au NPs are polycrystalline, as shown in the inset of the HRTEM in Fig. 2c. The spacings were measured to be 2.32 Å,
Figure 2: TEM image with size distribution and mean diameter of silica-Au NPs (a), and control Au NPs (b). HRTEM image with lattice spacing for silica-Au (c), and HRTEM image, lattice spacing and FFT of Au NPs (d).
2.10 Å, and 1.45 Å, corresponding to the (111), (200), and (220) planes of fcc-Au. The matrix containing the small Au NPs appears to be amorphous, since no lattice spacings were observed. The control Au NPs were also polycrystalline, with the 2.44 Å, 2.35 Å, and 1.39 Å spacings corresponding to the (111) and (220) planes of fcc-Au. The fast Fourier transform (FFT) of the Au NPs within the red square of Fig. 2d confirms the fcc-Au pattern.

HAADF-STEM images of the silica-Au NPs revealed white spheroid particles and grey amorphous material, corresponding to gold and silica, respectively. Due to the significantly different atomic numbers between gold and silicon, it is possible to visually identify the two elements: the higher atomic number element has higher contrast (gold = white) than the lower atomic number element (silicon = grey) [43]. The EDX spectrum in Fig. 3a taken of an isolated Au NP (white particle) inside the red circle shows the presence of both Si and Au.

Figure 3: HAADF-STEM image of silica-Au NPs with EDX spectrum taken of portion inside red circle.
While the area in the red circle appears to be all white, corresponding to Au, the Si detected could either be from surrounding Si in the matrix, or due to interstitial Si atoms within the Au crystal lattice. Since the XRD patterns of the silica-Au NPs and the control Au NPs match (Supplemental Material, Fig. S4), it is likely that the Si detected with EDX is predominantly from the amorphous silica near the free Au NP, although small amounts of interstitial Si in the Au NPs cannot be ruled out. In Fig. 3b, the EDX spectrum of a barely visible light particle inside the red circle contains mostly silicon and a small amount of gold, indicative of a small Au NP embedded in a large amount of silica. This result is consistent with the small particles visible in the TEM images in Fig. 2a and 2c consisting of small Au NPs embedded in a silica matrix.

The XPS spectra from the Au4f, Si2p, and O1s atomic orbitals for the silica-Au NPs, control Au NPs, and control silica NPs generated from ablating a silicon wafer in water are displayed in Fig. 4; the suggested species, deconvoluted peak binding energies, and atomic percentages of the species are presented in Table 1. The Au4f spectra reveal that the majority of the surface gold atoms are neutral, although the silica-Au NPs contain Au$^{1-}$, Au$^{1+}$, and Au$^{3+}$ surface species, and the control Au NPs contain Au$^{1-}$ and Au$^{1+}$. The lack of Au$^{3+}$ surface species in the control Au NPs is compensated for with the larger amount of Au$^{1-}$ and Au$^{1+}$ species. The presence of multiple Au oxidation species in both the control Au NPs and the silica-Au NPs is consistent with previous reports of PLAL synthesis of Au NPs from an Au target [17].

The Si2p spectrum for the silica-Au NPs in Figure 4b contains the expected peaks at 103.5 eV for SiO$_2$ [56–58] and 99.4 eV for Si$^0$ [56–58], with an additional peak at 98.0 eV, which has not been previously reported. Due to its proximity to the neutral Si$^0$ species, the peak at 98.0 eV is most likely negatively charged, since the Si$^{1+}$ is shifted up by ∼1 eV from the Si$^0$ peak [57–59]. The presence of this putative Si$^{1-}$ species is surprising due to the electropositive nature of Si, but the accessibility of metastable phases in the nonequilibrium environment formed at the plasma-water interface [3, 14, 43, 60] could enable the formation of such exotic species. The large peak centered around 103.5 eV in the silica-Au
NPs was deconvoluted into two peaks, which are likely two types of silica species with different electronic structures [56, 61], or silicon species with different oxide layer thicknesses [57, 62]. The more abundant peak at 102.9 eV could be a thin oxide layer [57], or it could be bound with gold particles, as reports with silica and colloidal Au may have a slightly lower binding energy to silica alone [54]. The peak at 104.6 eV is on the higher range of binding energies for silica, which could be due to a thicker oxide layer in the matrix or the presence of large silica particles [57, 62], based on a recent report of 104.3 eV binding energy of a 200 nm thick layer of silica [62]. Alternatively, the higher binding energy peak may arise from quartz based on previous XPS studies [50, 63]. The control silica NPs synthesized in water contain the same peaks in the Si2p spectrum, confirming that these species are formed from laser ablation of the silicon wafer in liquid, regardless of the presence of metal salt. A small peak (2%) corresponding to Si$^{3+}$ [57–59] was also present in the control silica NPs; the other peaks are shifted to slightly higher binding energies compared to the silica-Au NPs. This could also be due to the general oxide layers being thicker [57, 62], or due to the absence of Au NPs [56]. Gross et al. studied binding energy shifts of silica with and without colloidal gold, and found that with quartz species, the Si2p binding energy shifted down slightly when colloidal gold was present, while silica gel exhibited no binding energy shift whether the gold was present or not [56].

TEM, HRTEM, FFT and lattice spacing measurements of the control silica NPs (Fig. S5 of the Supplemental Material) show two populations of silica: amorphous and polycrystalline particles. This reflects the two deconvoluted peaks in the Si2p spectrum, although it is difficult to assign peaks to the different morphologies, due to overlapping binding energies reported for the different silica species [56, 61, 62, 64, 65]. The weak Si2p signal in the control Au NP sample may be partially oxidized Si species arising from contamination from the quartz cuvette used for irradiation experiments.

The O1s spectra in Fig. 4c show that most of the O1s surface species in the silica-Au NPs is from silica [61, 66], and a small percentage from oxidized gold (Au$_2$O$_3$ and Au(OH)$_3$) [67]. The binding energy assigned to SiO$_2$ at 532.6
eV matches closely to that reported by Gross et al. for quartz with colloidal gold (532.7 eV), and is close to the reported value for crystalline quartz [68]. However, the TEM and HRTEM images for the silica-Au NPs (Fig. 2) do not contain any crystalline silica species, but XPS analysis can identify species not visible with electron microscopy imaging. The control Au NPs contain mostly oxidized gold species, corresponding to surface hydroxides. The binding energy at 531.3 eV is close to that of Au(OH)$_3$ [67], giving the surface gold atoms a Au$^{3+}$ oxidation state that was not detected in the Au$^{4f}$ spectrum for the control Au NPs. Partial oxidation of the gold surface atoms is likely the case. Three peaks were deconvoluted in the control silica NPs O1s spectrum, with a small (1%) amount corresponding to that of amorphous silica [68], and the other two in the range of silica species [56, 57, 62, 65, 66]. The peak at 532.8 closely matches reported binding energy values for quartz (532.7 eV [68]), while the majority of the O1s signal comes from the peak deconvoluted at 533.1 eV, which is close to the 533.2 eV binding energy reported for silica [56, 57, 62, 65, 66]. It is difficult to assign species based on the Au$^{4f}$, Si$^{2p}$, and O1s XPS spectra due to overlapping binding energies reported; however, we hope to demonstrate the multiple types/populations of silica generated from our fs-RLAL approach.

Figure 4: XPS spectra for Au$^{4f}$ (a), O1s (b), Si$^{2p}$ (c) atomic orbitals for silica-Au NPs (blue), Au NPs (red), and silica NPs (black) with fitted peaks.

The Cl2p binding energies are presented in Table 1 and the spectra are
displayed in the Supplemental Material, Figure S6. The peaks correspond to metal chlorides, likely from the KAuCl$_4$ precursor [66].

<table>
<thead>
<tr>
<th>Species</th>
<th>silica-Au NPs</th>
<th>Au NPs</th>
<th>SiO$_2$ NPs</th>
<th>bulk (reference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$^{1-}$</td>
<td>82.9; 7%</td>
<td>82.8 eV; 30%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au$^0$</td>
<td>83.8 eV; 72%</td>
<td>84.0 eV; 55%</td>
<td></td>
<td>84.0 eV [64]</td>
</tr>
<tr>
<td>Au$^{1+}$</td>
<td>84.9; 13%</td>
<td>85.2 eV; 15%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au$^{3+}$</td>
<td>85.8; 8%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si$^{1-}$ *</td>
<td>98.0; 11%</td>
<td>98.3; 13%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si$^0$</td>
<td>99.4; 8%</td>
<td>99.8; 6%</td>
<td>99.4 eV [56, 58]</td>
<td></td>
</tr>
<tr>
<td>Si$^{1+}$ (Si$_2$O)</td>
<td>101.9; 100%</td>
<td>100.9; 2%</td>
<td>100.5 eV [57, 59]</td>
<td></td>
</tr>
<tr>
<td>Si$^{3+}$ (Si$_2$O$_3$)</td>
<td></td>
<td>103.4; 64%</td>
<td>102 eV [57]</td>
<td></td>
</tr>
<tr>
<td>Si$^{4+}$ (thin SiO$_2$)</td>
<td>102.9; 69%</td>
<td>102.6–104 eV [56, 58, 65, 69]</td>
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<td></td>
</tr>
<tr>
<td>SiO$_2$ (thick/quartz)</td>
<td>104.6; 12%</td>
<td>105.4; 15%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au$_x$O$_y$</td>
<td>529.0; 2%</td>
<td>529–530 eV [67]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au$_2$O$_3$</td>
<td>529.8; 1%</td>
<td>530.5; 5%</td>
<td>530.2 eV [67]</td>
<td></td>
</tr>
<tr>
<td>Au$_x$(OH)$_y$</td>
<td>531.2; 9%</td>
<td>531.3; 93%</td>
<td>531.2 eV [67]</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$ (amorphous)</td>
<td>530.7; 1%</td>
<td>530.7 eV [68]</td>
<td></td>
<td></td>
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<tr>
<td>SiO$_2$ (quartz)</td>
<td>532.8; 5%</td>
<td>532.9 eV [56, 60]</td>
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<td></td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>533.1; 94%</td>
<td>533.2–534 eV [56, 61, 62, 65, 66]</td>
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<td></td>
</tr>
<tr>
<td>Au-Cl</td>
<td>199 eV; 100%</td>
<td>198.5 eV; 100%</td>
<td>198.8–199.2 eV [66]</td>
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</table>

Table 1: Binding energy (eV) and atomic percent of various species deconvoluted from XPS analysis. Binding energy values correspond to Au$_{4f_7/2}$, Si$_{2p_3/2}$, O$_{1s}$, and Cl$_{2p_3/2}$ peaks.

*Suggested species not reported in literature. *$a$ value reported for Au(OH)$_3$. *$b$ binding energies reported for transition metal chloride compounds.

3.2. Catalysis

The reduction reaction of PNP by sodium borohydride was used to test the catalytic activity of the silica-Au NPs. This is a common model reaction that can be easily monitored via UV-vis spectroscopy by the decrease in absorbance of the para-nitrophenolate ion at 400 nm, allowing for direct extraction of the
pseudo-first-order rate constant [70, 71]. The PNP reduction reaction follows a two-step mechanism involving (i) the diffusion and adsorption of PNP to Au surfaces, and (ii) electron transfer mediated by the Au surface from BH$_4^-$ to PNP [72,74]. Therefore, designing Au nanocatalysts with high surface areas (small NP size) and available surface sites are expected to increase the catalytic activity. Experimental details and associated rate equations used to extract the rate constants reported below are provided in the Supplemental Material.

Table 2 displays catalytic rate constants for the silica-Au NPs, the control Au NPs, and selected Au NP catalysts recently reported. The rate constants $k_{\text{Au}}$ in Table 2 are reported with respect to the amount of gold added to the reaction rather than to the available surface area, i.e. as s$^{-1}$ $\mu$mol$^{-1}$ instead of s$^{-1}$ L m$^{-2}$ as commonly reported [73–75]. Normalizing the rate constant with respect to the amount of added Au provides a means to directly assess how efficiently Au atoms present in the nanocatalyst are used for the catalytic reaction, independent of the size dispersity of the nanocatalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>size (nm)</th>
<th>$k_{\text{Au}}$ (s$^{-1}$ $\mu$mol$^{-1}$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>silica-Au NPs</td>
<td>3.4±0.8; 7.3±2.1</td>
<td>0.101±0.010</td>
<td>this work</td>
</tr>
<tr>
<td>Au NPs</td>
<td>9.3±4.6</td>
<td>0.067±0.011</td>
<td>this work</td>
</tr>
<tr>
<td>bare Au NPs from PLAL</td>
<td>7.2±2.1a</td>
<td>0.037</td>
<td>[75]</td>
</tr>
<tr>
<td>Au@SiO$_2$ Yolk/Shell Nanoreactors</td>
<td>104±9 yolk; ~22 shell</td>
<td>0.0088</td>
<td>[76]</td>
</tr>
<tr>
<td>Au NP decorated ceria nanotubes</td>
<td>5</td>
<td>0.014</td>
<td>[9]</td>
</tr>
</tbody>
</table>

Table 2: Summary of rate constants extracted from model PNP catalytic reaction for samples discussed in this work and other references. *lognormal distribution of Au NPs revealed weighted mean size of 11.1 nm.

The silica-Au NPs synthesized in this work display the highest catalytic activity of the reported nanocatalysts, which were chosen based on their bare surfaces [75], Au-silica composition [76], and comparison with another common metal oxide support material [9]. The high catalytic rate constant of the silica-Au NPs is likely due to both the small size of the embedded Au NPs within the silica matrix and the accessible surface sites of the larger isolated Au NPs.
The larger size of the control Au NPs compared to both populations of the 
Au NPs in the silica-Au NPs sample is likely the main reason for their lower 
rate constant. The bare Au NPs synthesized via PLAL however, possessed sig-
nificantly lower catalytic activity compared to the control Au NPs in this work, 
despite their smaller size. It is not clear why the bare Au NPs from PLAL 
possess lower catalytic activity, since their Au NP surfaces should be highly ac-
cessible. It is possible that the electrostatically stabilized Au NPs from PLAL 
agglomerated upon addition to the catalytic reaction. A long (60 s) induction 
period was observed once the PLAL Au NPs were added to the catalytic re-
action, which was attributed to “surface restructuring” [75]. In contrast, there 
was no induction period observed when our control Au NPs were added to the 
catalytic reaction (Fig. S2b in Supplemental Material). While the control Au 
NPs reported here are also electrostatically stabilized, the small amount of elec-
trolytes in solution from the KAuCl$_4$ precursor [77], along with the slightly 
larger Au NP size, may prevent the Au NPs from agglomerating upon their 
addition to the catalysis reaction, thereby yielding a higher rate constant.

The other silica-Au nanocatalyst system was synthesized using a two-step 
wet-chemical method, in which colloidal Au NPs were prepared from a modified 
polyol process by refluxing HAuCl$_4$ in 1,5-pentanediol, poly(vinyl pyrrolidone), 
and a small amount of silver nitrate. The 120 nm gold particles were coated 
with silica via the Stöber method, with tetraethyl orthosilicate (TEOS) as the 
silica source in 2-propanol. The resulting rate constant of the Au-yolk@SiO$_2$-
shell nanoreactors was over an order of magnitude lower than the silica-Au NPs 
in this work. The low catalytic activity can be explained by the large size of the 
yolk-Au NPs, along with the slow diffusion of the substrate molecules through 
the thick silica shell. A diffusion coefficient for the silica layers of the shell was 
reported ($\sim 5 \times 10^{-19}$ m$^2$ s$^{-1}$), signifying a very slow rate of diffusion through 
the silica shell, depressing the rate constant [76].

While ceria is a common metal oxide support for Au NPs for CO oxidation 
and enhanced thermal stability, Au NP decorated ceria nanotubes synthesized 
by mixing PLAL-synthesized bare AuNPs with chemically-synthesized CeO$_2$
nanotubes [9] possessed poorer catalytic activity toward PNP reduction as compared to our silica-Au NPs. This is also surprising due to the small 5 nm size of the PLAL-generated Au NPs; however, it has been reported that along with the small size of the Au NPs, the support material also affects the catalytic activity toward PNP reduction [72]. Due to the high interfacial bonding of Au NPs on ceria, the catalytic activity was depressed [72, 78], compared to the weakly interacting silica support of our silica-Au NPs. The silica in our nanocatalysts is likely providing a bonding environment that promotes the adsorption and desorption of the substrate molecules and reduced products [64].

4. Discussion

To explain the formation of two populations of silica-Au NPs in fs-RLAL, we consider the timescales of chemical reactions in the initially generated plasma and material ejection from the Si wafer occurring in our experiments. Due to the extremely short duration of the femtosecond laser pulse as compared to the nanosecond pulses typically used in RLAL, both plasma reactions and material ejection can occur on significantly faster timescales than the ~µs timescales of cavitation bubble formation and collapse. Here, we will focus on how these early reactions taking place on timescales of tens of femtoseconds through nanoseconds can form two types of silica-Au NPs.

We first consider reactions in the initially formed plasma at the water-Si interface. The laser intensity used in our experiments exceeds the optical breakdown (OB) threshold of 10^{13} \text{ W cm}^{-2} for 800 nm, 30 fs pulses in water [26], and the fluence is sufficient to produce an electron-hole pair density at the Si surface exceeding the critical threshold of 10^{22} \text{ cm}^{-3} for ablation [79, 80]. The electrons generated in the OB plasma (eq 1-3) and ejected from the Si surface can induce Au^{3+} reduction (eq 5). The timescales for both electron formation processes are on the order of a few tens of femtoseconds [14, 79–82], and the resulting electrons become hydrated (eq 2) on a timescale of several hundred femtoseconds [83, 84]. Because hydrated electrons react with [AuCl_4]^- with a
diffusion-controlled rate constant of $6.1 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$ \cite{85} and have a lifetime in pure water of hundreds of ns \cite{86}. [AuCl$_4$]$^-$ reduction in solution can begin within hundreds of femtoseconds of the laser pulse and occur during the next several ns. As a result, a significant fraction of the available [AuCl$_4$]$^-$ near the laser focus may be consumed within $\sim$1 ns of the laser pulse. The OB plasma also contains OH radicals that lead to the formation of H$_2$O$_2$ (eq 1) on the timescale of $\sim$10 ns – 10 $\mu$s \cite{86}. This peroxide formation induces autocatalytic surface growth of the gold clusters to larger nanoparticles (eq 6) \cite{28,30}. We propose that this plasma-mediated mechanism that begins within tens of femtoseconds following arrival of the laser pulse drives the formation of the larger isolated Au NPs in our experiments.

$$\text{H}_2\text{O} \xrightarrow{n h\nu} \text{e}^- + \text{H}^+ + \text{OH}.$$ \hspace{1cm} (1)

$$\text{e}^- \longrightarrow \text{e}^-_{\text{aq}}$$ \hspace{1cm} (2)

$$\text{H}_2\text{O} \xrightarrow{n h\nu} \text{H} \cdot + \text{OH}.$$ \hspace{1cm} (3)

$$2\text{OH} \cdot \longrightarrow \text{H}_2\text{O}_2$$ \hspace{1cm} (4)

$$[\text{AuCl}_4]^\text{−} + 3\text{e}^-_{\text{aq}} \longrightarrow \text{Au}(0) + 4\text{Cl}^-$$ \hspace{1cm} (5)

$$[\text{AuCl}_4]^\text{−} + \frac{3}{2}\text{H}_2\text{O}_2 + \text{Au}_m \longrightarrow \text{Au}_{m+1} + \frac{3}{2}\text{O}_2 + 3\text{HCl} + \text{Cl}^-$$ \hspace{1cm} (6)

Second, we consider the dynamics of material ejection from the Si surface. After the removal of free electrons, a strong electrostatic field develops on the Si surface due to the charge separation, which ultimately pulls out silicon atoms and ions from the surface if the laser fluence is above the ablation threshold \cite{79,81}. Our fluence of 0.22 J/cm$^2$ exceeds the reported ablation threshold for Si in water with <100 fs laser pulses ($\sim$0.16 J/cm$^2$ \cite{87}) by a factor of $\sim$1.4. At fluences up to $\sim$3 times the ablation threshold, both experiments and molecular dynamics simulations report the beginning of material ejection on a timescale of tens or hundreds of ps after the laser pulse, depending on the target material and environmental conditions (Table 3) \cite{14,60,78,82,88}. While reported timescales for Si ejection are typically faster than 100 ps \cite{79,82,88}, these
studies were conducted in air or vacuum, without the confinement provided by the water environment. The slower timescales of 200−500 ps reported for Ag in water [13, 60] likely provide a better estimate for the ejection of Si atoms into the surrounding water in our experiments. Subsequent ejection of larger molten droplets can then occur on timescales of several ns [13]. These Si species in the expanding low-density Si-water mixing region or injected into the colder water above will undergo rapid oxidation and cooling, and can provide nucleation sites for nearby gold ions. We propose that the ejection of Si species on the sub-ns timescale leads to formation of the embedded silica-Au NPs. The small size of the Au NPs embedded in the silica matrix may result from either depleted [AuCl$_4$]$^-$ concentration due to the plasma reactions discussed above or silica species coalescing around the initially formed Au nuclei, halting further growth.

<table>
<thead>
<tr>
<th>material</th>
<th>pulse duration (fs)</th>
<th>environment</th>
<th>timescale (ps)/Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>130</td>
<td>air</td>
<td>20−100 [79]</td>
</tr>
<tr>
<td>Si</td>
<td>500</td>
<td>vacuum</td>
<td>25 [88]</td>
</tr>
<tr>
<td>Si</td>
<td>90</td>
<td>air</td>
<td>10−100 [82]</td>
</tr>
<tr>
<td>Ag</td>
<td>40</td>
<td>water</td>
<td>200 [60]</td>
</tr>
<tr>
<td>Ag</td>
<td>$10^4$</td>
<td>water</td>
<td>500 [13]</td>
</tr>
</tbody>
</table>

Table 3: Reported timescales for onset of material ablation with femtosecond pulses.

The proposed reactions and timescales in our experiments that lead to each population of silica-Au NPs are illustrated in Fig. 5. At early times during and immediately after the pulse, the plasma reactions begin. Free electrons generated in the plasma at the Si-water interface hydrate and react with the initially high concentration of [AuCl$_4$]$^-$, forming Au nuclei within hundreds of fs to a few ns. These can coalesce and react with the H$_2$O$_2$ generated beginning around 10 ns to predominantly form the larger isolated Au NPs. Meanwhile, surface reactions begin around 100 ps or later. The ejected Si atoms and liquid droplets oxidize and coalesce, at which point they can react with the remaining [AuCl$_4$]$^-$ and Au nuclei present. The expected low concentration of [AuCl$_4$]$^-$
near the Si-water interface at around 1 ns after the laser pulse could give rise to the predominant formation of ultrasmall Au NPs embedded in the Si that is ejected. Alternatively, the encapsulation of the growing Au nanoclusters by the Si species could quench the growth. The presence of some large Au NPs that appear to be attached to the Si matrix (Fig. 2a) may be accounted for by Au NPs formed in the plasma reactions coming into contact with the Si species prior to their cooling. Finally, we note that the formation of cavitation bubbles beginning approximately 100 ns after the laser pulse [54] could contribute to the observed silica-Au NP morphologies, particularly for the embedded Au NPs.

Figure 5: Proposed timescales of reactions in fs-RLAL.

Both the isolated and embedded silica-Au NPs formed in our experiments have significantly different morphologies as compared to silica-Au NPs prepared from ns-RLAL, indicating that completely different reaction dynamics from those depicted in Fig. 5 occur when ns lasers are used. Saraeva et al. generated small ~10 nm Au NP-decorated ~1 µm silica particles from ns-RLAL of a silicon wafer immersed in a [AuCl$_4$]$^-$ solution [45]. They reported that no Au NPs formed in the absence of the Si wafer, indicating that [AuCl$_4$]$^-$ reduction occurred primarily through reaction with ablated Si species through processes such as galvanic replacement [45]. In contrast, the formation of Au NPs from plasma reactions in water alone indicates that [AuCl$_4$]$^-$ reduction in fs-RLAL can occur without any Si species interactions, as we propose in Fig. 5. Liu et al. employed a double beam ns-RLAL approach using a 355 nm, 2 ns pulse for
ablation and a 532 nm, 10 ns pulse to irradiate the ablation plasma, resulting in
large silica particles (~200–500 nm) possessing wrinkled surfaces, silica parti-
cles with veins of gold throughout, and silica-core/Au-shell particles \[43\]. They
reported that irradiation of the plasma region at a wavelength resonant with
the Au SPR frequency facilitated the reduction of \([\text{AuCl}_4^-]\) to form Au NPs
that encapsulate the ejected Si species \[43\]. The simultaneous material ejection
and metal salt reduction timescales over hundreds of ns in the latter experi-
ments are distinct from the likely separate timescales of metal salt reduction
and material ejection that can occur in fs-RLAL. Further investigation of the
different nanoparticle formation mechanisms in ns- and fs-RLAL is needed to
fully understand the origin of the distinct particle morphologies produced.

5. Conclusions

This work introduced a fs-RLAL approach as a facile route to silica-Au NPs
with significantly smaller Au NP sizes than accessible in previously reported
ns-RLAL studies. The silica-Au NPs were found to be highly active towards
catalytic reduction of PNP by NaBH\(_4\) as compared to the control Au NPs
synthesized in the absence of Si and several other gold nanostructures recently
reported. Characterization of the products revealed two populations of Au NPs-
(i) larger, predominantly isolated Au NPs (7.3±2.1 nm), and (ii) small Au NPs
(3.4±0.8 nm) embedded in an amorphous silica matrix, along with previously
unreported silica species deconvoluted in the Si2p XPS spectra. Considering
the timescales of reactions in a fs-laser optical breakdown plasma and material
ejection from ablation, we proposed formation mechanisms for the two observed
populations of silica-Au NPs. Unlike in ns-RLAL, we expect that photochemical
reduction of metal ions can occur before material ejection in fs-RLAL, poten-
tially enabling unprecedented control over accessible particle morphologies due
to the separation of the reduction and ablation steps. Further elucidation of
the distinct chemical reactions and timescales occurring in ns- and fs-RLAL
is needed to advance the rational design and synthesis of catalytically active
nanostructures using this readily generalizable approach.

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Supplemental Material

UV-vis spectra at intermediate laser irradiation times; UV-vis spectrum of control Au NPs; characterization of silica NPs; details of PNP catalytic reactions; additional TEM images of silica-Au NPs; and Cl2p XPS spectra.

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