Nanoengineering Multiples Plasmonic Hotpots in Individual Gold Nanodentrites For Boosting Hot Electron Formation for Plasmonic Catalysis

Carlos Castro,1 Scarllett L.S. de Lima,1 Jules Gardener,2 Marcos V. Petri,3 Guilhermo Solórzano,1 Tommaso Del Rosso,1 Anderson G.M. da Silva,1

*1Departamento de Engenharia Química e de Materiais-DEQM, Pontifícia Universidade Católica do Rio de Janeiro (PUC-Rio), Rua Marquês de São Vicente, 225 - Gávea 22453-900 Rio de Janeiro – RJ, Brazil.*

*2Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748, 05508-000, São Paulo, SP, Brazil*

*3Center for Nanoscale Systems, School of Engineering and Applied Sciences, Harvard University.*

Resumo/Abstract

RESUMO - Os plásmons, oscilação coletiva de elétrons livres em nanopartículas metálicas, são excitados pela luz e geram campos elétricos localizados conhecidos como hotspots, que promovem reações de transferência de carga na interface metal-molécula e aumentam a eficiência do processo fotocatalítico. O efeito dos hotspots na atividade fotocatalítica de nanopartículas metálicas tem sido extensivamente estudado, com ênfase na morfologia e anisotropia das nanopartículas. A morfologia altamente ramificada e anisotrópica dos nanodendritos de ouro (AuNDTs) confere a eles propriedades plasmônicas únicas, que foram avaliadas em testes experimentais utilizando as moléculas *p*- aminotiofenol (PATP) e anilina. O estudo mostrou que a oxidação fotocatalítica do *p*- aminotiofenol e da anilina usando nanodendritos de ouro (AuNDTs) apresentou maiores taxas de conversão sob excitação de luz visível em comparação com o uso de partículas de nanoesfera de ouro (AuNSPs). Isso indica que os AuNDTs possuem maior atividade catalítica na promoção de reações de transferência de carga na interface metal-molécula.

*Palavras-chave: Fotocatálise; plasmônica; nanopartículas de ouro; oxidação; SERS; nanoestruturas.*

ABSTRACT - Plasmons, the collective oscillation of free electrons in metal nanoparticles, are excited by light and generate localized electric fields known as hotspots, which promote charge transfer reactions at the metal-molecule interface and enhance the efficiency of the photocatalytic process. The effect of hotspots on the photocatalytic activity of metal nanoparticles has been extensively studied, with an emphasis on nanoparticle morphology and anisotropy. The highly branched and anisotropic morphology of Au nanodendrites (AuNDTs) gives them unique plasmonic properties, which were evaluated in experimental tests using *p*-aminothiophenol (PATP) and aniline molecules. The study showed that the photocatalytic oxidation of *p*-aminothiophenol and aniline using Au nanodendrites (AuNDTs) exhibited higher conversion rates under visible-light excitation compared to using Au nanospheres (AuNSPs). This indicates that the AuNDTs possess greater catalytic activity in promoting charge transfer reactions at the metal-molecule interface.

*Keywords: Photocatalysis; plasmonics; gold nanoparticles; oxidation; SERS; nanostructures.*

## Introdução

Metal nanoparticles have unique optical properties that make them promising for various applications such as photonics, electronics, and sensing. Localized surface plasmon resonance (LSPR) is an important feature of these nanoparticles that can lead to larger enhancements of the electric field around them. Plasmonic catalysis is a process that relies on the energy generated by LSPR excitations in plasmonic nanoparticles to drive, accelerate, and/or control molecular transformations (1-3).

The use of gold and silver nanoparticles in plasmonic catalysis is particularly strong due to their ability to support LSPR excitation in the visible and near-infrared ranges with tunable wavelengths. Anisotropy is an important factor affecting the photocatalytic properties of these nanocomposites, with highly branched and anisotropic morphology showing unique plasmonic properties (4-5). Au nanostars and Au nanodendrites are examples of these nanocomposites that have been studied for their ability to locally create extremely large electromagnetic field enhancements in their spikes or hotspots (6-7).

The objective of the comprehensive experimental and theoretical analysis is to study the influence of nanoparticle anisotropy on the photocatalytic properties of these nanocomposites. The study will focus on Au nanodendrites, which exhibit unique plasmonic properties due to their highly branched and anisotropic morphology (8). Specifically, the role of nanoparticle morphology and the degree of anisotropy in enhancing the plasmonic response were investigated. The presence of hotspots and their effect on the photocatalytic activity of metal nanoparticles were also examined, with the aim of promoting charge transfer reactions at the metal-molecule interface and improving reaction rates and selectivity.

## Experimental

*Materials and instrumentation*

Analytical grade chemicals sodium citrate dihydrate (C6H5Na3O7.2H2O, 99%, Sigma-Aldrich), chloroauric acid trihydrate (HAuCl4.3H2O, 99.9%, Sigma-Aldrich), sodium hydroxide (NaOH, anhydrous ≥98%, Sigma-Aldrich), hydroquinone (C6H6O2, 99%, Vetec), polyvinylpyrrolidone (PVP, Sigma-Aldrich, Mw 55 000 g/mol) were used as received.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL 1010 microscope operating at 80 kV or a JEOL JEM 2100 microscope operated at 200 kV. Samples for TEM and HRTEM were prepared by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. UV-Vis spectra were obtained from aqueous suspensions containing the nanostructures with a Perkin Elmer Lamba 650 spectrophotometer. Raman spectra were acquired on a Renishaw Raman InVia equipped with a CCD detector and coupled to a Leica microscope that allows a rapid accumulation of Raman spectra with a spatial resolution of about 1 µm (micro-Raman technique). The laser beam was focused on the sample using a 50x lens. The experiments were performed under ambient conditions using a back-scattering geometry. The samples were irradiated with the 633 line of a He-Ne laser (Renishaw RL633 laser), and a solid-state diode laser, respectively, using controlled laser power outputs of 0.02-0.66 mW and employing the exposure time up to 30 s.

*Synthesis of Au Nanospheres (AuNSPs)*

The Au nanospheres (AuNSPs) were synthesized using a colloidal seeded growth technique (9). Briefly, for the synthesis of Au seeds, 150 mL of a 2.2 mM sodium citrate aqueous solution was heated in a 250 mL round flask at 100 °C under magnetic stirring. After 15 min, 1 mL of 25 mM AuCl4 solution was added, the reaction mixture kept at 100 °C under vigorous stirring for 30 minutes. For the first deposition step, 1 mL of 60 mM sodium citrate solution was added to same 250 mL round flask under magnetic stirring at 100 °C. After 5 min, 1 mL of 25 mM AuCl4 solution was injected to mixture at 100 °C for another 30 min. For a second deposition step, another 1 mL of 60 mM sodium citrate solution was injected, followed by the addition of 1 mL of AuCl4 25 mM for another 30 min.

*Synthesis of Au Nanosdendrites (AuNDTs)*

Primary, Au seeds were prepared by adding 17.6 mL of ultrapure water to a 20 mL round flask, which was then preheated at 70°C under magnetic stirring. After 10 minutes, 2 mL of HAuCl4 solution and 2 mL of 8.8 mM NaOH were injected into the flask. After 1 minute, 600 µL of 170 mM trisodium citrate aqueous solution was added, and the reaction was allowed to proceed for 30 minutes.

For the synthesis of Au nanodendrites, a combination AuCl4 as the Au precursor like growth approach was employed, Au NPs spheres as seeds, hydroquinone as a reducing agent and polyvinylpirrolidone (PVP) as a stabilizer. Firstly, 10 mL of 0.2 mM PVP aqueous solution (1 mg/mL) was added to a 50 mL glass flask at room temperature, followed by 400 µL of as-prepared Au seeds and 85 µL of 25 mM HAuCl4 solution, while stirring the mixture continuously. After 3 minutes, 1 mL of 30 mM aqueous hydroquinone solution and 300 µL of 34 mM trisodium citrate aqueous solution were injected simultaneously. In a few seconds, the reaction proceeded, resulting in the formation of a blue suspension.

## Results and Discussion

The morphological analysis of these Au NPs has been carried out by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). It can be observed from the TEM imagens (Fig. A and C) the Au nanodendrites (AuNDTs) displayed a several spikes around a core, and the tip of the spike is curved (Fig. E).

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Figure 1. TEM (A), HRTEM (C and E) imagens for Au dendrites. TEM (B), HRTEM (D and F) imagens for Au nanospheres.

Histograms were plotted to analyze the distribution of Au nanoparticles obtained from Figure 1. The Au nanodendrites exhibited a total size of 26 ± 1.5 nm in diameter (Figure S1A), while the core of the Au nanodendrites displayed a diameter of 11.5 ± 0.8 nm (Figure S1B). Furthermore, the Au nanospheres exhibited a diameter of 16.5 ± 0.45 nm. These findings contribute to the characterization and understanding of the size variations within the synthesized Au nanoparticles.

The important differences in the absorption signatures of the three different morphologies chosen for this study (AuNSPs and AuNDTs) can be clearly observed in Figure 2. AuNSPs with a diameter of 14 nm present a single and narrow absorption band with a maximum centered at 522 nm while the anisotropic particles exhibit more complex fingerprints (10). The Au nanodendrites show two plasmon bands represented the core (shoulder at 522 nm) and outer spikes (broad band centered at 656 nm) typical of these nanostructures.

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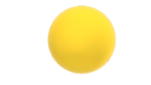
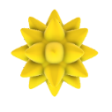


Figure 2. Normalized UV-Vis extinction spectra recorded from aqueous suspensions containing AuNSPs and AuNDTs (blue and red traces, respectively).

Hot electrons are produced when Au nanodendrites undergo SPR excitation, occupying energy states above the Fermi level during plasmon oscillation. These electrons can be transferred to an adsorbed molecule, triggering charge-transfer transformations. In the context of SPR-mediated *p*-aminothiophenol (PATP) oxidation, hot electrons produced from SPR-excited Ag nanomaterials can be transferred to adsorbed O2 molecules, which are activated to O22- ions. This process subsequently contributes to the *p*-aminothiophenol (PATP) oxidation to p,p′-dimercaptoazobenzene (DMAB) at the metal surface, as shown in Figure 3A. To further understand the photocatalytic properties of these nanocomposites, experimental and theoretical analyses focusing on the influence of nanoparticle anisotropy have been conducted. Au nanostars, known for their ability to create large electromagnetic field enhancements in their spikes, were used as photosensitizers to increase the population of hot electrons near the metal-molecule interface (11).

The SERS spectra of Au nanodendrites functionalized with PATP are presented in Figure 3B-C, with the laser power being the variable. Meanwhile, Figure 3B displays the DMAB:(DMAB + PATP) 1433 cm-1:1081 cm-1 intensity ratios in relation to the laser power. The SERS effect made it possible to identify the PATP and/or DMAB bands in all spectra, such as the A1 modes of PATP at 1081, 1188, 1489, and 1593 cm-1, and the Ag modes of DMAB at 1081, 1142, 1390, 1433, and 1575 cm-1. The Raman intensities of the Au modes related to DMAB and DMAB:(DMAB + PATP) 1433 cm-1:1081 cm-1 intensity ratios increased proportionally to the laser power, confirming an SPR-mediated reaction mechanism (12,13). The irradiation time-dependent SERS spectra and DMAB:(DMAB + PATP) 1433 cm-1:1081 cm-1 intensity ratios recorded using a 0.30 mW laser power are displayed in parts D and E of Figure 3, respectively. The Raman intensities attributed to DMAB increased with the laser irradiation time, which is also consistent with an SPR-mediated mechanism.

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Figure 3. Strategy for the SPR-Mediated Oxidation of PATP to form DMAB (A) Catalyzed by Au nanodendrites using 633 nm as the incoming electromagnetic radiation. Laser-power (B) and irradiation-time (C) dependent SERS spectra for Au nanodendrites that had been functionalized with PATP employing 25 s as the exposure time (B) and 0.30 mW as the laser power (C) (D-E) Show the DMAB:(DMAB+PATP) 1433:1081 intensity ratios obtained from (B) and (C), respectively.

Figure 4A shows the SERS spectra recorded under 632.8 nm excitation for nanodentrites (AuNDTs) and nanospheres (AuNSPs) and functionalized with PATP (blue and black traces, respectively). Th qe intensity ratios of DMAB:(DMAB + PATP) at 1433 cm-1:1081 cm-1 were strongly influenced by the shape of Au dendritic with hotspots injecting hot electrons in catalysts (14).

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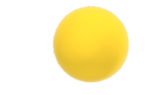
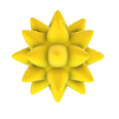


Figure 4. SERS spectra that had been functionalized with PATP employing 25 s as the exposure time and 0.30 mW as the laser power.

To gain deeper insights into the utilization of light energy by nanoparticles to drive catalytic reactions on the surface, we focused our attention on the employment of AuNSPs and AuNDTs as plasmonic catalysts (see Figure 5). Specifically, we investigated their effectiveness in the visible-light-driven oxidation of aniline under ambient conditions (room temperature, 1 atm of O2), employing a 300 W tungsten lamp as the excitation source. These experimental conditions were chosen to match those described elsewhere (15). It is important to note that the traditional synthesis of aromatic azocompounds from amines typically involves multiple reaction steps and the use of stoichiometric amounts of nitrite salts (NaNO2), as well as toxic oxidants (16).

Figure 5A illustrates the time-dependent conversion (%) of aniline under various reaction conditions, including the use of catalysts (AuNSPs - red trace, AuNDTs - blue trace) and the absence of a catalyst (blank - black trace). The employment of AuNDTs resulted in approximately 95% conversion of aniline after 8 hours, which was significantly higher compared to AuNSPs, achieving only about 20% conversion. This hybridization of Au NPs (AuNDTs) demonstrated a higher and faster conversion of aniline when compared to core-shell metallic nanorattles reported in another study conducted by our group (15).

Figure 5B illustrates the impact of visible light on the photocatalytic activity of AuNDTs. Three different conditions were applied for the oxidation of aniline: light on, light off, and light off after 3 hours. The results revealed that in the absence of visible light excitation, the conversion (%) remained low, with only 10% conversion observed after 10 hours at 34°C. In contrast, under visible-light excitation, complete conversion (100%) was achieved after 10 hours. Figure 5B provides further evidence of the role of visible-light excitation by demonstrating the catalytic conversion for 3 hours under visible-light excitation followed by turning off the light source. Notably, no significant conversion occurred after the light source was turned off, aligning with previous studies that propose the reaction to proceed through an electron transfer mechanism. (17,18).

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Figure 5. Conversion (%) of aniline as a function of time catalyzed by AuNSPs and AuNDTs (blue and red traces, respectively) (A) Conversion (%) of aniline employing Au nanodendrites as catalysts in the absence of visible light or by turning the light off after 3 h (B).

## Conclusion

The study investigated the morphological and photocatalytic properties of gold nanoparticles (AuNPs) with different shapes. The AuNPs were characterized using transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The results showed that the Au nanodendrites (AuNDTs) had several spikes around a core, while the Au nanospheres (AuNSPs) were spherical. The absorption signatures of the two different morphologies exhibited differences in their absorption spectra. The photocatalytic properties of AuNDTs were investigated by functionalizing them with PATP, and it was found that the conversion was influenced by hot electrons transfer in the AuNDTs. The study demonstrated that AuNDTs had enhanced photocatalytic properties compared to AuNSPs, and this was attributed to their anisotropic shape.

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