Tuning plasmon transitions and their applications in organic photochemistry*

Juan C. Scaiano[‡], José C. Netto-Ferreira, Emilio Alarcon, Paul Billone, Carlos J. Bueno Alejo, Charles-Oneil L. Crites, Matthew Decan, Chiara Fasciani, María González-Béjar, Geniece Hallett-Tapley, Michel Grenier, Katherine L. McGilvray, Natalia L. Pacioni, Andrea Pardoe, Laetitia René-Boisneuf, Rachel Schwartz-Narbonne, M. Jazmín Silvero, Kevin G. Stamplecoskie, and Tse-Luen Wee

Department of Chemistry, Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

Abstract: The ketone-photoinduced formation of Au, Ag, and Cu nanoparticles from their corresponding ions in solution has been carried out using benzoin photoinitiators. Ketones are good photosensitizers for nanoparticle synthesis not because of the energy they can absorb or deliver, but rather because of the reducing free radicals they can generate. Efficient photochemical nanoparticle generation thus requires a careful selection of substrates and experimental conditions such that free radical generation occurs with high quantum efficiency, where metal ion precursors do not inhibit radical formation. A key consideration to achieve nanoparticle synthesis with short exposure times is to minimize excited-state quenching by metal ions.

Applications of nanostructures in catalysis require control of the nanoparticle characteristics, such as dimension, morphology, and surface properties. Part of this article describes the strategies to modify photochemically prepared particles. Finally, we illustrate some of the nanoparticle applications that interest us, with some emphasis on plasmon-mediated processes.

Keywords: catalysis; nanoparticles; noble metals; photoinitiator; photochemistry; plasmon.

INTRODUCTION

Research in nanomaterials in the last two decades has intensified and led to a wide range of organic and inorganic nanostructures, with rich current and future applications [1]. This contribution concentrates in recent work on metal nanostructures from our group at the University of Ottawa. Noble metal nanomaterials have a characteristic absorption band described as the surface plasmon resonance band (SPB), or simply the "plasmon band". For spherical nanoparticles of Au, Ag, and Cu the SPB absorption falls in the visible region of the spectrum and is responsible for the characteristic color of these materials in colloidal suspensions [2]. Metal nanoparticles can be prepared from metal salts by thermal or photo-

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[‡]Corresponding author

chemical methods, or directly from metallic substrates; in the latter case, the synthesis frequently involves ablation of the bulk metal [3,4]. In the case of Au nanoparticles (AuNPs), reduction with citrate or sodium borohydride is quite common [5,6]. Our group focuses on metal nanoparticle synthesis using photochemical methods [7–13].

The SPB can be described as the collective oscillations of conduction band electrons following variations of the electric field vector of the incident beam; such a description, while correct, fails to provide any insights as to how a chemist could find potential applications for the interesting phenomena underlying SPB transitions. Figure 1 illustrates some of the processes that can be triggered by photo-excitation in the SPB region; these processes can in turn be an integral part of photoinitiated catalytic processes. In order to successfully direct plasmon processes to implement the different pathways in Fig. 1, it is essential to be able to synthesize, modify, and derivatize metal nanoparticles. The first sections of this contribution outline methodologies for photochemical nanoparticle synthesis in a systematic manner, controlling nanoparticle size, shape, surface reactivity, and environment, such as solvent or support materials.



Fig. 1 Different processes that can be initiated by excitation of metal nanoparticles in their SPB absorption.

Figure 2 shows typical SPB spectra for colloidal aqueous noble metal nanoparticles. The spectra are extracted from data in earlier contributions; in the case of CuNPs the signals before normalization were weaker than for AuNPs and AgNPs, and as a consequence scattering effects are more important (and appear as a drifting baseline). Details of the synthesis are available in the original contributions [9,10,12].

Photochemical synthesis of metal nanoparticles can be performed in a variety of ways, but this paper concentrates on those developed in our laboratory, that make use of photogenerated ketyl radicals and/or α -aminoalkyl radicals as reducing agents.



Fig. 2 Normalized absorption spectra for aqueous noble metal nanoparticles. The boxes above each spectrum identify the metal, and also provide the common range for spectral maxima for monomeric spherical nanoparticles in each case.

PHOTOCHEMICAL SYNTHESIS OF METAL NANOPARTICLES

Many syntheses of metal nanoparticles are mediated by reducing free radicals, whether or not these are identified mediators in the process. Among reducing free radicals, ketyl radicals and α -aminoalkyl radicals are easy to prepare photochemically, and many precursors are available, since these molecules are frequently employed as free radical initiators for polymerization or as photocuring agents. The two photoinitiators most widely used by us are Irgacure-2959TM (I-2959) and Irgacure-907TM (I-907), both shown in Scheme 1, along with their photocleavage reaction via the Norrish Type I reaction [14].



Scheme 1 Photoinitiators I-2959 and I-907, along with their Norrish Type I photoreaction.

While we initially assumed that the benzoyl radicals of Scheme 1 did not play a significant role, recent experiments show that air oxidation of these radicals yield the corresponding carboxylic acids, and these contribute to the stabilization of aqueous nanoparticles prepared by these methods. While α -aminoalkyl radicals are potent reducing agents [15,16], more so than ketyl radicals, we have generally preferred the latter as reductors, largely because their precursors (e.g., I-2959) are not reducing agents until they undergo photocleavage; in contrast, one can anticipate that free amines (e.g., the morpholino group in I-907) will be able to reduce some ions, even if some of these processes may be quite

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slow. There is also a need for metal nanoparticles that do not contain nitrogen or sulfur stabilizers [17], another reason to favor I-2959. As a result, we have generally used I-2959, and substituted for I-907 when the former proved to be a sluggish reducer.

The chemistry that follows the generation of radicals is simple and well understood, and is illustrated in Scheme 2 for the ketyl radical systems. It should be noted that other ketyl radicals show comparable behavior to that illustrated here [8]. The rate constant k_3 , approaches diffusion-controlled kinetics ($k_3 \ge 10^9 \text{ M}^{-1} \text{ s}^{-1}$) in aqueous solvents [8,13], but there are indications the process is slower in nonpolar organic solvents.

$$\rightarrow OH + M^{n+} \xrightarrow{k_3} \rightarrow O + H^+ + M^{(n-1)+}$$
 (3)

$$M^{(n-1)+} \xrightarrow{\text{reduce}} M^{(n-2)+} \xrightarrow{\text{reduce}} \longrightarrow M^{0}$$
(4)

 $m M^0 \rightarrow \rightarrow \rightarrow MNP$ with m atoms (5)

$$2 M^{X+} \xrightarrow{k_6} M^{(X+1)+} + M^{(X-1)+}$$
(6)

Scheme 2 Reductive and disproportionation processes converting metal ions to atomic metals and from these to nanoparticles.

The simplest system from a mechanistic point of view is Ag. Given that the oxidation state changes from +1 to zero, only reactions 3 and 5 are relevant. In contrast, in the case of AuNP the ketyl radicals are involved in the reduction Au(III) \rightarrow Au(I) and Au(I) \rightarrow Au(0), but Au(II) is quite unstable and undergoes disproportionation (reaction 6), 2 Au(II) \rightarrow Au(III) + Au(I). In the case of Cu, Cu(I) undergoes a counter-ion dependent disproportionation, a process that controls the efficiency of the process and the polydispersity of resulting CuNPs [10].

We have observed in the past a wide range of reaction times in the photochemical synthesis of nanoparticles [8]. We have learned that the key factor controlling reaction times is the rapid quenching of excited states by noble metal ions [8,11,13]. For example, Au's common precursor, AuCl₄⁻, quenches the triplet state of azaxanthone in aqueous solution with a rate constant of $1.03 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [8]. The exceptional efficiency of I-2959 (nanoparticles in minutes at irradiance around 50 W m⁻²) is due to three factors: (i) excellent absorbance in the UVA region, (ii) high quantum yield of reaction ($\Phi = 0.29$), and a triplet lifetime of only 11 ns [18]. The last parameter is key to the excellent performance of I-2959; the fact that this initiator is also sufficiently soluble in a wide range of solvents, from water [9] to toluene [19], adds to its versatility.

While AuNPs prepared by the I-2959 method are stable for months to years in the absence of covalently bound stabilizers, it is important to note that both chloride anions (from $AuCl_4^-$) and organic byproducts are important contributors to AuNP stability. In the experiment of Fig. 3, an equal volume of ethyl acetate (upper phase) was added to aqueous AuNPs. The pink solution turned blue, suggesting surface changes and likely particle aggregation. The solution was manually stirred, and we arbitrarily refer to time zero (t = 0) to the moment stirring stops. Figure 3 shows still images extracted from a movie clip. After about 1 s the separation of the ethyl acetate phase is evident, while at the bottom one can see an almost colorless aqueous phase, with the nanoparticle-rich region in the center. The separation continues for about 10 s, and then approximately at 11 s the blue particles start to climb the tube



Fig. 3 Sample of aqueous AuNPs prepared from 0.33 mM $HAuCl_4$ and 1.0 mM I-2959 exposed to 40 W/m² UVA and treated with an equal volume of ethyl acetate. The sample is contained in a borosilicate glass tube, and the still frames were extracted from a 20 s video clip. See text for more details.

walls, a process that takes about 2 s to complete. The total climb exceeds 1.0 cm from the top of the ethyl acetate layer (see the last two frames). If viewed from the top (axially) the solution looks clear, so all the particles are on the glass surface. Adhesion is fairly reversible, and the overall process can be repeated by shaking the tube again. While we refrain from calling these particles "naked", it is clear that their surface exposure exceeds that of any other nanoparticles prepared by chemical methods.

The methods mentioned above for the synthesis of monometallic colloidal nanoparticles can also be adapted to the synthesis of alloys and core-shell particles [7], as well as supported particles, both employing solution- and solid-state methods. One of these approaches is presented later in this paper for AuNP-decorated nanodiamonds that were subjected to laser ablation.

The photoinitiator I-2959 has also proven versatile enough to allow for the solid-state synthesis of AuNPs on various supports, such as TiO_2 and alumina, suggesting that the ketyl radicals are sufficiently mobile to cause Au salt reduction even in solid systems, a characteristic that may be attractive from the perspective of green synthesis of supported catalysts. A photograph of the home-made set-up is shown in Fig. 4. This work will be published elsewhere.

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Fig. 4 Set-up used for the irradiation of solid samples contained in rotating vials, thus ensuring homogeneous exposure. The upper exposure panel has been lifted for display purposes, but is normally parallel to the hot dog cooker surface.

Beyond Au, Ag, and Cu

The examples provided in this section involve Co, Pt, and Ru, all metals with recognized catalytic properties. Most important, these examples illustrate the versatility of the photochemical strategies developed in our laboratory; these allow the synthesis of many nanostructures with only mild, noncovalent stabilizers that allow easy exchange and expose the metal surface for additional derivatization and/or catalytic applications.

Cobalt nanoparticles (CoNPs)

CoNPs are of particular interest because of their strong paramagnetism [20,21]; unfortunately, they are very unstable toward oxygen and aggregate readily at room temperature.

Based on the methods discussed above, I-907 was preferred to photochemically reduce Co^{2+} to CoNP. Irgacure-907 generates a strongly reducing α -aminoalkyl radical as shown in Scheme 1 and reduces $CoCl_2$ to form polydisperse CoNP in acetonitrile (Fig. 5). The black, insoluble particles are paramagnetic but upon exposure to air, they become gray/white and do not exhibit paramagnetic behavior (based on the same qualitative experiment).



Fig. 5 SEM image of CoNP formed after 20 min UVA exposure of 1 mM $CoCl_2$ and 2 mM I-907 in N₂-saturated acetonitrile. Following exposure, the particles were insoluble and were concentrated using a small magnet and resuspended. Inset: Picture of the insoluble CoNPs attracted to a small magnet being held outside of the glass test tube.

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Plasmon transitions

Platinum nanoparticles (PtNPs)

PtNPs have been less studied than AuNP and AgNP toward catalysis, but have shown to be effective in catalyzing reactions such as hydrogenation, alcohol oxidations, and carbon monoxide oxidation [22]. Photochemical synthesis of PtNPs was successful using K_2PtCl_6 (0.3 mM), with I-2959 (1.2 mM), and tetra-methyl ammonium bromide (TMABr, 0.2–1.1 mM) in water and irradiation with UVA light (ca. 70 W m⁻²) for 30 min, yielding a brown solution showing extensive light scattering at $\lambda < 700$ nm. Other stabilizers including CTAC and SDS show some nanoparticle formation, but not as effectively as TMABr. The PtNP are ~3.0 nm in diameter as seen by transmission electron microscopy (TEM), Fig. 6.



Fig. 6 TEM images of PtNPs made in the presence of 0.8 mM TMABr. Inset (top right); TEM at higher resolution than the main panel in the figure; Inset (bottom right): Absorption spectrum before and after irradiation of K_2 PtCl₆ with I-2959 and 1.1 mM TMABr.

Ruthenium nanoparticles (RuNPs)

Another metal in the noble metal group that has potential catalytic applications is Ru [23–25]. Contrary to other noble metals such as Au or Ag, Ru metallic nanoparticles do not display an SPB, probably due to their frequent very small diameter (<3 nm), providing very high surface area. Our photochemical approach offers the advantage of mild stabilizing agents, and thus renders the surface more available.

As mentioned earlier, I-2959 is usually favored for the photochemical reduction of salts. Ru is an example where I-907 has been preferred due to its stronger reducing ability. The Ru precursor, $RuCl_3$, is reduced in a similar fashion to Au with the α -aminoalkyl radical shown in Scheme 1. Depending on the subsequent environment required for catalytic applications, the Ru salt can be reduced readily in either acetonitrile or a water:ethanol (1:1) mixture, and results in monodispersed nanoparticles, below 2 nm diameter. The synthesis is accompanied by the bleaching of the characteristic 406 nm Ru(III) absorption, followed by the development of a scattering spectrum similar to that shown for PtNPs (see Fig. 6). These particles appear to be monomeric rather than the chain-like structures produced by other methods, such as poly(vinyl pyrrolidone) (PVP) reduction [24]. Figure 7 shows a high-resolution TEM image of these particles.



Fig. 7 High-resolution TEM image of RuNP prepared using I-907 as a radical source. The size bar is 5 nm.

CUSTOM MODIFICATION OF METAL NANOSTRUCTURES

Photochemical synthesis of nanoparticles with the methods presented yield particles in the 2–100 nm range such that size can be controlled by adjusting the conditions during synthesis [9], or by post-synthesis modification. This section presents some of the strategies that we are currently using in our laboratory to tune the properties of the nanoparticles. Not all these processes are initiated by light, but combined with photochemical techniques they provide a useful toolkit to control nanoparticle properties. No attempt has been made to be truly comprehensive; the examples provided here are simply vignettes of the strategies used in our laboratory.

Seeding of photochemically derived AuNPs

While much success has been established over the generation of AuNPs in the 2–15 nm range employing either NaBH₄, citrate or ketyl radicals as reducing agents [5,6,9], control over particle size and shape has frequently come at the expense of increased polydispersity for particles in the 20–80 nm size range, where a lack of uniformity of particle size decreases industrial appeal towards imaging, surfaceenhanced Raman spectroscopy (SERS), and drug delivery applications.

The unprotected nature of photochemically generated aqueous AuNPs has proven advantageous for the enlargement of AuNPs through seed-mediated growth. Addition of photochemically generated AuNPs to a dilute solution of the metal salt and mild reducing agent (growth solution) resulted in reduction of the metal salt via particle-mediated catalysis. The choice of mild reducing conditions is paramount to minimize the generation of new AuNPs, termed "secondary nucleation" [26]. Ascorbic acid has been a common choice in similar approaches as originally devised by Natan et al. [27] with citrate-mediated AuNP seeds.

We have examined the seed-mediated growth of photochemically derived AuNPs using hydroxylamine hydrochloride (NH₂OH·HCl) as a mild reducing agent using an approach previously developed for other reductants [27,28]. Control over size and rate of particle growth was achieved by controlled addition of variable amounts of 12 nm photogenerated AuNP seeds to growth solutions containing hydroxylamine hydrochloride and HAuCl₄⁻. An autocatalytic growth occurred, as characterized by an induction period and a signature sigmoidal growth curve where the rate of particle growth increased with increasing seed concentration. However, lower seed concentration led to much larger particles, with the expected red-shift of the SPB due to both size and presumably aggregation.

Because the particle surface itself is a site of reduction, the growth behavior is intuitive in that new layers of particles form faster when more reducing agent is present and the concentration of HAuCl₄ is held constant. Furthermore, larger particles are formed when lesser concentrations of seed are added, as indicated by a greater bathochromic shift and broadening of the SPB [29]. The broadening of the resonance band is also indicative of particle agglomeration, which is also confirmed by SEM. The average particle size for AuNPs prepared from 0.45 μ M Au⁰ measured 166.2 ± 44 nm, while particles prepared from 4.53 μ M Au⁰ were 36.4 ± 17 nm.

The unprotected surface of the Au particles, essentially stabilized with mildly associated chloride and 4-hydroxyethoxy benzoic acid, a photoproduct of the photoinitator I-2959 under ambient conditions, allows for rapid seed-mediated catalysis at the particle surface. Cognitive of various commercial AuNPs stabilized with numerous protecting ligands, the seed-mediated growth of AuNPs protected with different thiols was compared in the present study. We tested 16-mercaptohexadecanoic acid (MHDA) and mercaptothiazoline (MTHZ) [30], a smaller and hydrophilic thiol. In order to functionalize the photogenerated AuNPs, they were treated in the presence of $1.0 \,\mu$ M thiol for 16 h prior to incorporation to the growth solution. This approach (rather than using commercial nanoparticles) assures that all seeds originate from the same batch and have the same AuNP core. While addition of nonfunctionalized AuNP seeds to the growth solution resulted in the instant red coloration and growth of the SPB of AuNPs and enlargement of AuNPs as verified by SEM, the addition of thiol-functionalized seeds resulted in a very pale turbid blue/green color over the course of several minutes. The SEM imaging revealed the formation of irregular-shaped nano-snowflakes in the presence of various 12 nm AuNP seeds. These stunning results are shown in Fig. 8 and demonstrate the exceptional surface exposure of particles prepared from I-2959.



Fig. 8 Seed-mediated growth of AuNPs over time using 3.31 μ M Au⁰ (non-functionalized) prepared from I-2959 (\bigcirc), 1.0 mM MHDA (\Box), and 1.0 mM MTHZ (\triangle) functionalized AuNPs as seeds in the presence of 0.25 mM HAuCl₄, 0.4 mM NH₂OH–HCl.

Particle modification via LED exposure

In the case of AgNP we have reported [12] that when the I-2959 method is combined with citrate in situ treatment, it leads to very small AgNPs (~3 nm) that can be used as seeds (their spectrum has been included in Fig. 2). We find that it is possible to modify these seeds to produce a range of particle morphologies by simply irradiating the seeds with visible light from narrow-band light-emitting diode (LED). Morphology changes are accompanied by particle growth and changes in spectroscopic properties, effectively leading to a colorful gamut of nanoparticle samples; the spectra for two of these samples are shown in Fig. 9.



Fig. 9 Ag nanostructures from LED irradiation at 455 and 627 nm of citrate-stabilized seeds, as shown in Fig. 2 for AgNPs. Exposure at 455 nm leads to decahedra and 627 nm to triangular and hexagonal platelets.

We are frequently asked if the growth and morphology changes can be reversed. The next section provides an example where this is the case.

Particle modification via laser ablation

Laser ablation can be used in order to modify simple colloidal nanoparticles, or supported particles. In this method, a pulsed high-energy laser beam is concentrated, but not focused, on a small volume sample containing nanoparticles. Work in our laboratory frequently uses the *laser drop technique* [31,32], which allows high-intensity sample exposure, but avoids unnecessary exposure of already exposed samples. A typical drop is <10 μ l and receives energy doses \leq 50 mJ per drop. Below we provide two examples of laser ablation of nanoparticles. Some photographs are shown later in the section on alcohol oxidation.

Laser exposure of colloidal AgNPs

For many applications, the size of the nanoparticles needs to be reduced in order to gain contact surface (catalysis) or reach target molecules (bioapplications). For these purposes they have to be very small, and it is also desirable to have a uniform size distribution; i.e., it is frequently advantageous to have small, monodisperse nanoparticles. In the example presented here we submit aqueous AgNPs to laser exposure using the laser drop technique [31]. In this method, we generate drops of the nanoparticle solution $(8-10 \ \mu l)$ and irradiate them with a pulsed laser. Depending on the wavelength used we obtain different size distributions. In the case of spherical AgNPs with an SPB absorption at ~400 nm, irradiation at long wavelengths gives a monodisperse size distribution. Using 440 nm laser pulses we obtain sizes from 2 to 20 nm. If we utilize a laser pulse at 532 nm we obtain sizes from 5 to 7 nm, and if we

irradiate at 650 nm we obtain AgNPs from 4 to 7 nm. In all cases we expose each drop to 100 laser shots, collect the solution, and submit it to SEM.

Interestingly, laser ablation can also be used to reverse the growth and change in morphology achieved by LED irradiation, as those in Fig. 9. Figure 10 shows how triangular plates absorbing at long wavelengths can be reconverted to small, predominantly spherical AgNPs absorbing around 400 nm. Notice that the exact final spectrum depends on the laser wavelength employed for particle ablation.



Fig. 10 Initial triangular Ag platelets (dashed line and inset) lead to conventional AgNP when excited by laser pulses at 650 or 440 nm using the laser drop technique.

In the case of AuNPs, we have also achieved size reduction and a good uniformity. Irradiation of AuNPs with 8–25 nm diameter, leads, following 532 nm irradiation (near the maximum of the SPB) or at 650 nm, to AuNPs showing a distribution of sizes from 3 to 5 nm.

Exposure of nanodiamond-supported AuNPs

Nanocrystalline diamonds (NCDs) are a solid carbon-based material with various uses in modern technology due to their unique physical properties, such as thermal conductivity, hardness and inertness [33]. NCDs provide an excellent support for catalysts [34] and are well suited for biotechnological applications [35,36]. These nanomaterials are biocompatible and the surface can be easily functionalized with carboxyl or amino groups. Specifically, nanodiamonds have a large specific surface area that shows an exceptionally high affinity for proteins in aqueous solution after treatment with acid, a property that can also be exploited for metal nanoparticle applications [33,35,36].

NCDs with low-field electron emission properties are a promising candidate as a supporting material for Au-based catalysts. Reactivity of Au on diamond nanoparticles prepared as a highly efficient Fenton catalyst has been reported recently [34]. The Au from $HAuCl_4$ has been supported by the conventional deposition/precipitation method on Fenton-treated diamond nanoparticles followed by hydrogen reduction at 300 °C.

Here we report a facile photochemical synthesis by reduction of $HAuCl_4$ in deionized water by using I-2959 as photoreducing agent, and mixing with 350-nm diamond particles. Upon UVA irradiation (15 min), the light yellow milky solution of $HAuCl_4$ with diamonds gradually turned into milky red solution. From the TEM images, the nucleation of Au nanocrystals on the diamond surface can be clearly seen; the average size of the Au particles on the diamond surface is about 10–20 nm (Fig. 11A). The total Au content loading in the final Au-diamond catalyst was about 2.5 wt %. Any excess of free AuNP and I-2959 was removed by performing centrifugation–redispersion cycles.

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Fig. 11 TEM images (JEOL JEM-2100F) showing the effect of laser ablation (532 nm) on aqueous AuNPdecorated nanodiamonds. Panels A and C before ablation and panels B and D after ablation using the laser drop technique. Top panels, at lower magnification (scale bar is 100 nm), show the actual NCD before and after exposure, while the lower panels (scale bar is 10 nm) show details of the fragmentation of the AuNPs.

The morphologies and microstructures of Au on diamond before and after 532 nm laser ablation are shown in Fig. 11. The average size of AuNPs on diamond decreased after laser excitation (\leq 5 nm) (Figs. 11B,D).

Previous studies have demonstrated that the formation of nanoparticles under laser irradiation of a metal target immersed into a liquid proceeds via local melting of the metal [37]. Electron–phonon coupling leads to a transfer of the electronic excess energy into lattice heat. As a result of thermal equilibration between electrons and the lattice, the heat is released to the surrounding environment, and finally, the ejected fragments and atoms form particles with the stabilizer/capping agents on their surface [37].

In summary, the laser drop ablation results suggest that Au and other metallic atoms and fragments can be ejected in solution forming new particles or can be relocated and coordinated onto the support surface, and our laser drop ablation in liquid media is an alternative, efficient technique to fine-tune metallic nanoparticle size.

APPLICATIONS OF METAL NANOSTRUCTURES

Figure 1 shows some of the areas of application of nanomaterials that possess a SPB absorption; a few that are currently explored in our group are outlined below. Beyond photochemical applications that involve SPB excitation, the materials discussed above offer numerous opportunities for catalysis (e.g., involving C–H bonds [38]) and for diagnostics and treatments [39].

Plasmon-mediated enhanced triplet-state formation

When light interacts with nanomaterials that have a SPB transition, the nanostructure can behave as an antenna (sometimes described as a lightning rod [40]) that concentrates the electromagnetic waves in the vicinity of the surface and can induce excitation enhancements in surrounding molecules [41,42]. For instance, photophysical properties of a molecule in the proximity of a metallic nanoparticle surface could be modified by SPB interactions undergoing transmitter/antenna effects [41,43]. Thus, a molecule near a nanoparticle surface can behave as a receiver (the nanoparticle being the transmitter), while the excited state of the same molecule is a transmitter with the nanoparticle as the receiver (see right section in Fig. 1). Excited molecules at contact or near-contact distances from the surface are quenched efficiently by the surface, and only those a bit further (typically 2–20 nm) benefit from plasmon enhancement [41,44].

In our laboratory we have examined the AuNP-methylene blue (MB) system [45]. In this system the relevant excited state is the triplet state of MB that can be readily detected using laser-flash photolysis (LFP) techniques. When examining the quenching of MB triplet by AuNP we measured an apparent rate constant of 6.4×10^{13} M⁻¹ s⁻¹ [45]. This rate is 3–4 orders of magnitude faster than expected even for a diffusion-controlled process [14].

We observed that the anomalous kinetics were accompanied by a 2.2-fold higher enhancement in MB triplet quantum yield in the presence of AuNP (\approx 1.2 nM) upon 650-nm laser excitation (see Fig. 12). This enhancement has been attributed to an antenna effect, which favors excitation of MB molecules near AuNP, i.e., a rich concentration of excited triplets is formed in the proximity of the AuNPs. Those located in a "pseudo" MB monolayer at the metallic surface are completely quenched. Thus, this "excited MB transient shell" is spatially set up for antenna-like enhancement effects, but once formed, it is also the subject of effective quenching and an anomalous quenching rate constant of 6.4 × 10¹³ M⁻¹ s⁻¹ was determined. Zeta potential measurements of AuNPs in the presence of different AuNP/MB ratios showed that AuNPs became essentially neutral as a result of electrostatic interaction of MB with the AuNP surface.



Fig. 12 Plasmon effects on excited states. The top trace shows the distance dependence of excitation for molecules at different distances from the surface. At contact distances we observe quenching, rather than enhancement, represented by a black line in the bottom part of the figure. The enhancement region (in graded gray) fades as the distance increases. Bottom right: transient LFP signal from MB triplet showing enhancement, but also a fast decay. Note that the apparent horizontal line is in fact a decay that occurs in the microsecond time scale.

The plasmonic effect with larger AuNPs is currently being explored. Preliminary results suggest that bigger AuNP sizes provoke higher antenna effect. Figure 12 shows in schematic form the quenching and enhancement effects in the vicinity of the AuNPs.

Applications of SPB to heat conversion (photothermal processes)

The fact that excitation of metal nanoparticles in their SPB can lead to thermal processes on their surface is well established [46,47]. We were intrigued by the magnitude of the effect, frequently described as "extreme heat". We wondered what temperature a molecule placed at the surface of a nanoparticle actually "feels" (as opposed to the temperature effects within the nanostructure [48]). For this purpose we decided to select a molecule that could be our reporter, in other words, a molecule that effectively could act as an in situ thermometer. This molecule was dicumyl peroxide, which upon thermolysis yields cumyloxy radicals [49,50] that abstract hydrogen to yield the alcohol; the reaction is illustrated in Fig. 12. The results suggest that the peroxide is exposed to temperatures of ~500 °C for submicrosecond times [51]; thus, plasmon transitions provide the means to carry high-energy reactions at room temperature.

Catalytic oxidation of citrate and diverging AgNP growth

Small "seed" metal nanoparticles can be used as nucleation sites on which to grow larger particles. Often, however, this seeded growth has two competing processes; (1) addition of reduced metal atoms to the seed particles as desired or (2) new nucleation of nanoparticles from reduced metal atoms and clusters. New nucleation is a problematic side effect of seeded growth when the common goal is to generate monodispersed sizes of larger particles since new nucleation during the growth process inevitably results in polydispersity [26]. A new, plasmon-mediated approach to photochemical seeded growth and generation of larger AgNPs is attempted here. The idea is to excite the SPB of AgNP seeds and cause reduction of the nanoparticle seeds instead of metal salt. The metal seeds then grow by the addition of positively charged metal salt to the reduced seeds as shown in Scheme 4. Maillard et al. [52] claim that the excitation of metal nanoparticles with citrate results in citrate reduction of the particles, but this speculation was not previously confirmed.

To test this mechanism, a solution of ~3.3 nm AgNP and 2.7 mL of H₂O was placed in two cells of an oxygen uptake apparatus, as previously described [53]. Various amounts of a solution containing 5 mM AgNO₃ and sodium citrate (as indicated in Fig. 13) were injected to both cells prior to irradiation. One cell (the reference) was covered with aluminum foil, while the other sample was irradiated with 400 nm light from an LED. The change in pressure with respect to the reference sample is recorded with the oxygen uptake apparatus and can be correlated (after calibration) with a volume and/or molarity of gas produced. The pressure increase is monitored in time until a plateau as shown in Fig. 13 below. Upon addition of various quantities of trisodium citrate and AgNO₃, the increase in pressure upon irradiation is shown. The initial rapid increase in pressure is due to an increase in temperature when the LED turns on presumably due to heating of the AgNPs, while the following linear increase in pressure is due to gas produced. From Scheme 3, the CO₂ produced can be correlated with the oxidation of citrate. It is important to note that there is no increase in pressure when the LED is off, and also that the 400 nm LED is chosen to selectively excite the AgNP SPB and not the reducing agent (citrate) that absorbs only in the UV region. We note that quantitative analysis shows that the amount of gas produced correlates with either citrate or $AgNO_3$ added, whichever is the limiting reagent. Therefore, both reagents are needed for citrate to reduce the AgNPs and Ag⁺ to add in the growth mechanism in Scheme 4.



Fig. 13 (left) Pressure change over irradiation time of samples of AgNP after adding 50, 100, and 200 μ L of 5 mM AgNO₃/citrate; (right) UV–vis absorption spectra of solutions of AgNP seeds after 100 μ L additions of 5 mM AgNO₃/citrate and 400 nm LED exposure.



Scheme 3 The thermal decomposition of dicumyl peroxide leads to cumyl alcohol in the presence of small concentrations of methanol and was used to estimate the surface temperature of AuNPs excited in the SPB.



Scheme 4 Citrate reduction for plasmon-mediated growth of AgNPs.

The plasmon absorption after successive additions of $AgNO_3$ and citrate was also recorded using a CARY 100 UV–vis spectrophotometer. One can see from Fig. 13 that the plasmon absorption increases systematically after each irradiation. This increase in absorption and red-shift of the SPB is consistent with the addition of Ag and the formation of larger AgNP [12,54,55]. This process can be repeated by rediluting the particle solutions and reusing them as seeds for new citrate/AgNO₃ growth solutions.

Plasmon-mediated catalytic oxidation of alcohols

The plasmonic transitions of AuNPs provide the opportunity to exploit these materials as potential photocatalysts for a variety of simple, organic reactions through both photocatalytic and photothermal reactions. Specifically, alcohol oxidations are of interest due to the importance of this process in the manufacturing industry of paints and various synthetic materials [56,57]. Currently in our group, AuNP-assisted benzylic alcohol oxidations are being investigated through the use of the aforementioned laser drop technique. Irradiation of a solution containing 12 nM AuNPs, 0.55 M benzyl alcohol, and 0.77 M H_2O_2 with 532 nm laser pulses results in a distinct color change of the AuNP solution from pink to violet and increasingly efficient conversion to benzaldehyde with the number of laser shots incident on the sample drop (Fig. 14). Following 100 laser shots per drop, the percent conversion of the alcohol to the aldehyde was observed; however, formation of benzaldehyde is negligible in the absence of AuNPs, indicating that nanoscale Au is required for the oxidation to occur.



Fig. 14 Plot illustrating the effect of the number of laser shots/drop on the oxidation of benzyl alcohol to benzaldehyde (% conversion) as determined by HPLC-UV spectroscopy. Inset shows the drops of AuNP solution before and after 532 nm laser excitation. While not visible in the B/W version, the color changes from pink to violet upon laser excitation. Note additional bubbles after excitation.

Optimizing SERS

The use of Raman spectroscopy as an analytical tool has been hindered since its discovery due to inherently low intensity signals. Metal nanoparticles have more recently been used to enhance Raman signals of analytes on the surface of the particles predominantly through an electromagnetic field (EM) enhancement provided by the particles. However, the size and shape of AgNPs can have a dramatic effect on the overall intensity of the Raman spectrum. In recent work, we have controlled the size of AgNPs between 20–70 nm and determined an optimal size of AgNPs for enhancing the Raman spectrum of rhodamine 6G (R6G) [58]. Theoretically, as particle size increases, there is a subsequent increase in the EM field around the particles, and it is this increase in EM field that results in stronger Raman signals for molecules bound to larger particles. However, due to a decrease in overall surface area as well as an increase in inelastic scattering with increasing particle size. It was found that the optimal size of AgNPs for detecting R6G is approximately 50 nm and that this result should be transferable to other analytes studied under similar experimental conditions (off resonance excitation with a 785-nm laser).

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CONCLUSION

Photochemistry is a powerful tool for the synthesis and modification of nanomaterials. Plasmon excitation, as shown in Scheme 1, offers new ways of tuning size and morphology, and to trigger new reactions, through the various pathways shown. As illustrated above, these materials also become useful as catalysts for reactions that may or may not require light.

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