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High-Temperature Organic Reactions at Room Temperature Using Plasmon Excitation: Decomposition of Dicumyl Peroxide

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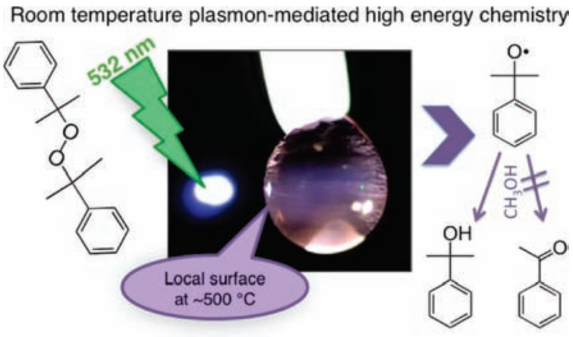
ABSTRACT



Photoexcitation of gold nanoparticles in their plasmon transition around 530 nm provides the means to carry high-energy reactions at room temperature. In the case of dicumyl peroxide (with activation energy of 34.3 kcal/mol) the reaction occurs in less than 1 min under 532 nm laser excitation. The results suggest that the peroxide is exposed to temperatures of ~500 °C for submicrosecond times, and provides a guide as to which type of organic reactions may benefit from plasmon-mediated energy delivery.

Nanoparticles of several metals, in particular gold, silver, and copper, present plasmon absorptions in the visible region of the spectrum.[1] In the case of spherical gold nanoparticles (AuNP) this absorption is around 530 nm. Excitation in the surface plasmon band (SPB) can be viewed as a collective motion of electrons that result in transient polarization of the particle. The energy associated with this phenomenon can be harvested in a variety of ways, including electronic excitation of nearby molecules[2,3] in a process sometimes described as undergoing transmitter/receiver antenna interactions.[3,4] In another example excitation provides an efficient conversion of light-to-heat that can then transfer energy to the microenvironment directly around nanoparticles.[5] Key pathways are illustrated in Figure 1, where pathway **Tc** corresponds to

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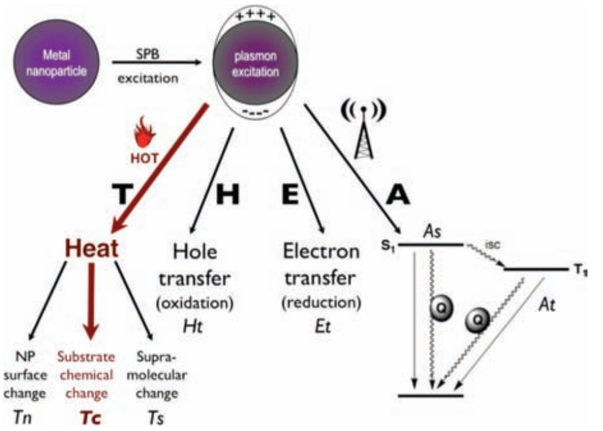
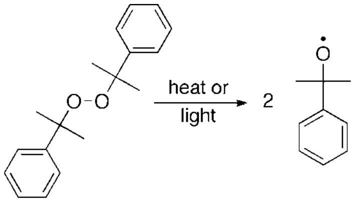


Figure 1. Plasmon excitation leads to a range of effects on molecules adsorbed, bound, or in proximity to a nanoparticle, as well as changes in the nanoparticle itself. In the presence of a suitable receiver, antenna effects (**A**) can result in excited state processes (**As** and **At**). Plasmon relaxation can lead to thermal effects (**T**) that can themselves induce supramolecular changes in guest molecules (**Ts**), chemical change (**Tc**) sometimes referred to as photocatalysis, or changes in the nanoparticle itself (**Tn**) of either a physical or chemical nature (e.g., oxidation). Under plasmon excitation the nanoparticle can act as an electron donor (**Et**) or as an electron acceptor (**Ht**). Color arrows are used for mechanism **Tc**, the one explored in this paper.

the process examined in this communication, in other words, triggering thermal chemical reactions through SPB excitation.

The reaction that we use to probe SPB photocatalysis is the decomposition of dicumyl peroxide (DCP), illustrated in reaction 1, that can be triggered thermally or photochemically; in the latter case the reaction requires ultraviolet irradiation.



(1)

Reaction 1 is quite endothermic, requiring heating at >140 °C for hours for decomposition to occur. The activation energy for thermal decomposition can be estimated as 34.3 kcal/mol (see the Supporting Information), and corresponds to the bond dissociation energy (BDE) for the peroxide bond.

Our choice of reaction may seem unusual, but in fact we wanted a system that, while well understood, challenged the limits of plasmon photothermal effects in order to evaluate to what extent plasmon methodologies can become an effective tool to perform high-energy organic reactions at near-ambient temperatures.

Several examples that take advantage of plasmon-induced photothermal effects have been established in systems that because of favorable thermodynamics, or strong (e.g., covalent) surface attachment[5] find favorable conditions for SPB catalysis. Aldeman et al. have also observed decomposition of ethanol in water−ethanol mixtures.[6] A recent publication reports a temperature of 330 °C under plasmon irradiation (and much higher when CO oxidation occurs). Plasmon heating therapeutic applications have recently been reviewed.[7]

In this paper we combine laser excitation of the AuNP SPB with the laser-drop technique developed in our laboratory[8] to study photothermal effects in the plasmon-mediated decomposition of DCP.

Gold nanoparticles were prepared photochemically and their surface was largely unprotected;[9,10] their shape was mainly spherical and their diameter 12.7 nm, showing a SPB absorption at 530 nm (see the Supporting Information). The synthesis was carried out in water typically obtaining 1 nM concentration of nanoparticles. Laser excitation was performed with the frequency doubled 532 nm (∼8 ns) pulses from a Nd/YAG laser; the beam was concentrated, but not focused on the sample drops. Focused laser pulses readily lead to drop explosions and prevent the multiple laser pulse exposures required for low conversion reactions. Typical doses were 50 mJ/pulse. This common laser wavelength is particularly well suited for spherical AuNP that absorb around 530 nm.

The laser-drop system consisted of a computer-controlled syringe pump that delivered the sample to the exposure region through a Teflon needle with an external diameter of 1.6 mm (used as a ruler to measure the drop size). The volume delivered and the number of laser pulses per drop (delivered at 1 Hz) was programmable. The irradiated drops were collected in a cuvette and analyzed by HPLC using a reverse phase C18 zorbax column eluted with 80:20 acetonitrile/water. The only products from DCP detected were 2-phenyl-2-propanol and acetophenone, along with small peaks derived from Irgacure-2959, the benzoin initiator used in the synthesis of AuNP.[10] The drop volumes (typically 7 μL) were calculated based on the drop photographs (see Figure 2), approximating the drops as spherical.

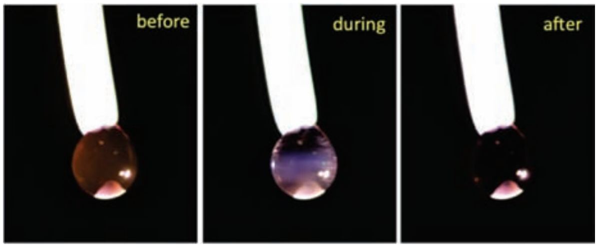
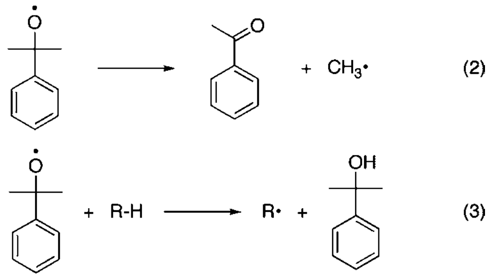


Figure 2. Laser drop pictures before, during, and a few milliseconds after 532 nm laser excitation. Note a slight blueish tint during excitation. A 532 nm notch filter was used in front of the camera lens, to make it "blind" to the green laser beam and to prevent camera damage.

The drop images were captured with a Nikon D90 DSLR camera, equipped with a Sigma 105 mm *f*2.8 macro lens, controlled by the laser-drop system. Figure 2 illustrates drops photographed before, during, and a few milliseconds after excitation. The drops remained clear during these experiments.

The products 2-phenyl-2-propanol and acetophenone are anticipated from a competition of the reactions in Scheme 1.

Scheme 1. Reactions of Cumyl Radicals



In an alternate mechanism, one could propose electron transfer from AuNP to the peroxide to give RO$^•$ + RO$^-$ (R = cumyl); if this was the case the maximum yield of acetophenone (reaction 2) would be 50%. However, in the absence of hydrogen donors (e.g., methanol, see below) the acetophenone:cumyl alcohol ratio is as high as 97:3, ruling out electron transfer as the dominant mechanism.

The change of color noted during excitation persists for milliseconds, but its blue tint is not present after the experiment. These red shifts are usually attributed to changes in surface molecules and/or aggregation.

To verify if the effect observed was a true photothermal effect, we also exposed the solutions of DCP with and without AuNP to microwave (MW) irradiation. No reaction was observed after 20 min at 80 °C with a MW power of 300 W with no AuNP and 47% conversion with AuNP. This confirms that we are not simply observing bulk heating of the solution; gold is also a good microwave absorber and prolonged heating under these conditions does lead to some conversion. Note that in the case of the laser excitation, the conversion after 25 s (25 equal laser shots) exceeds that obtained after 20 min of microwave irradiation.

As another method of photoexcitation, we repeated the experiment using a custom-designed LED irradiator consisting of four LedEngin 10 W LZ4-40G110 emitters (λ_{exc} 530 nm, see the SI). The data obtained with this method are compared with MW in Figure 3. Despite the lower LED intensity compared with the laser, we still obtain 21% conversion after 1 h of irradiation with AuNP. LED sources may offer an inexpensive alternative to lasers and microwaves for organic reactions.

Reaction 1 is clearly possible, yet inefficient under SPB-mediated photolysis, and may thus provide an idea of the limitations of this methodology. A particularly interesting aspect relates to the actual temperatures that can be achieved on the surface of the AuNP.

The calculation of eqs 4 and 5, where C_p corresponds to the heat capacity of water and ~1.0 g/mL is its density, leads to a bulk heating of 1.7 K for a 50 mJ laser pulse (2.2 × 10^{-7} einstein) and a 7 μL drop, even if the light was totally absorbed (vide infra). The calculation assumes an adiabatic drop, something that is probably a good approximation for a single laser pulse, but not for the experiment lasting minutes (at 1 Hz, as many seconds as laser pulses). Given the stability of DCP under microwave conditions, bulk heating of the drops cannot explain the chemistry observed.

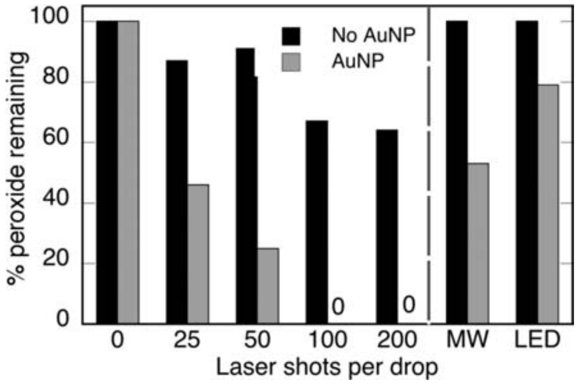


Figure 3. Graph of conversion vs number of shots per drop for 1 mM of dicumyl peroxide in H_2O with 5% of MeOH irradiated with a 532 nm laser with different number of shots per drop. The power of the laser used is 50 mJ/shot. In all cases the black bar is the control experiment with no AuNP. The right panel in the graph shows the results using a microwave (300 W, 20 min) and a 530 nm set of LED (4 × 15 W, 35 °C, 60 min).

$$\Delta T\ (\text{K}) = \frac{\text{energy (J)}}{C_p\ (\text{J/g K}) \times \text{mass (g)}} \tag{4}$$

$$\Delta T\ (\text{K}) = \frac{0.05J}{4.2\ (\text{J/g K}) \times 0.007\ \text{mL} \times 1.0\ \text{g/mM}} \cong 1.7\ \text{K} \tag{5}$$

In another extreme case, we assumed that during the 8 ns laser pulse the AuNP themselves behave as adiabatic units that in this time do not exchange heat with surrounding molecules; this treatment resembles an ideal gas of nanoparticles. A typical 7 μL drop may contain 10^{-7} g of gold ($C_p = 0.129$ J/g K). Thus, a similar calculation as eq 4 leads to $\Delta T > 10^6$ K, clearly not realistic. Even taking into account incomplete light absorption (absorbance ~0.05 in the drop diameter, but enhanced by internal reflections), ΔT values are in the 10^6 K range. The melting point of nanoparticles is lower than that of the bulk material.[11] For bulk gold its melting point is 1337K, while for the particles used here it is probably around 1200K.[11] Laser excitation of AuNP can lead to surface changes, suggesting that temperatures near the AuNP melting point are achievable. Combining these

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observations and calculations one can estimate that high temperatures, but below 1200 K can be achieved.

Another approach to understanding the achievable temperatures is to base the estimate on the actual chemical changes taking place; perhaps somewhat empirical, knowledge of what temperature a molecule "*feels*" is useful for organic chemistry applications. For reaction 1 values of the Arrhenius parameters of $E_a = 34.3$ kcal/mol and a pre-exponential factor of $4.7 \times 10^{14}\ \mathrm{s}^{-1}$ ($\log A = 14.67$) can be calculated from the reported kinetic data.[12] With these values on hand, simple application of the Arrhenius equation gives the rate constants as a function of temperature, Figure 4.

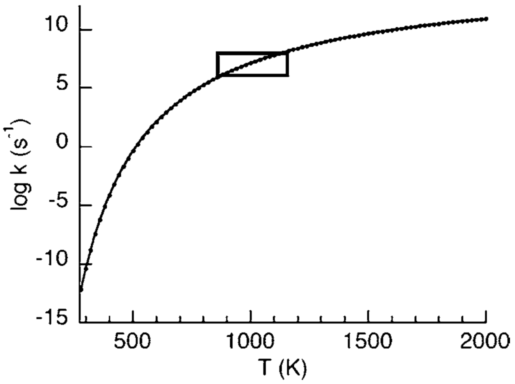

Figure 4. Calculated rate constant for reaction 1 at various temperatures, based on $E_a = 34.25$ kcal/mol and $\log A = 14.67$. The rectangle shows the range of temperatures where the lifetime of DCP would be between 10 ns and 1 μs.

We know that 100% conversion is achieved in ca. 75 shots (Figure 3), giving the per-laser-pulse conversion as 1.3%. We can now calculate the rate constant and from it the temperature if we know the duration of the SPB heating. Assuming that plasmon effects last 100 ns in the AuNP surrounding organic layer, we have:

$$\log \frac{c_0}{c} = \log \frac{100}{98.7} = 0.0057 = kt = k \times 10^{-7}\ \mathrm{s} \quad (6)$$

leading to $k \approx 57\,000\ \mathrm{s}^{-1}$ and a temperature (see Figure 4 and eq 7) of 760 K.

$$\log (57000) = 14.67 - \frac{34250}{2.3 \times R \times T} \Rightarrow T \approx 760\ \mathrm{K} \quad (7)$$

For the 10 ns to 1 μs range the temperatures required for 1.3% conversion per shot fall in the 680 to 830 K range. We note that reported time-resolved studies indicate energy release from the nanoparticle occurs in <1 ns;[13] however, these studies analyze the particle heat release, but not the behavior of the surrounding organic layer (bound or solvent) that is key to any substrate chemical changes. The actual time is unlikely to be shorter than the laser pulse itself, since irradiation continues for that period, or longer than 1 μs, since early heat exchange with the bulk solvent must be fast. Of course, the temperature itself is a time-dependent parameter and the value estimated should be treated as a "nominal" temperature, i.e., *chemical changes happen as if the temperature was between 680 and 830 K*. Note also that the data was treated as if all DCP molecules had a chance of exposure to plasmon fields, but this is likely an approximation. Reducing the DCP fraction exposed to the AuNP would lead to even higher ΔT values.

We note also that in experiments with 5% and 0.5% methanol, the only product was 2-phenyl-2-propanol; in fact the only condition under which acetophenone was detected was when no hydrogen donor was added. Reaction 2 has an activation energy of only 8.6 kcal/mol,[14] i.e., much lower than that for peroxide decomposition. The fact that α-cleavage does not compete with the hydrogen abstraction of reaction 3 ($\mathrm{R{-}H} = \mathrm{CH_3OH}$), even when only 0.5% methanol is present, suggests that the cumyloxyl radicals are for all practical purposes already thermalized, essentially at ambient temperature. This emphasizes the short duration of the plasmon temperature jump experienced by molecules at or near the particle surface, with several hundred degrees difference for the reagents and the products of reaction 1.

Thus, we conclude that for molecules that are not covalently bound to the AuNP surface, plasmon-assisted photothermal effects are likely to operate for unimolecular processes with activation energies below 40 kcal/mol. Achievable nominal temperatures are in the 500 ± 100 °C range for submicrosecond times. These are the first temperatures estimated for plasmon effects in organic chemistry[15] and can serve as a rough guide to select organic reactions worth screening under conditions of plasmon-mediated energy delivery. We note that LED irradiation provides a very inexpensive alternative to laser and even microwave techniques.

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Supporting Information Available: Spectroscopic, kinetic, and imaging data. This material is available free of charge via the Internet at http://pubs.acs.org.

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