Plasmon-Mediated Catalytic Oxidation of sec-Phenethyl and Benzyl Alcohols

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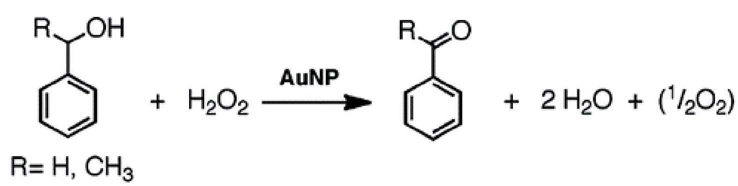

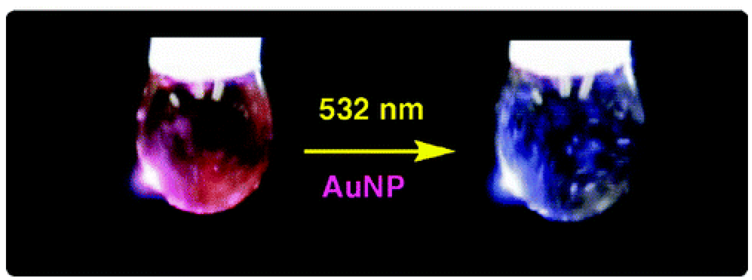

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M S Bootharaju
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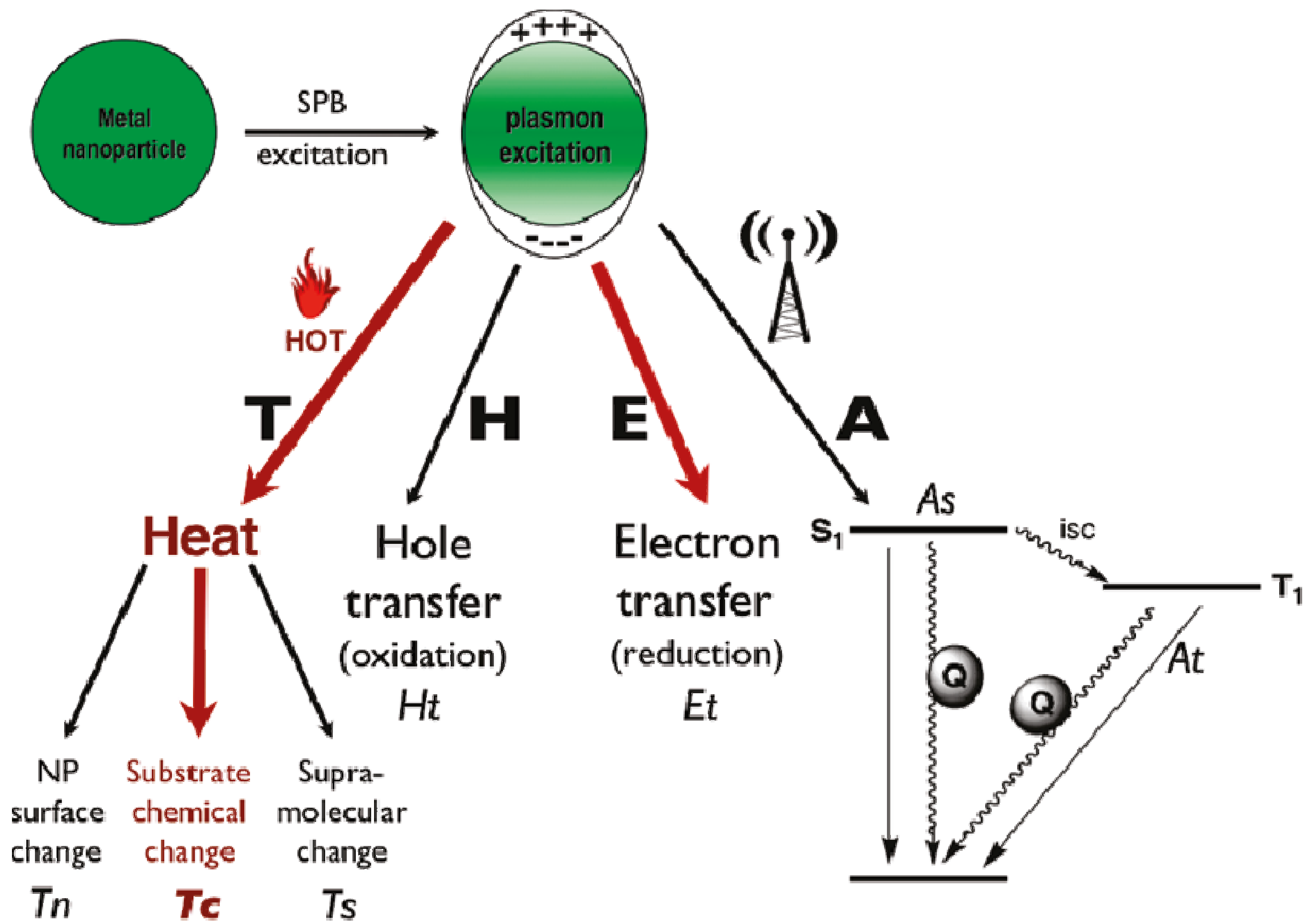
Introduction

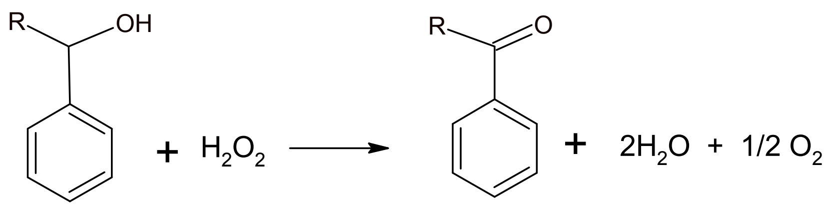
1. Alcohol oxidation products are important in industrial materials like perfumes, paints, and plastics.
2. Conventional methods using chromates and permanganates are environmentally unfriendly and they are toxic too.
3. In most recent people started to use greener oxidants such as hydrogen peroxide for oxidation of aromatic alcohols in aqueous media in place of organic solvents.
4. Gold nanoparticles (AuNP) have been proven to oxidize a variety of organic alcohols in the absence of harsh chemicals or reaction conditions .
5. The excitation of AuNP to produce chemical transformations in nearby molecules is described as plasmon-mediated catalysis (PMC).
6. Local surface temperature can cause chemical transformations at ambient conditions which may occur at higher temperatures.

7. The induced electromagnetic field formed upon absorption of visible light by the AuNP plasmon can also be used to exploit the photochemical activity of metal nanoparticles.

8. Direct excitation of metal nanoparticles is thought to favor ejection of electrons, crucial when considering AuNP as participants in a variety of photoinitiated electron transfer pathways.



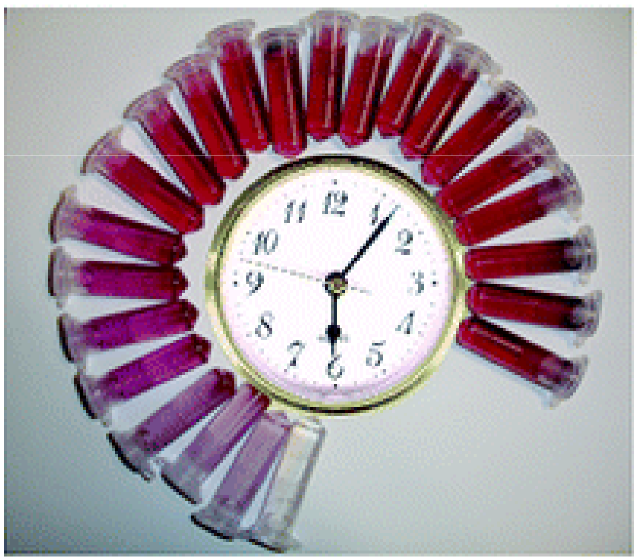
Experimental

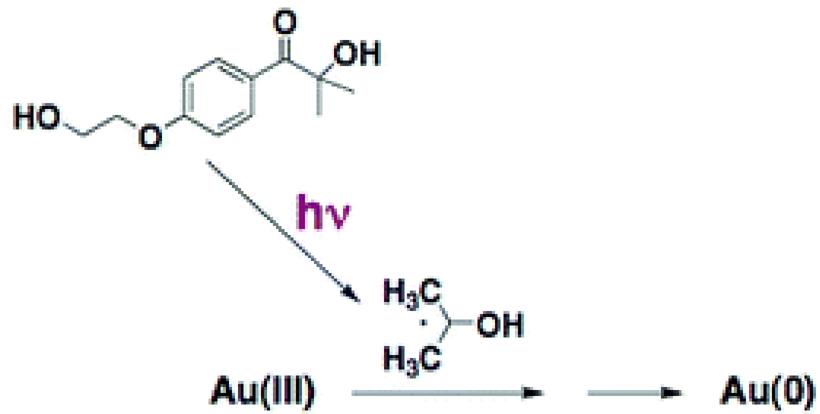


Synthesis and Characterization of AuNP

1 mL NP + 99 µL sec-phenethyl

+ 50 µL 50% H_2O_2





McGilvray, K. L.; Decan, M. R.; Wang, D.; Scaiano, J. C. *J. Am. Chem. Soc.* **2006**, *128*, 15980.

Results

Laser Drop Technique

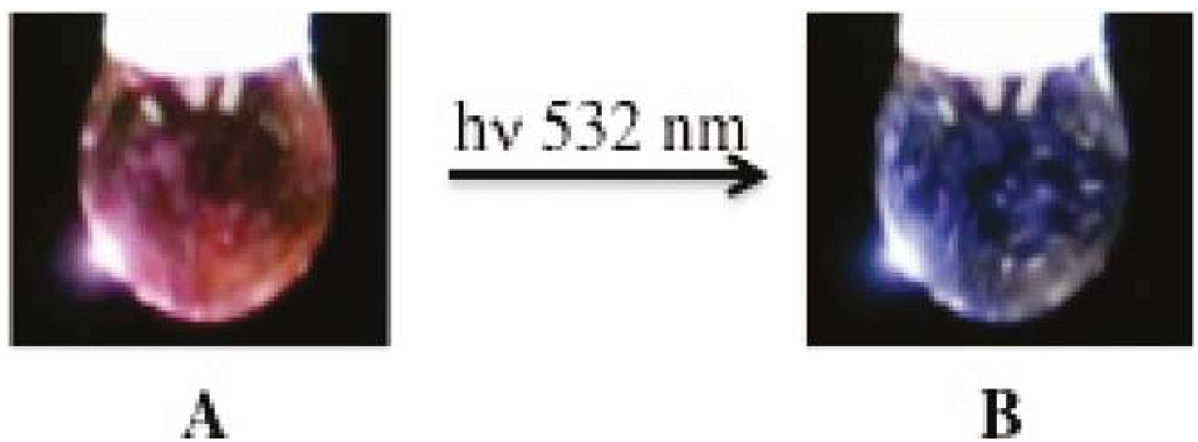
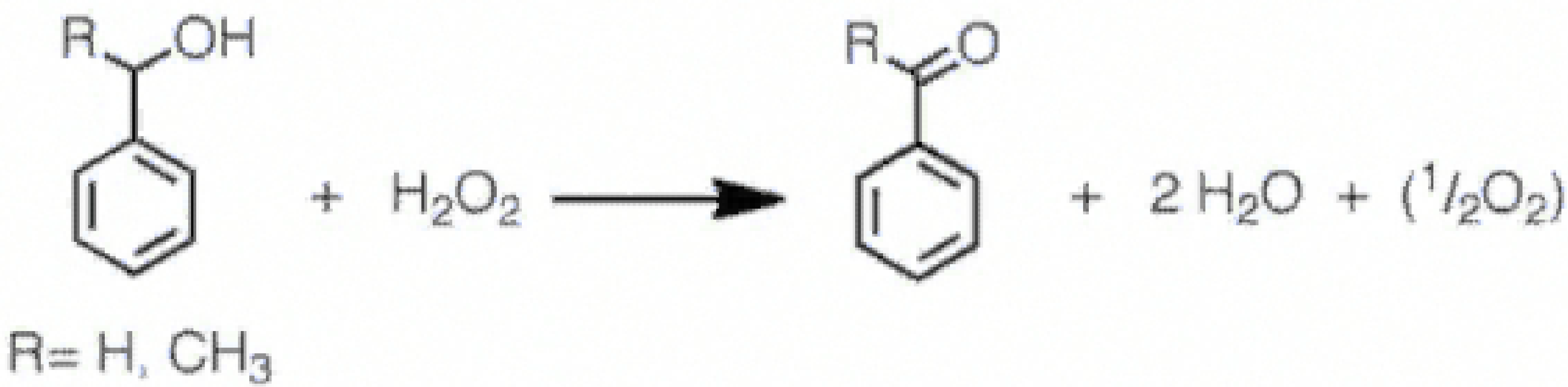


Figure. Color of the laser drop sample before (A) and after (B) a single pulse of 532 nm laser excitation. Note the distinct color change from pink to violet following laser exposure.

Oxidation of alcohols by H_2O_2 catalyzed by gold nanoparticles



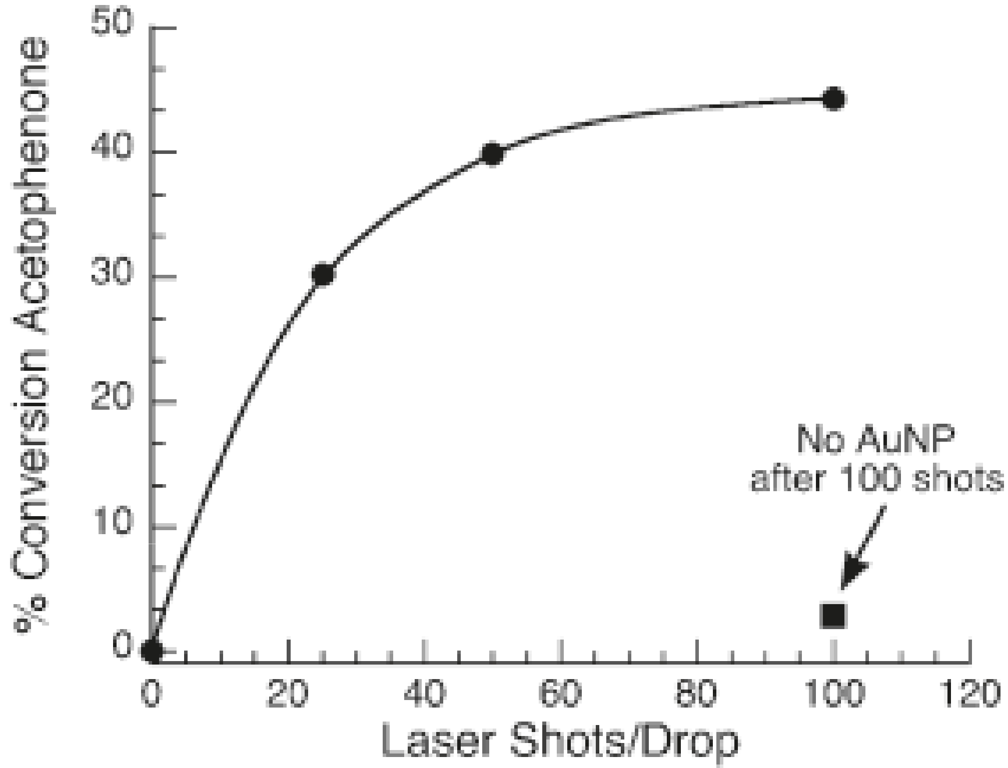


Figure. Acetophenone percent conversion as a function of laser dose (HPLC $\lambda_{monitor}$ = 245 nm).

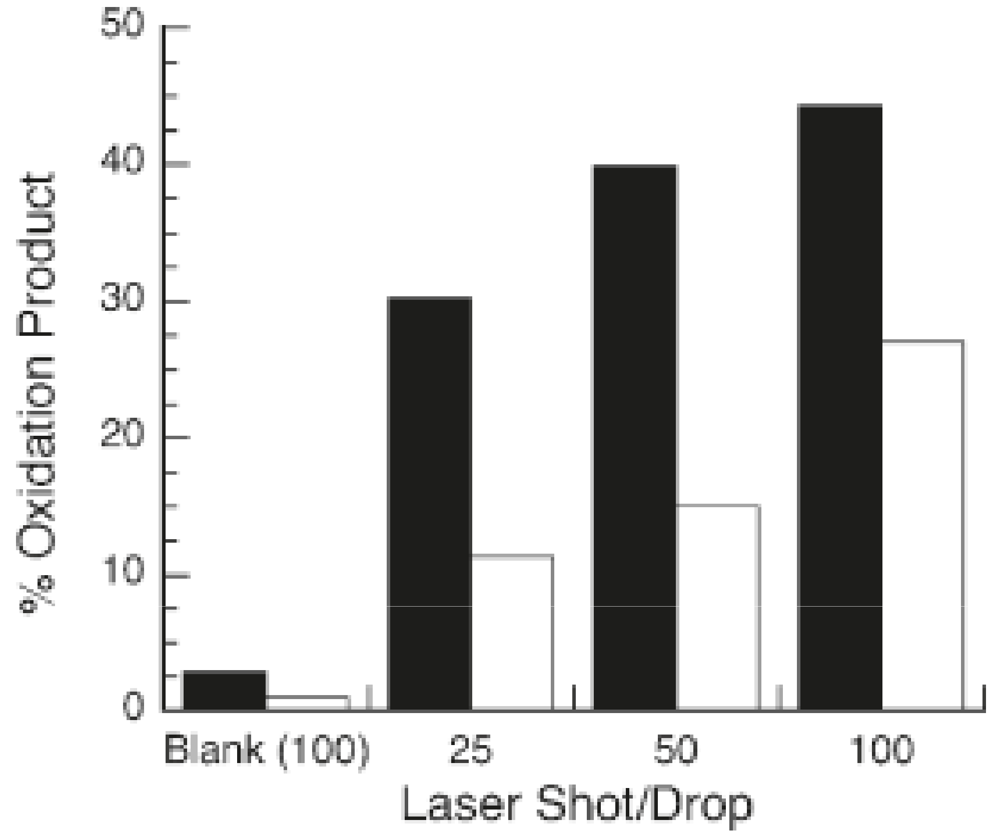


Figure. Bar graph illustrating the percent conversion to benzaldehyde (open) as compared to the percent conversion to acetophenone (solid) following 532 nm laser drop excitation in the presence of AuNP. In the absence of AuNP, minimal conversion to either oxidation product was observed.

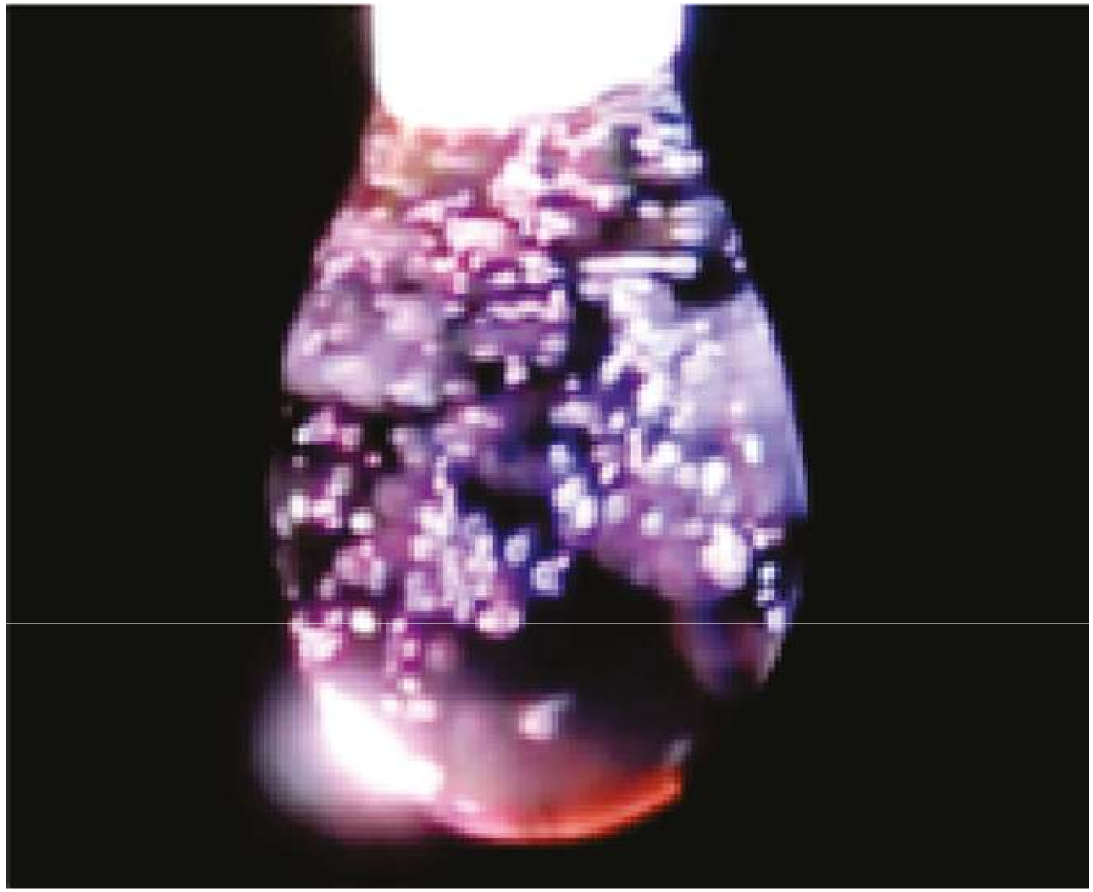


Figure. Still shot of the drop taken at the end of 532 excitation of secphenethyl alcohol, H_2O_2, and 13 nM AuNP (from a movie clip). Note how the bottom of the drop is slightly pink in color due to back flow of the original solution.

LED Photoexcitation at 530 nm

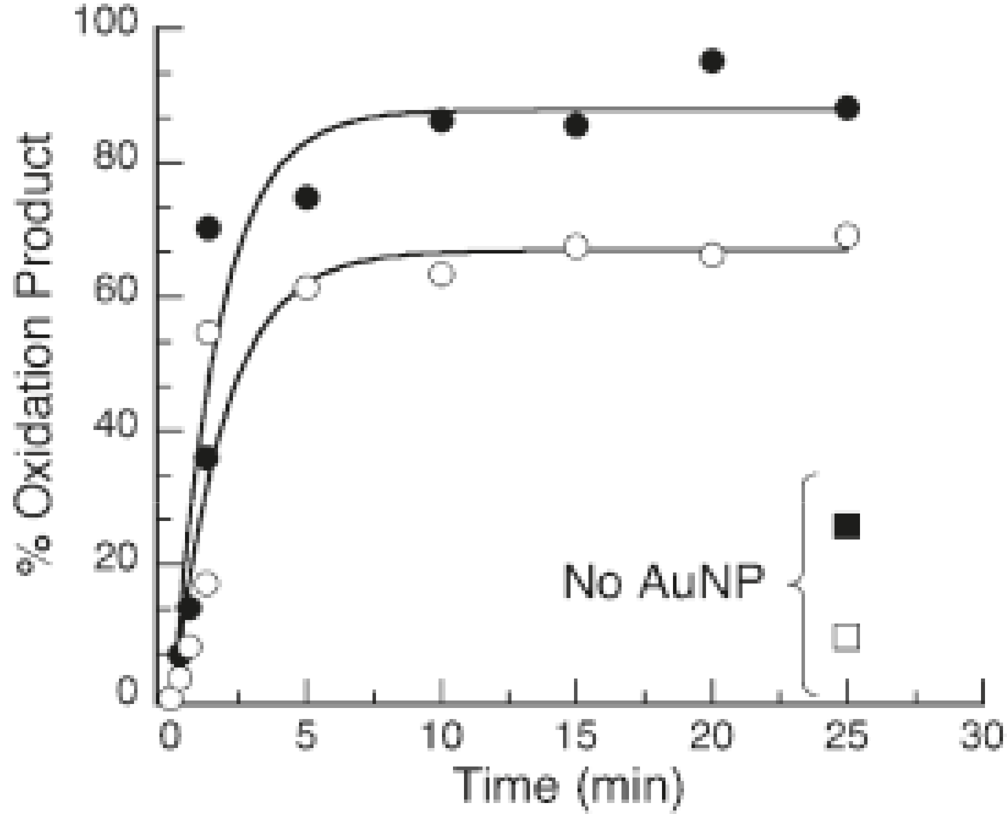


Figure. Acetophenone (●) ($\lambda_{monitor}$ = 245 nm) and benzaldehyde (O) ($\lambda_{monitor}$ = 250 nm) conversion as a function of LED photoexcitation time. Note the reduced conversion to acetophenone (■) and benzaldehyde (□) in the absence of AuNP.

Table 1. Summary of the Percent Conversions of sec-Phenethyl and Benzyl Alcohol Obtained Using Laser, LED, and Microwave Irradiation

Method	sec-phenethyl alcohol % conversion[a]	benzyl alcohol % conversion[b]
LD 100 shots/drop	44.3	27.0
LD blank (100 shots/drop)	2.8	1.0
LED 100 s	70.2	54.6
LED 20 min	95.2	66.3
LED blank (25 min)	25.7	9.1
microwave 1 min	81.7	18.4
microwave 10 min	98.2	31.5
microwave blank (10 min)	2.8	2.8

[a] Conversion to acetophenone. [b] Conversion to benzaldehyde

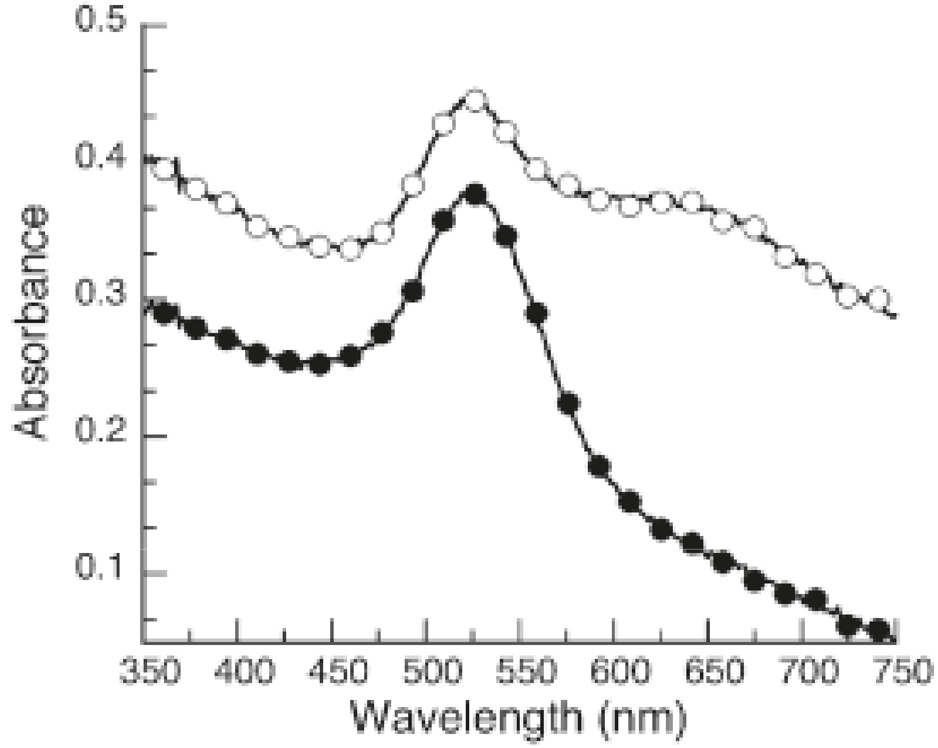


Figure. UV-vis spectra taken before (●) and after (O) 532 nm laser excitation of sec-phenethyl alcohol, H_2O_2, and 13 nM AuNP.

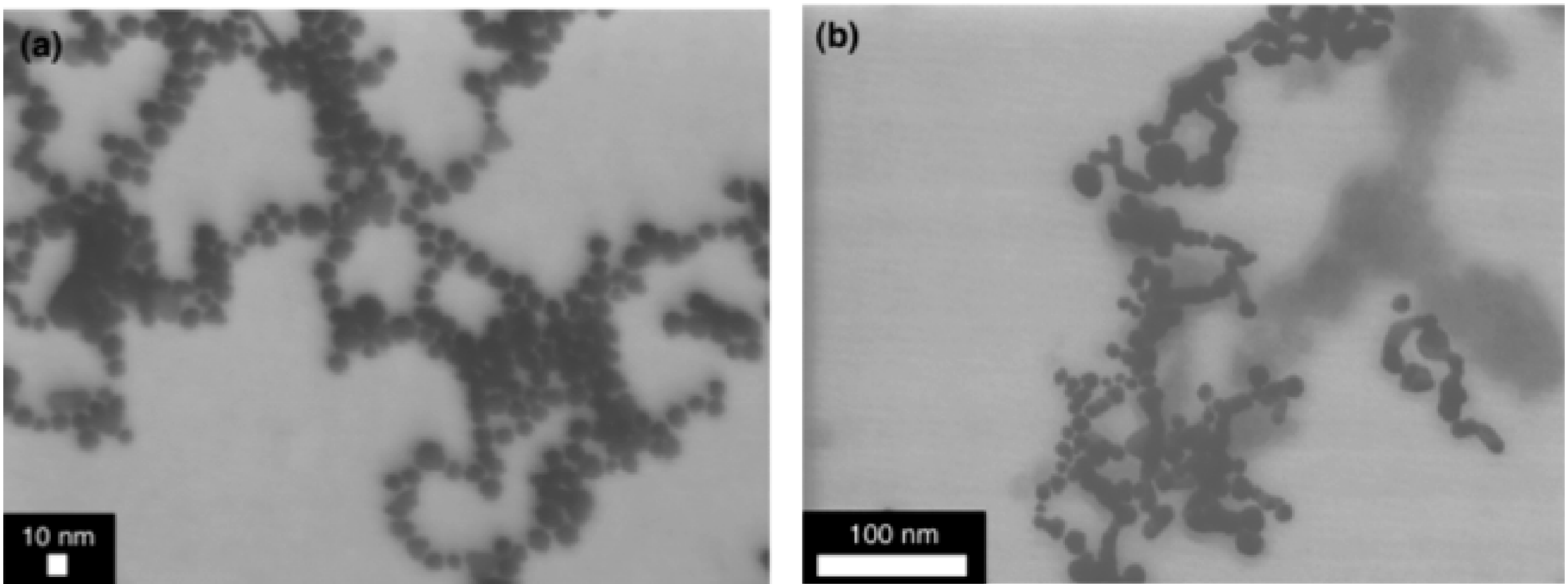


Figure. SEM images of 13 nM AuNP (a) before and (b) after 532 nm laser excitation in the presence of sec-phenethyl alcohol and H_2O_2.

Discussion

1. Oxidation of alcohols is achieved and it is enhanced in the presence of NP.
2. Physical change, interparticle distance decrease.
3. Sufficient number of particles are there in solution.
4. Reason for reduced interparticle distance.
5. Gas evolution.
6. $OH^{\bullet}$ radical formation.

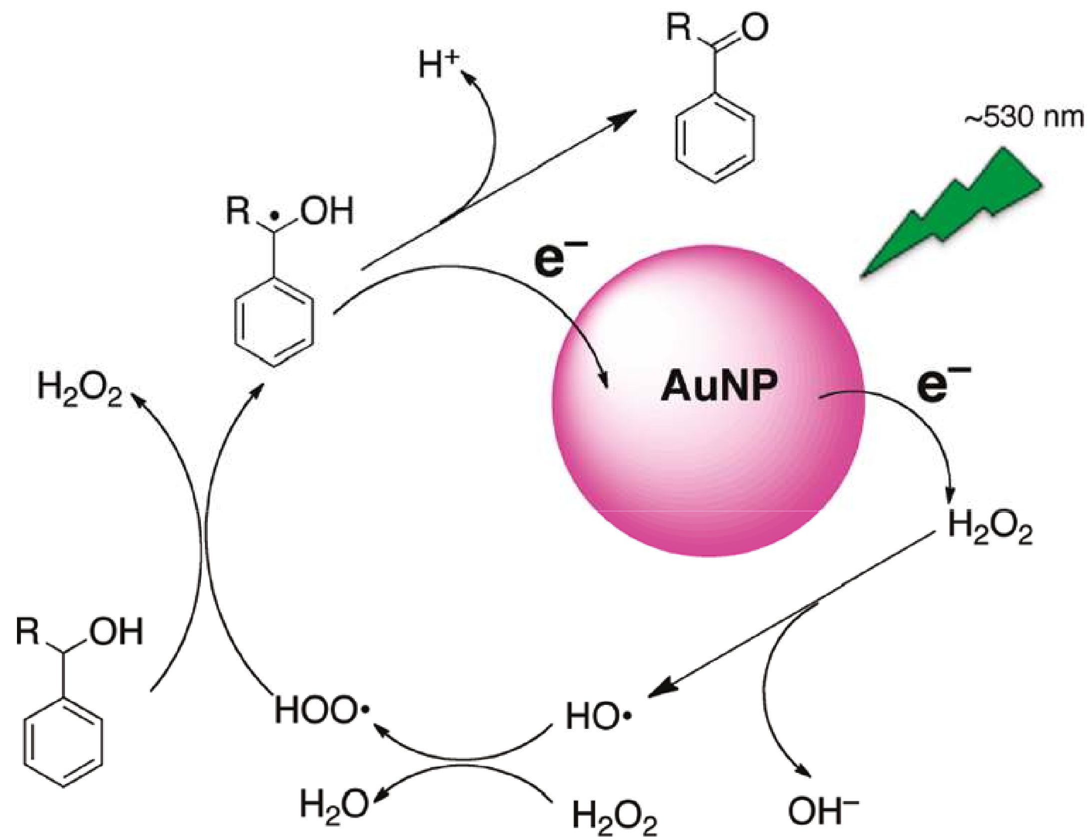


Figure. Proposed mechanism for the plasmon-mediated oxidation of sec-phenethyl alcohol ($R = CH_3$) and benzyl alcohol (R = H) by AuNP.

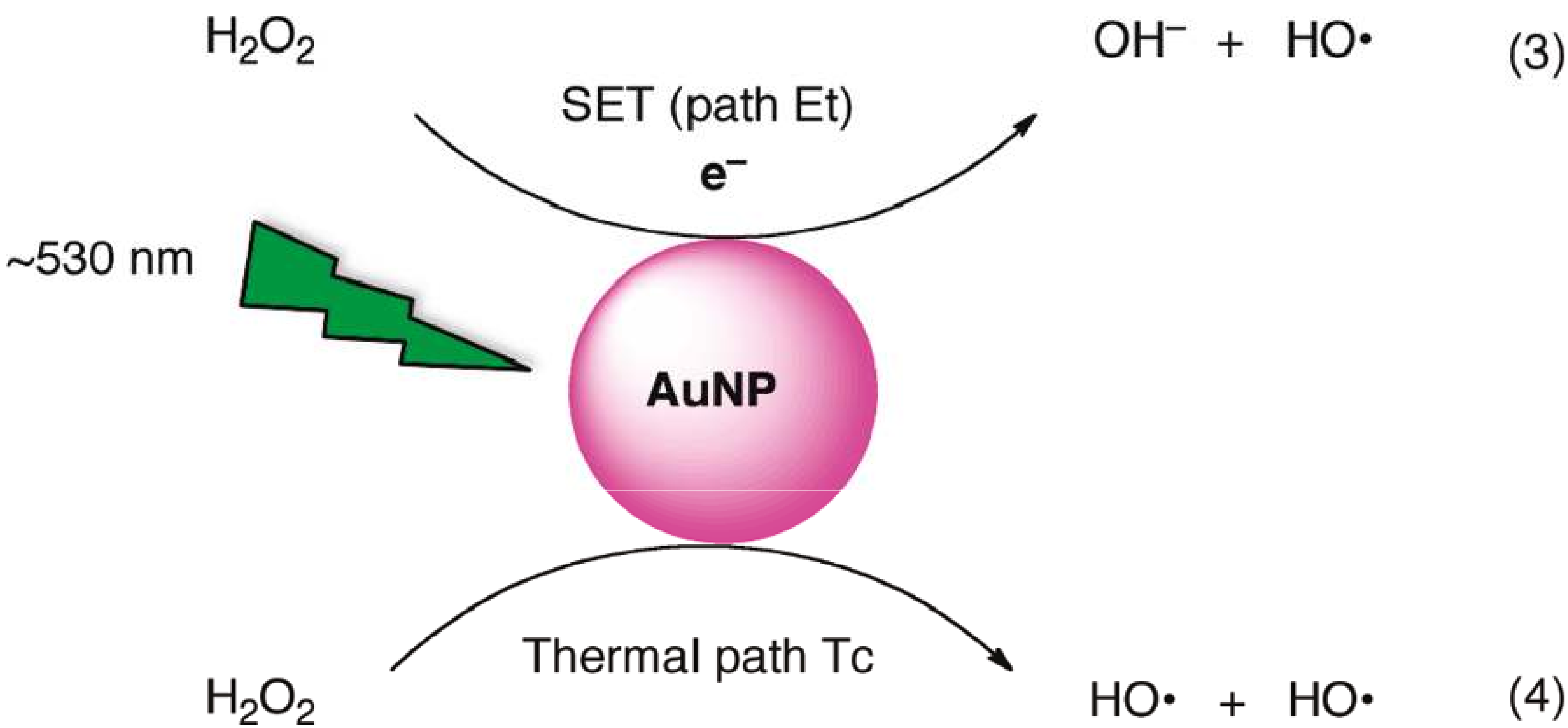


Figure. Possible reaction pathways for the plasmon-mediated photoinitiation reactions leading to hydroxyl radicals. The paths indicated for reactions 3 and 4 correspond to the same labels used in Figure 1.

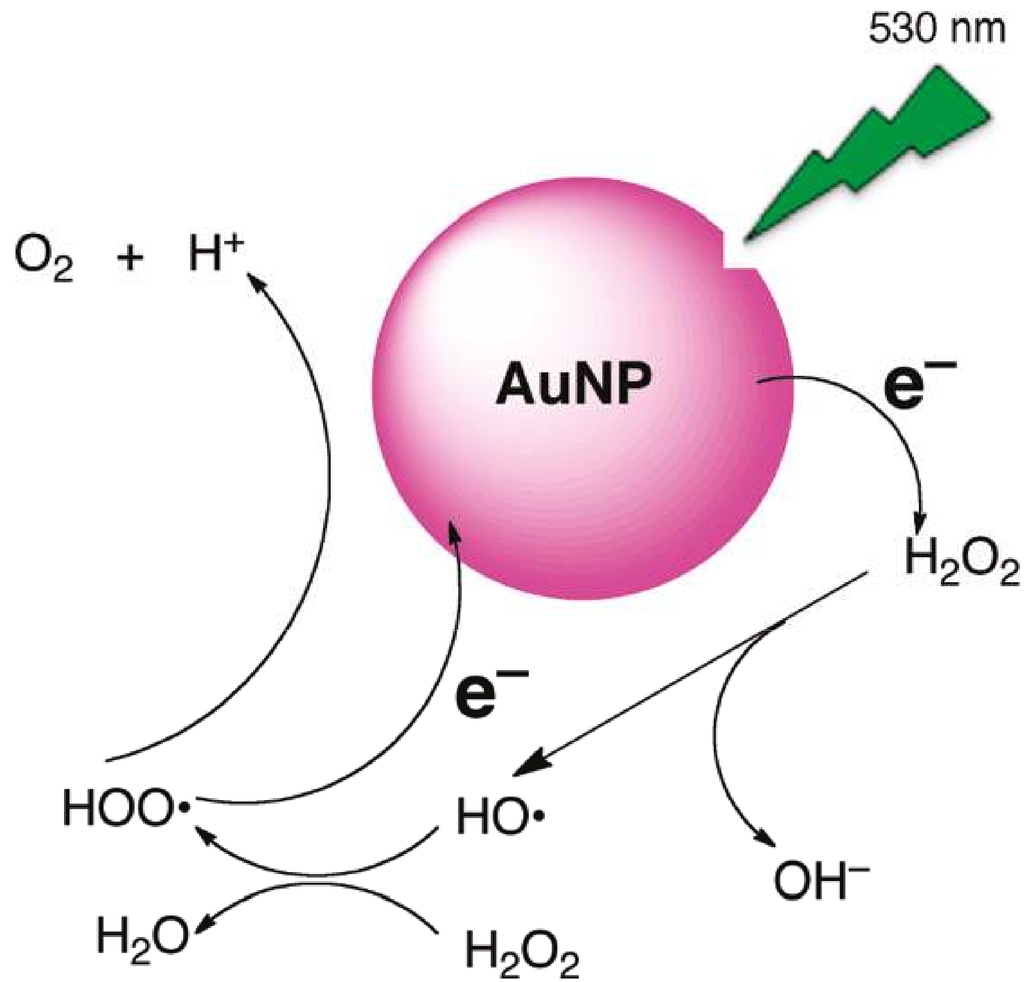


Figure. Photocatalytic degradation of H_2O_2 mediated by AuNP and photoinitiated by plasmon band excitation.

Conclusions

• Sec-phenethyl alcohol conversion was calculated to be 95% in 20 min when monochromatic 530 nm LEDs were used.

• The mechanism for plasmon-mediated AuNP alcohol oxidations was discussed in detail and is proposed to involve both photochemical and photothermal components.

• The reaction proceeds through the formation of peroxyl, ketyl radicals as intermediates.

• O_2(g) is evolved through both photothermal and photocatalytic decomposition of excess H_2O_2 present in the reaction mixture.

Thank you

Future plan

Application of new silver and gold quantum clusters in the catalysis of

Organic named reactions, rearrangements, photochemical reactions, etc.