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Nanocatalysts by Quantum Electrodynamics Induced Electromagnetic Radiation

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Abstract: Gold has been regarded as a poor heterogeneous catalyst because it is generally considered a nonreactive metal. But as nanocatalysts, gold and other metals somehow significantly enhance reactivity. It is generally thought chemical bonds of reactants are weakened by adsorption to nanocatalysts thereby allowing reactions to proceed more rapidly, but how this reaction proceeds to completion is not well understood. Here gold nanocatalysts are treated as unsupported nanoparticles (NPs) in a solution of reactant molecules from which extensions are made to gold NPs supported on titanium dioxide. Whether the NPs are supported or unsupported, enhanced catalytic reactivity depends on absorbed thermal kT (k is Boltzmann's constant and T is absolute temperature) energy accumulated from prior collisions of reactant molecules. The accumulated kT energy is treated as electromagnetic thereby allowing frequency up-conversion by quantum electrodynamics (QED) to the confinement frequency of the NP, typically beyond the vacuum ultraviolet (VUV). By this theory, the chemical reaction of reactant molecules having bonds weakened by adsorption is completed by QED induced VUV photolysis.

Key words: nanocatalyst; nanoparticle; gold; quantum electrodynamics

Density functional theory (DFT) has now well established that nanocatalysts comprising metal nanoparticles (NPs) provide an interface whereby adsorption of reactant molecules decreases dissociation barriers to allow chemical reactions to proceed more rapidly [1]. Indeed, gold NPs deposited on select metal oxides have recently been found to be very reactive for the removal of offensive odor from gases while improving electrochemical reactions in aqueous media [2]. More recently, gold NPs in catalyzed hydrocarbon oxidation have been attributed to free radical mechanisms [3] while in luminol-hydrogen peroxide solutions have been shown to enhance chemiluminescence [4]. However, gold NPs are not unique among nanocatalysts. The oxidation of tetralin in the liquid phase is found to increase and saturate with the number of vanadium atoms in the NP heteropolyanion [5].

However, DFT only explains how bond weakening depends on the adsorption of reactants. No guidance is offered as to the source of electromagnetic (EM) energy necessary to complete the bond breaking and initiate the chemical reaction.

In this paper, the EM energy necessary to initiate chemical reaction is QED induced EM radiation finding basis in quantum mechanics (QM) by the EM confinement of kT energy accumulated in collisions of reactant molecules with supported or unsupported NPs, the accumulated kT energy frequency up-converted by QED to VUV levels.

NPs under molecular collisions find similarity with quantum dots (QDs) under near infrared (NIR) laser radiation in that both NPs and QDs absorb EM radiation [6]. In QDs, NIR laser radiation is absorbed; whereas, in NPs the kT energy at far infrared (FIR) frequencies is absorbed by molecular collisions. Like the QDs, the NPs are absent specific heat and therefore cannot conserve the accumulated kT energy by an increase in temperature. Conservation may only proceed by the NPs inducing the accumulated kT energy to undergo frequency up-conversion to the EM confinement frequency of the NP, typically beyond VUV frequencies.

Consider an unsupported NP having kT energy accumulated from prior collisions of reactant molecules A and B that by QED is induced to undergo frequency up-conversion to VUV levels. Subsequently, A and B molecules react to form AB by VUV photolysis as depicted in Fig. 1.
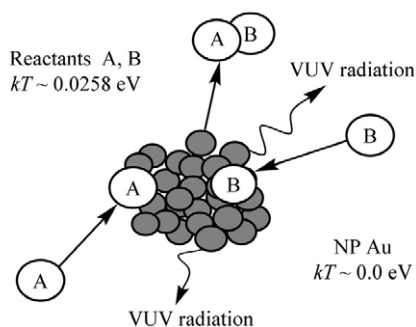
Similar to photo-assisted nanocatalysts, the reactant A and B molecules upon adsorption are excited by the VUV radiation induced within the NP to promptly initiate the chemical reaction [7],

$$A + B + h\nu \rightarrow AB \tag{1}$$

Fig. 1. Catalysis of A and B reactants by unsupported NP under QED induced EM radiation.

where, h is Planck's constant and v is the frequency of the EM confinement. By this theory, the QED induced VUV radiation in the NPs provides the EM energy necessary beyond bond weakening by adsorption necessary for the chemical reaction to form the product AB.

It is important to note the EM confinement frequency of the NP excited by FIR radiation from collisions of reactant molecules is not that of plasmon lattice vibrations at microwave frequencies. Instead, the quasi-bound Mie resonant radial mode is excited at VUV frequencies having sufficient Planck energy to activate adsorbed oxygen molecules [8], and if not leaks the VUV to the surroundings to excite other reactant molecules in solution.

Under EM confinement, QED restricts the kT energy of the NP atoms to vanishing small levels; whereas, the colliding reactant A and B molecules absent EM confinement have full kT energy of 0.0258 eV. This may be understood by the Einstein-Hopf relation [9] for the harmonic oscillator at 300 K shown in Fig. 2.

Typically, NPs as nanocatalysts have diameters $D < 50$ nm and EM confinement wavelengths $\lambda < 200$ nm [2]. Fig. 2 shows at ~5 microns, $kT = 10^{-5}$ eV, and therefore at $\lambda < 200$ nm, $kT \ll$
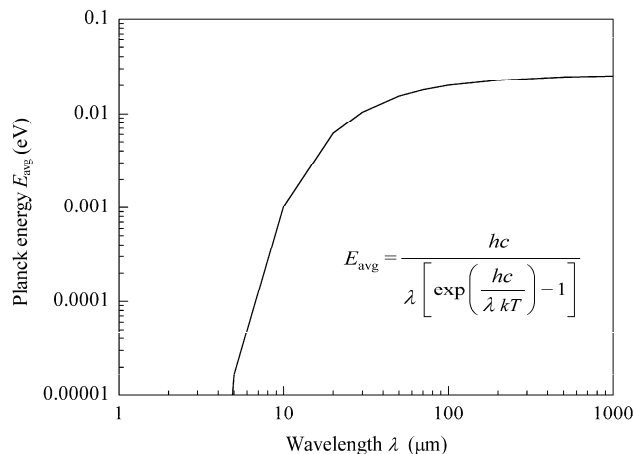
Fig. 2. Harmonic oscillator at 300 K. In the inset formula, c is the speed of light, and λ is wavelength.

10^{-5} eV. Hence, kT vanishes for NP atoms; whereas, colliding reactant molecules A and B not under EM confinement have full kT energy in the FIR, say for $\lambda > 100$ microns in Fig. 2.

Since A and B molecules are small in relation to the NPs, collisions transfer full kT energy to the NPs. However, the absence of specific heat forbids the kT energy to be conserved by an increase in temperature, and therefore conservation proceeds by the accumulation of Planck energy at the EM confinement frequency of the NP. For nanocatalysts having NP diameters $D < 50$ nm, the Planck energy exceeds 6 eV, which is more than sufficient to complete the bond dissociation begun by adsorption to initiate the chemical reaction.

The generality of QED induced EM radiation finds application to EM radiation at VUV levels in diverse applications, e.g., the oxidation and aging of hydrocarbon liquids in flow electrification by NP impurities [10] and the thermal conductivity of nanofluids [11].

The purpose of this paper is to extend QED induced EM radiation to nanocatalysts under molecular collisions.

1 Theory

1.1 EM confinement

Before considering NPs absorbing EM radiation from molecular collisions, it is instructive to consider the QD theory under NIR laser radiation for the case of $D > \lambda$ shown in Fig. 3 [6]. For clarity, a single NIR photon is depicted to excite the polar, radial, and equatorial modes of the NP [8].

The equatorial mode shows the EM radiation trapped in the NP by total internal reflection (TIR), but the case of interest is $D \ll \lambda$, which can be understood by the number n of reflections of wavelength λ around the NP circumference, $n \sim \pi D/\lambda$. As $n \to 1$, the ratio $\lambda/D \to \pi$. For $n > 1$, the speed of light c is reduced in the NP, giving frequency f_{TIR},

$$f_{TIR} = \frac{c/n_r}{\pi D} = \frac{c}{\pi n_r D} \qquad (2)$$

where, n_r is the index of refraction.

For NPs having $D \ll \lambda$, the TIR frequency f_{TIR} is analogous to the QM analogy of creating photons of wavelength by supplying EM energy to a QM box with walls separated by $\lambda/2$. For NPs of diameter D, the EM confinement frequency f and
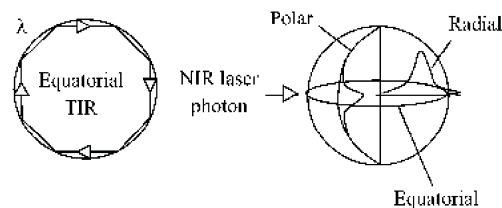
Fig. 3. EM energy interaction with NP for $\lambda < D$.

Planck energy E_P,

$$f = \frac{c}{\lambda}, \lambda = 2n_r D, \text{ and } E_P = \frac{hc}{\lambda} = \frac{hc}{2n_r D} \qquad (3)$$

1.2 Vanishing specific heat

Classical heat transfer conserves absorbed EM energy by an increase in temperature but is not applicable to NP atoms because of the EM confinement of thermal kT energy. Equivalently, the specific heat of NPs may be said to vanish. To show this, the Einstein specific heat for the NP atoms as harmonic oscillators is modified to that for the vibration of thermal photons with EM confinement.

Einstein assumed that the atoms in solids are harmonic oscillators vibrating independent of each other. However, the thermal photons as oscillators vibrate coherently at the EM confinement frequency of the NP imposed by TIR, the oscillations taking the shape of the Mie resonant modes shown in Fig. 3. Taking one thermal photon for each degree of freedom, the energy U of a NP with N atoms,

$$U = 3N \frac{hc}{\lambda \left[\exp\left(\frac{hc}{\lambda kT} \right) - 1 \right]} \qquad (4)$$

For the specific heat C given by $\partial U/\partial T$, the dimensionless specific heat C^* is,

$$C^* = \frac{C}{3Nk} = \frac{\left(\frac{hc}{\lambda kT} \right)^2 \exp\left(\frac{hc}{\lambda kT} \right)}{\left[\exp\left(\frac{hc}{\lambda kT} \right) - 1 \right]^2} \qquad (5)$$

At 300 K, Fig. 4 shows that dimensionless specific heat C^* vanishes for $\lambda = 2n_r D < 4$ μm [8]. Absorbed EM energy is therefore conserved by a temperature increase for $\lambda > 4$ μm while EM emission occurs for $\lambda < 4$ μm. For index $n_r > 2$, the NP temperature increases for $D > 1$ μm.
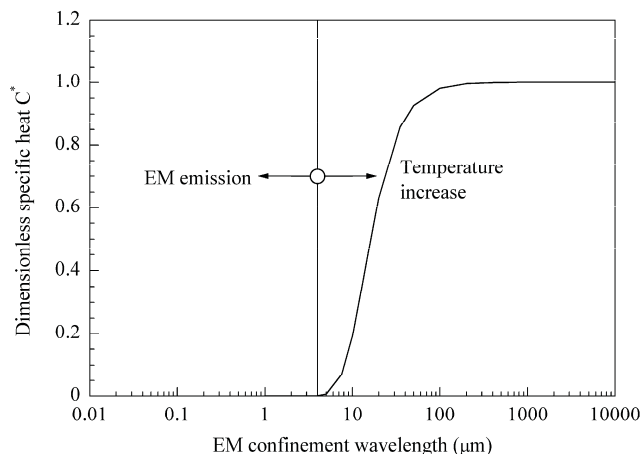
1.3 Collision induced EM radiation

The collisional EM energy Q_C transferred to the NP is [12],

$$Q_C = \frac{\pi}{2\sqrt{3}} pPD^2 \sqrt{\frac{kT}{m}} \qquad (6)$$

where, p is the probability of EM energy transfer, and P is the ambient pressure. The mass m of colliding molecules is $m = M_W/\text{Navag}$, where M_W is molecular weight and Navag is Avagadro's number.

1.4 QED induced EM energy and photon rate

Absent an increase in NP temperature, the collisional EM power Q_C is conserved by the emission of EM radiation,

$$E_P \frac{dN_P}{dt} = Q_C \qquad (7)$$

where, E_P is Planck energy, dN_P/dt is the rate of QED photons produced. Combining,

$$\frac{dN_P}{dt} = \frac{\pi}{2\sqrt{3}} \frac{pPD^2}{E_P} \sqrt{\frac{kT}{m}} \qquad (8)$$

For NPs having $D < 50$ nm and $n_r > 2$, $E_P > 6.21$ eV and the EM radiation is emitted in the VUV where most reactant molecules are activated. For probability $p = 1$ of full kT transfer, the E_P and power Q_C at Planck energy E_P for water and n-hexane having $M_W = 18$ and 86 are shown in Fig. 5.

Under absorbed collisional kT energy, the NP is induced by QED to produce EM radiation at a power Q_C depending on its diameter D. For $D = 5$ nm NPs in benzene and water, Fig. 5 shows the QED induced power $Q_C \sim 0.4$ nW of EM radiation at ~ 60 eV.

2 Extensions

The theory for unsupported NPs is extended to hemi-

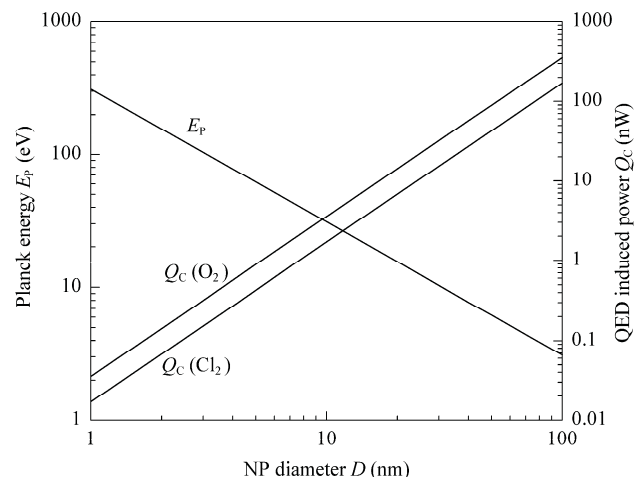

Fig. 4. Dimensionless specific heat (C^*) at 300 K.

Fig. 5. QED induced NP power Q_C and planck energy E_P.

spherical gold NPs supported on substrates. The metal oxide considered is TiO_2 because of high synergy with gold in the catalytic oxidation of CO [13]. Of importance is the QED effects of substrate size on the reactivity of attached gold particles. For Pt/TiO_2 composites, the optimum TiO_2 size is less than 35 nm [14], although TiO_2 substrates from 1 nm to 1 mm are cited in the literature.

2.1 EM confinement

The hemispherical gold NPs supported on the TiO_2 particle substrate absorbing EM radiation from molecular collisions is depicted in Fig. 6.

Unlike the unsupported spherical gold NP, the geometry of the hemispherical gold NP on the TiO_2 particle is complex. The Mie EM confinement frequencies under TIR are even more complex as they are not simple in the unsupported spherical NP. For the purposes here, the fundamental Mie resonant frequency f_C for the Au/TiO_2 composite is,

$$f_C \sim c/2\delta \qquad (9)$$

where, δ is the longest dimension across the composite as shown in Fig. 6.

The EM confinement frequency includes the TiO_2 particle support having a large area to accumulate kT energy that may be transferred to the gold NP through the Au/TiO_2 interface. Otherwise, the transfer of kT energy directly to the gold NP is far significant because of the small area compared to the TiO_2 particle.

2.2 Vanishing specific heat

Upon absorption of kT energy from reactant molecules, the EM radiation is confined within the geometry of the Au/TiO_2 composite. Fig. 4 shows the dimensionless specific heat C^* vanishes for $D < 4$ μm. For $n_r > 2$, the dimension δ necessary

for the Au/TiO_2 composite to have vanishing specific heat is < 1 μm.

2.3 QED induced EM energy and photon rate

Generally, optimum Au/TiO_2 reactivity is found for submicron TiO_2 supports having $\delta < 35$ nm [14]. It is therefore likely that this would also be the case for Au/TiO_2. On this basis, the QED induced power Q_C may be estimated by taking $D = \delta$ in Fig. 5.

3 Discussion

Over the past decade, the emphasis in gold nanocatalysts has been prompted by the discovery by Haruta that led to a review of gold in catalysis [2]. However, the history of nanocatalysts by ubiquitous NPs began about 200 years ago.

In 1817, Davy showed chemical reactions to occur between gaseous reactants at a metal surface without the latter being chemically changed [15]. Davy used a fine Pt wire heated to a high temperature to catalyze the chemical reaction between H_2 and O_2 gases, although with finely divided Pt, the reaction could proceed at room temperature. By QED induced EM radiation, Davy's findings are interpreted in terms of the ubiquitous NPs: the finely divided Pt most likely included many NPs for the chemical reaction to be initiated at room temperature; but to initiate chemical reaction with the fine Pt wire, high temperatures were required to raise the kT energy to compensate for the fewer NPs.

Like DFT, QED induced EM radiation is one of many theories proposed to explain catalysis over the past decade [16]. To limit the scope of this review, emphasis is placed on the activation of adsorbed oxygen in supported Au/TiO_2 thought to enhance catalytic activity caused by surface defects [2]. How QED induced EM radiation may supplement surface defects in activating oxygen adsorbed to Au/TiO_2 nanocatalysts is discussed as follows.

3.1 Supported

With regard to CO oxidation to CO_2, gold can act as a novel catalyst once oxygen is activated on the defective surface or excited by other means [2]. QED induced EM radiation from gold NPs provides a means by which oxygen may be activated other than by defective surfaces, say at the Au/TiO_2 interface. That QED induced EM radiation is a credible activation mechanism of oxygen is suggested by the finding that gold deposited on the inside of the quartz tube of a CO_2 laser shows CO oxidation at room temperature only during laser operation [17].
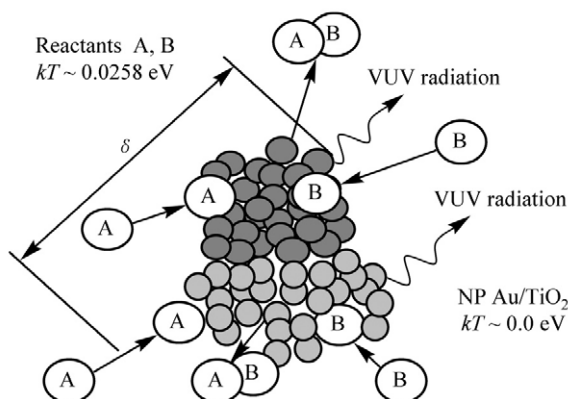
Fig. 6. Catalysis of A and B reactants by supported NP under QED induced EM radiation.

Indeed, QED induced EM radiation may be considered a FIR laser converting the accumulated kT energy of colliding reactant molecules into VUV radiation having the Planck energy to activate adsorbed oxygen.

Currently, high Au/TiO$_2$ activity at low temperature is thought caused by the contact structure, which yields the longest perimeter interface [18,19], or equivalently the hemispherical gold bump geometry. However, if the Au/TiO$_2$ support particle is viewed as the area for gathering kT energy from colliding reactant molecules and transferring that EM energy to the gold NP through the contact area, the enhanced activity would also be consistent with a contact structure yielding the longest distance of perimeter interface.

In QED induced EM radiation, the size of the TiO$_2$ support particle is required to be submicron for the EM confinement to induce Planck energy at the necessary VUV levels to activate oxygen adsorbed on the gold bump, say $D < 35$ nm for Au/TiO$_2$ composite [14]. Otherwise, the Au/TiO$_2$ support induces low level Planck energy that cannot activate the adsorbed oxygen except by defect surfaces.

Hence, the reason for the enhancement of catalytic activity seen upon the addition of gold NPs to metal oxide supports may simply be the larger area of the supports that allows more kT energy to be absorbed from collisions of reactant molecules and subsequently transferred to the gold NP through the contact area. Indeed, the adsorption isotherms of CO by TiO$_2$ supports are almost the same as that of the Au/TiO$_2$ composite while that of the gold NP bumps is at least an order of magnate less [13].

QED induced VUV photolysis is expected to liberate electrons leaving gold in a positive charged state. Indeed, Au$^+$ and Au^{3+} but not Au- are found in the support surface consistent with QED induced VUV photolysis [20].

However, the catalytic activity of gold NPs supported on metal oxides cannot rely on QED induced EM radiation alone as this would incorrectly imply activity is independent of defects and the chemical selectivity between the reactant molecules and support. Indeed, it is known that gold supported on metal oxides other than SiO$_2$ and Al$_2$O$_3$ is much more active for CO while unsupported gold is more active for H$_2$ oxidation [13]. All sources of oxygen activation need to be considered in enhancement of catalytic activity by nanocatalysts.

3.2 Unsupported

Gold NP clusters are thought reactive at room temperature with oxygen because of electrical charge and the number of atoms in the clusters [21]. However, the gold clusters may be charged by QED induced EM radiation through the photoelectric effect.

But charging is inconsequential to excitation of adsorbed oxygen on the surfaces of the gold clusters that oxidizes CO to CO$_2$. It is the EM radiation at VUV levels induced by QED that activates adsorbed oxygen on gold NPs to oxidize CO to CO$_2$.

4 Conclusions

QED induced EM radiation relying on the transfer of kT energy to supported or unsupported nanocatalysts in collisions of reactant molecules acts to assist bond weakening of adsorbed reactant molecules thereby completing the bond breaking to initiate the chemical reaction.

Supported NPs on submicron metal oxide particles provide higher catalytic activation of adsorbed oxygen than with unsupported NPs. But this is only true by activation under QED induced EM radiation at VUV levels as the activation mechanism. NPs supported on supermicron particles are not excited by VUV radiation, but rather low level IR Planck energy incapable of activating adsorbed oxygen. Supermicron particles require defective surfaces as the source of activation.

Similar to photo catalysis, QED induced EM radiation only provides a way of activating reactant molecules with VUV radiation. The VUV radiation is almost independent of the nanocatalyst, say gold or another material. However, this does not imply that all nanocatalysts will catalyze a reaction more or less as gold. The chemistry of the nanocatalyst in relation the support must be considered to catalyze a particular chemical reaction.

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