



Charge transfer and heat in photocatalysis
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Abstract

Photocatalysis occurs very often in the life of ordinary people. Its simplest example is the photosynthesis of plants and algae. It is difficult to overestimate how important this photochemical reaction is because the possibilities of its application are ranging from water purification to the development of a cheap bombed energy source. This work is aimed at a more detailed investigation of the photocatalytic reaction. For this purpose, the present work presents the analysis of the latest and most important research in the field of plasmon-induced photocatalysis. As a model system, the authors mainly used molecules of the thiol group such as nitrobenzenethiol or nitrophenol adsorbed on plasmonic nanoparticles. To characterize the resulting systems, Raman spectroscopy (SERS) was used. It is reported that the main mechanism for triggering photocatalytic reactions is the transition of hot charge carriers under the influence of light, which leads to a local surface plasmon resonance (LSPR) and a change in temperature by internal or external heating of the system. It should be noted that the main factor influencing the photocatalytic activity was not fully determined due to the numerous diverse opinions on the issue.

Keywords: Photocatalysis, catalysis, photochemistry, electromagnetic field, temperature, plasmons, nanoparticles, Raman spectroscopy, SERS, molecules, hot-electrons, hot-holes;

1. Introduction

Photocatalysis is becoming an increasingly relevant research topic due to its wide range of applications in the fields of energy and environmental conservation, including self-cleaning surfaces, air and water purification systems, sterilization, hydrogen evolution, photoelectrochemical conversion, solar energy harvesting, and even theranostics of cancerous tumors.

At present, there is no consensus on the exact mechanism of plasmon-induced photocatalysis. There is a debate in the scientific community and there are some scientific studies and articles. Scientists discuss what affects this type of reaction to a greater extent: localized surface plasmon resonance (LSPR), internal or external heating, charge transfer, or each of the listed phenomena equally.

Photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalytic photolysis, light is absorbed by the adsorbed substrate. In photogenerated catalysis, photocatalytic activity (PCA) depends on the ability of the catalyst to create electron-hole pairs that generate free radicals (for example, hydroxyl radicals: $\bullet\text{OH}$) that can enter secondary reactions. Its practical application became possible due to the discovery of water electrolysis using titanium dioxide (TiO_2) [7]. When developing new photocatalysts, many candidates with a higher photocatalytic activity than TiO_2 were studied, most of which have a wide band gap and are active only in UV light [2].

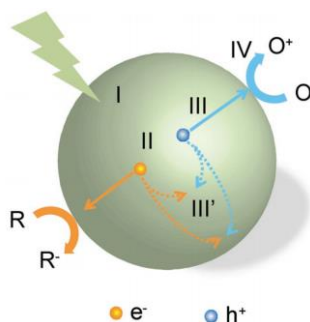


Figure 1. Stages of photocatalytic reactions. R: chemicals in reduction reactions, O: chemicals in oxidation reactions. [20].

Photocatalysis, while varying in detail in terms of reactions and mechanisms, can be described by four important steps (shown in Figure 1): (I) absorption of light to create electron-hole pairs; (II) separation of excited charges; (III) transfer of electrons and holes to the surface of photocatalysts; and (IV) using surface charges for redox reactions. At the third stage, most of the electron-hole pairs recombine either on their way to the surface or on the sections of the surface [11, 19]. Recombination dissipates the collected energy in the form of heat (non-radiative recombination) or light emission (radiative recombination). Long-lived photogenerated charges on the surface can contribute to various redox reactions the details of which depend on the donor or acceptor properties of particles absorbed by the surface [4].

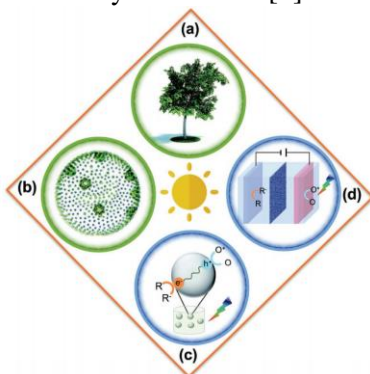


Figure 2. Types of photocatalytic reactions. a) natural photosynthesis in plants, b) photosynthesis of microalgae, c) photocatalysis of nanoparticles, d) photoelectrocatalysis [20].

In an effort to classify existing photocatalysis approaches, Figure 2 presents four classes of reactions. In the first category (Figure 2a), we see natural photosynthesis. An ingenious result of billions of years of nature evolution. This process has become the main source of our energy supply. Carbohydrates are the key products of these reactions [4]. A variation of this reaction is shown in Figure 2b where microalgae carry out reactions similar to those of plants but synthesize unique chemicals such as H_2 or other valuable chemicals (ethanol, butanol, glycerin and isoprene) [4]. When it comes to artificial photosynthesis systems, there are many variations. They can be grouped into two general types as shown in Figures 2c and 2d. When the reduction and oxidation reactions are not specifically separated. This category can include reactions involving both heterogeneous and homogeneous catalysts. A key distinguishing feature of Figures 2c and 2d is physical separation of the reduction and oxidation centers by a reasonable distance (more than a few hundred nanometers) [20].

2. Materials and methods

The use of surface plasmons as a catalyst for surface reactions has attracted great interest of scientific researchers in recent years. The authors have shown that the excitation of local surface plasmon resonance increases the rate of chemical reactions due to the excitation of hot charge carriers and a local temperature increase [5, 10]. The oxidation of p-aminothiophenol (PATP) was used as a model reaction to study the catalytic activity of various substrates [1]. PATP strongly interacts with the metal and binds to its surface through the thiol group forming a covalent bond [8]. It was shown that upon deposition on silver nanoparticles, p-aminothiophenol (PATP) dimerizes to a new compound p, p'-dimercaptoazobenzene (DMAB). In this reaction, the amino groups (-NH₂) of two PATP molecules are oxidized and become azo bonded (N = N bond is formed). It is generally accepted that the excitation and transfer of hot electrons / holes from metal nanoparticles form the main mechanism responsible for the photocatalytic reactions studied on noble metal substrates.

After the excitation and decay of a localized plasmon, hot charge carriers are generated in the metal. These hot charge carriers transform into the excited state of the adsorbed molecules and provide the activation energy for the chemical reaction. During PATP dimerization, hot electrons are adsorbed on O₂ molecules from the air and generate reactive components ³O₂ while hot holes are active particles responsible for the oxidation reaction [1]. PATP can also be directly oxidized to p-nitrophenol (PNTF) by adding a supplementary source of electrons and holes to the system. In this process, a nitro group (-NO₂) is formed.

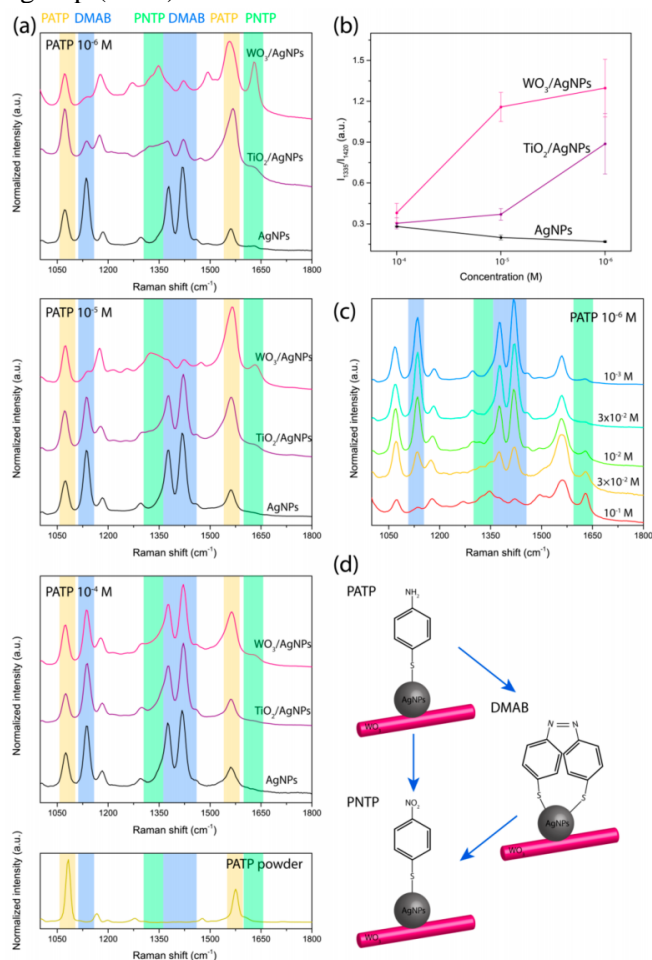


Figure 3. Raman spectra and schematic transition of PNTP reagent molecules and DMAB/PATP product molecules [1].

Figure 3 depicts: (a) Normalized SERS spectra for PATP at various concentrations applied only to WO_3/AgNP , TiO_2/AgNP , and AgNP substrates, compared to the Raman spectrum of PATP powder applied to a glass substrate. (b) Ratio of PNTP / DMAB composites for PATP at different concentrations applied to different substrates. (c) Normalized SERS spectra of PATP molecules at low concentration supported on a WO_3/AgNPs substrate. (d) Schematic of the oxidation reaction and the formation of DMAB and PNTP from PATP. As a result of this study, we can say that the composite material WO_3/AgNPs is an effective substrate for initiating catalytic redox reactions based on the model oxidation reaction of PATP to PNTP.

It should be noted that during the excitation and decay of plasmons, hot charge carriers are formed in gold nanoparticles (AuNP) which are transferred to surface molecules and cause chemical transformations. In one of the latest scientific studies, it was reported that channels for the transfer of electrons and holes must be opened to initiate the reactions [8, 9]. The joint interaction of hot electrons and hot holes explains many of the previous observations. The reaction from NTP or NBT to DMAB does not occur on gold nanoparticles without a reducing agent [12]. Reducing agents (e.g., 4 BH⁻) consume hot holes on AuNP, which facilitates the transfer of hot electrons from AuNP to NBT molecules, which in its turn leads to the formation of DMAB (see Figure 4) [9]. Schlücker et al found that the addition of halide anions reduces NBT to ABT on Ag nanoparticles (AgNP) [18]. This can be explained by the fact that halide anions collect hot holes from AgNP, which greatly accelerates the transfer of hot electrons to NBT. As a result, the rate of the reaction is significantly increased by converting NBT molecules to ABT replacing the nitro group with the amino group. This model is also applicable to the oxidation process.

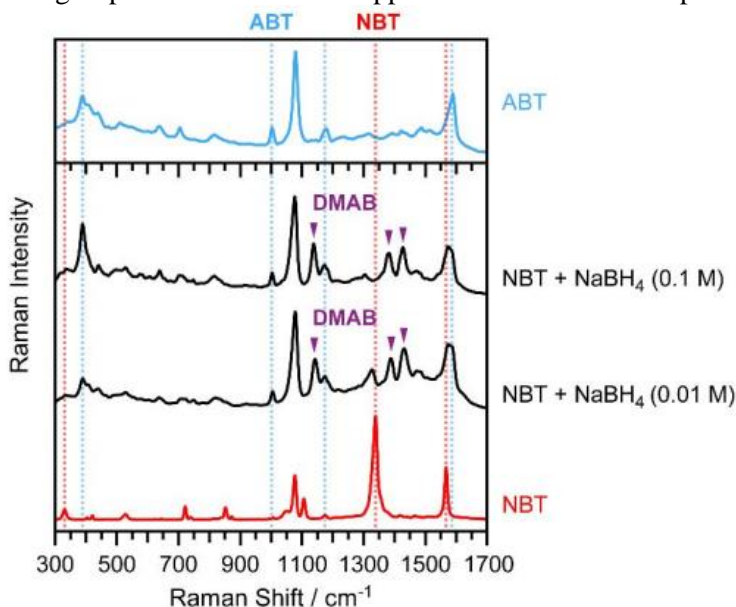


Figure 4. Plasmonic reduction of NBT to DMAB (and further to ABT) requires the addition of a reducing agent (NaBH_4). The SERS spectrum for NBT molecules from SAM in NPoM increases with the addition of NaBH_4 . The peaks of SERS intensity characteristic of the DMAB molecule (purple triangles) and ABT (light blue пунктирные линии) are illustrated [9].

Habteyes et al observed that cetyltrimethylammonium bromide (CTA) coated gold nanorods (AuNR) were more reactive to convert ABT to NBT than citrate coated AuNRs or pure AuNRs.

CTA cations combine with hot electrons on AuNR, excited by plasmon. Then, excess hot holes more quickly pass into ABT molecules, which leads to the generation of NBT molecules [13].

It is worth noting another study that contributes to a fundamental understanding of plasmon-induced transfer of hot electrons and photocatalysis at plasmon interfaces [16]. In order to further confirm the mechanism of interphase transfer of hot electrons and expand it to more practical systems, the authors of this work presented plasmonic nanoparticles with a core-shell structure with various shell materials that can be used in photoelectrochemical splitting water in addition to the above-described model oxidation reaction pATP (NBT) to DMAB. Photoelectrochemical water splitting is known to be one of the most important reactions in the energy sector and a promising way of sustainable hydrogen production [6, 14]. In this photoelectrochemical system, pure Au nanoparticles or nanoparticles of a core-shell structure with a shell of 2 nm are used as a working electrode. Hot electrons generated in pure Au nanoparticles and core-shell particles pass to the platinum counter electrode through the external circuit and induce the hydrogen evolution reaction (HER) (Figure 5A). The cyclic voltammogram of pure Au nanoparticles shows the strong oxidation peak of about 0.65 VSCE (Figure 5B) which can be attributed to oxidation of the gold surface. This peak completely disappears for the following core-shell structures: Au@SiO₂, Au@TiO₂, and Au@Pd indicating that the surface of the Au core is completely covered with SiO₂, TiO₂, and Pd, respectively.

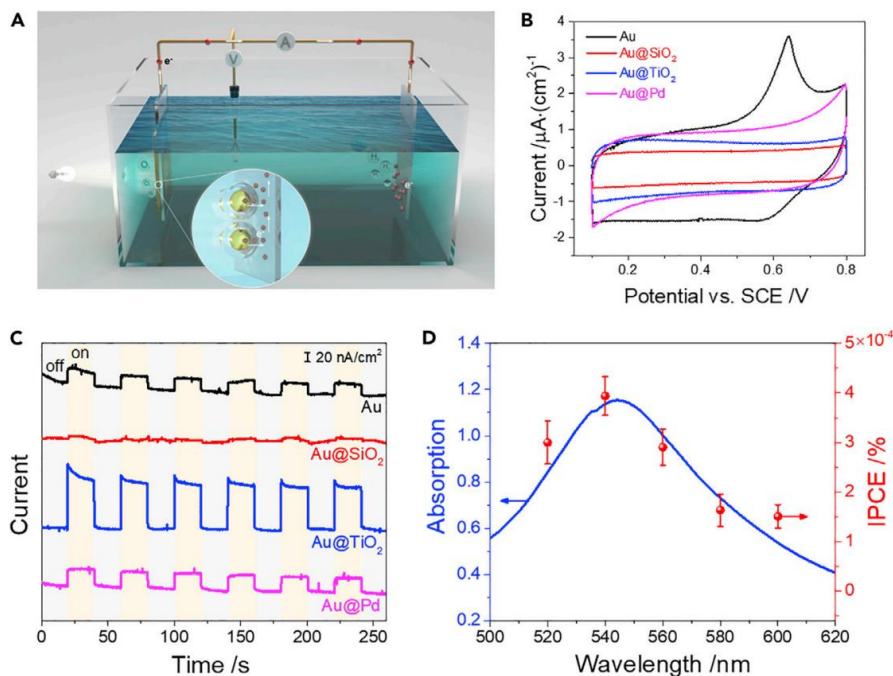


Figure 5. Photoelectrochemical splitting of water using plasmonic nanoparticles with a core-shell structure [16].

Figure 5C shows the i-t amperometric curves for pure Au nanoparticles and various nanoparticles with a core-shell structure at the constant voltage of 0.7 VSCE. A periodic high frequency photocurrent can be clearly observed for pure Au nanoparticles. This photocurrent almost completely disappears for nanoparticles of the Au @ SiO₂ core-shell structure. This result further confirms that silica shells can block hot electron transfer, which is in good agreement with the detection of plasmon-mediated conversion of pATP to DMAB. A similar photo-response is observed for nanoparticles with the Au@Pd structure. However, everything is different for the

Au@TiO₂ structure. The photo response in this case is more intense than in the previous cases, which indicates a more active transition of charge carriers.

Such fundamental study is confirmed by the results of the photoelectrochemical splitting of water using nanoparticles of the core-shell structure [14]. This work deepens the fundamental understanding of the hot electron transfer mechanism at plasmon interfaces and contributes to the creation of highly efficient plasmon-enhanced photocatalysts.

3. Discussion

In addition to plasmon-enhanced action, photocatalytic activity can be increased by internal or external heating of the system under study. However, it is difficult to separate the relative thermal and nonthermal impacts to plasmon-induced reactions. Temperature measurements at the nanoscale are technically challenging, and macroscale experiments are often characterized by collective heating effects that tend to make the actual temperature rise unpredictable. The authors of this paper demonstrate the methods [3] which make it possible to experimentally detect and quantify photothermal effects in plasmon-induced chemical reactions, to distinguish their contribution from photochemical processes and to take a critical look at the current controversial situation.

The effective absorption of a sample can be easily characterized with an infrared camera by measuring the temperature rise at two orthogonal polarizations. Alternatively, the optical properties of the sample can be measured with a conventional spectrometer, but taking into account the fact that regular transmission measurements usually give an extinction spectrum that can differ from the absorption spectrum due to strong scattering effects in plasmon nanostructures [3].

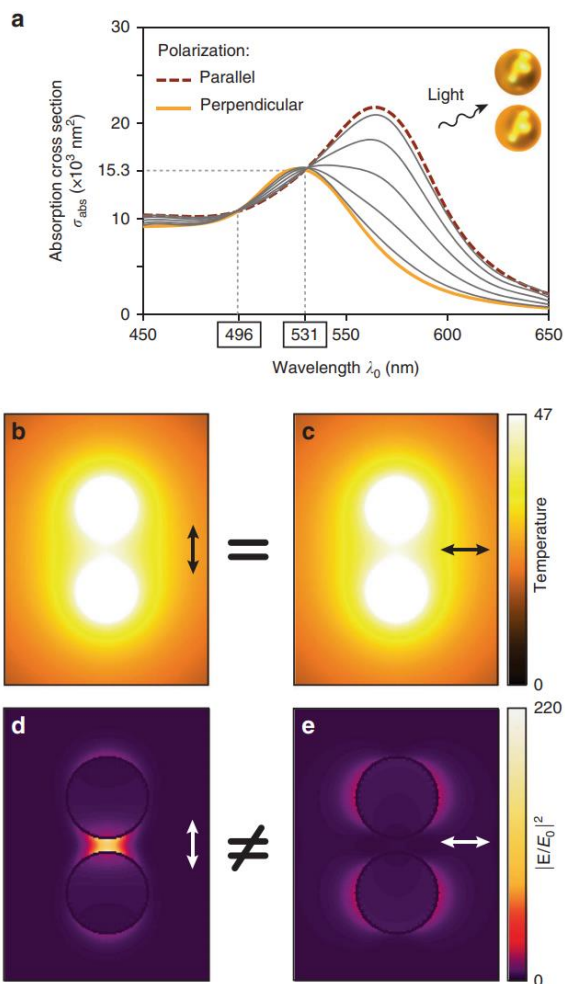


Figure 6. Temperature maps and corresponding increases in electric field intensity for longitudinal and transverse polarization of incident light for a dimer illuminated by a laser with the wavelength of 531 nm at the light intensity of $1 \text{ mW}/\mu\text{m}^2$ [3]

This method is not suitable for nanoparticles randomly deposited on a substrate as it is usually the case in plasmon chemistry experiments, since all plasmonic structures must be aligned in the same direction. However, this procedure can be used with samples from plasmonic nanostructures fabricated by nanolithography methods such as electron beam lithography, conformal substrate imprint lithography, nanosphere or colloidal hole mask lithography, or reduced hole colloidal lithography [15].

An important contribution to the study of the temperature effect on photocatalytic activity is the previously mentioned work by Sarhan et al. The paper discusses the temperature dependence of the 4-nitrothiophenol (4-NTP) dimerization in DMAB adsorbed on gold nanofibers using surface-enhanced Raman scattering (SERS) [17]. Raman thermometry shows significant optical heating of the particles (Figure 7).

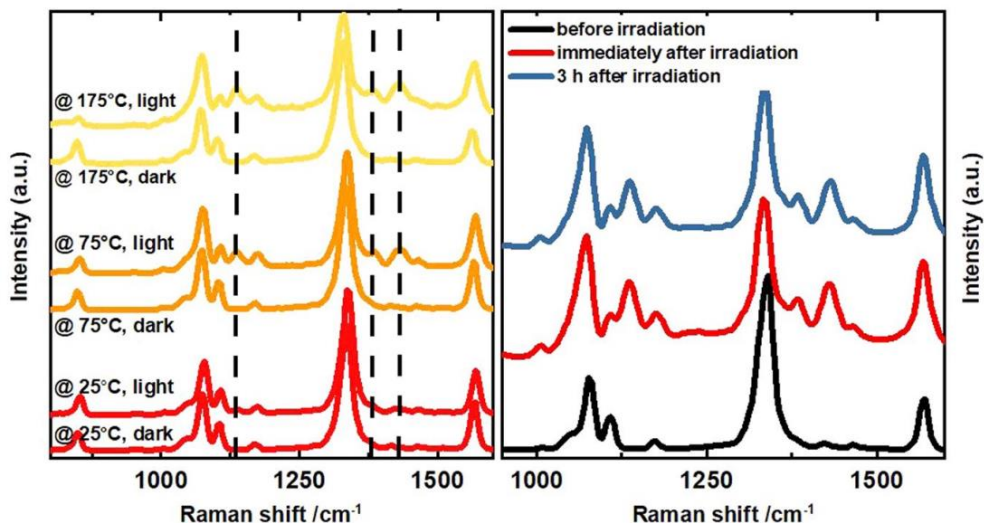


Figure 7. (a) Temperature-dependent SERS spectra of 4-NTP molecules obtained with the 2.44 kW/cm² Raman laser after exposing the laser beam to dark (without light) and bright (25.4 kW/cm² for 5 minutes) sample sections. SERS spectra were measured at the intensity of 2.4 kW/cm². (b) SERS spectra of 4-NTP confirming the stability of the DMAB product [17].

The ratio of Stokes and anti-Stokes Raman signals demonstrates that the temperature of the molecules during the reaction exceeds the average temperature of the plasmon particles crystal lattice. The product stripes are even hotter than the reagent stripes, which makes it possible to suppose that the reaction takes place predominantly in hot spots. In addition, kinetic measurements of the reaction with external heating of the reaction environment show a significant increase in the reaction rate with the temperature. Despite this significant heating effect, comparison of the SERS spectra obtained after heating the sample with an external heater and the spectra recorded after prolonged illumination shows that the reaction is strictly photocontrolled. Although the temperature rise is comparable in both cases, dimerization occurs only in the presence of light. Intensity dependent measurements at fixed temperatures confirm this result [17].

4. Conclusion

Photocatalysis is becoming an increasingly relevant research topic due to its wide range of applications in the fields of energy and environmental conservation. It includes self-cleaning surfaces, air and water purification systems, sterilization, hydrogen evolution, photoelectrochemical conversion, solar energy harvesting, and even theranostics of cancerous tumors. Currently, there is no consensus on the exact mechanism of plasmon-induced photocatalysis. In the scientific community, there are disputes and a big number of scientific papers discussing to what extent the following phenomena are important for this type of reaction: localized surface plasmon resonance (LSPR), internal or external heating, charge transfer. This work proves that current understanding of plasmon photocatalysis is incomplete without taking into account the interactions between photothermal, electronic and photonic factors, which open up new, as yet unexplored possibilities for developing improved photocatalytic activity, selectivity, and the possibility of creating a new class of photocatalysts.

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