Review

Recent advances in research on plasmonic enhancement of photocatalysis

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Abstract

The purpose of the present work is to review the results of the research on the plasmonic enhancement of photocatalytic activity of composite nanostructures consisting of metal and oxide semiconductor nanoparticles (NPs). Besides the separation of electrons and holes photoexcited in an oxide semiconductor resulting in the reduction of their recombination rate, the plasmon resonance in metal NPs deposited on or embedded into the oxide semiconductor significantly enhances the photon absorption by the nanocomposite compared with that by the single oxide semiconductor, i.e. the plasmonic enhancement. The main content of this review is a presentation of the study of various nanocomposite photocatalysts with enhanced activities due to the plasmonic enhancement effect, i.e. the plasmonic photocatalysts. Results of the study of many two-component nanocomposite plasmonic photocatalysts are presented. The simplest one consists of Au NPs or Ag NPs embedded into TiO\textsubscript{2}. The other ones consist of Au nanorods (NRs) elaborately arranged on the TiO\textsubscript{2} surface, Au NPs deposited on different supports such as hydrotalata (HT), \(\gamma\)-Al\textsubscript{2}O\textsubscript{3}, n-Al\textsubscript{2}O\textsubscript{3}, ZnO as well as TiO\textsubscript{2} NRs, CeO\textsubscript{2}-coated bimetallic nanocomposites Au@Pd and Au@Pt, and the metal nanocrystal core@CeO\textsubscript{2} shell nanostructure. Besides these various two-component nanocomposite photocatalysts, several three-component ones have also been studied by many authors. The results of research on Au@TiO\textsubscript{2}/Pt, Au@TiO\textsubscript{2}/Pd, Au/TiO\textsubscript{2}/Pt, Au@Pd/TiO\textsubscript{2}, Au@SiO\textsubscript{2}/TiO\textsubscript{2}, SiO\textsubscript{2}@TiO\textsubscript{2}/Au, Au/mp-TiO\textsubscript{2}/FTO, Au/mp-TiO\textsubscript{2}/ITO, Au/mp-TiO\textsubscript{2}/glass, where mp-TiO\textsubscript{2} means mesoporous titania, as well as Ag@AgCl/CNTs, Ag@AgBr/CNTs and Ag@AgI/CNTs, are also presented. The plasmonic coupling of metallic NPs in the networks of NPs generates the complementary enhancement effect. The results of the study on the physical mechanisms of the plasmonic coupling are also included.

Keywords: plasmonic, enhancement, photocatalyst, nanocomposite

Classification numbers: 2.09, 4.00, 4.02, 5.07

1. Introduction

Titania (TiO\textsubscript{2}) nanoparticles (NPs) have been immobilized in photocatalytic membranes of the pilot plants for the photocatalytic degradation of toxic solutions since the 1990s\textsuperscript{[1–4]}\textsuperscript{[2043-6262/15/043001+17$33.00 © 2015 Vietnam Academy of Science & Technology].} However, for photocatalytic degradation under irradiation by sunlight, the use of pure TiO\textsubscript{2} has a drawback: the absorption spectrum of TiO\textsubscript{2} mainly belongs to the region of UV radiation and makes up only a very small portion (~4%) of sunlight energy. One of the most efficient ways to overcome this difficulty is to deposit NPs of some noble metal (such as Au or Ag) onto the surface of a TiO\textsubscript{2}NP. Kamat \textit{et al}\textsuperscript{[5]} have shown that photoexcited semiconductor NPs undergo charge equilibration when they are in contact with metal NPs. Such a
charge redistribution induces the shift of the Fermi level in semiconductor NPs to a more negative potential. The transfer of electrons to AuNPs was probed by exciting TiO$_2$NPs and determining the apparent Fermi level of the TiO$_2$/Au composite system. The Fermi level shift is size-dependent: 20 and 40 mV for AuNPs with diameter of 8 nm and 5 nm, respectively.

The influence of excitation wavelength (UV or visible) on the photocatalytic activity of TiO$_2$ containing AuNPs for the generation of hydrogen or oxygen from water was investigated by Garcia et al [6]. These authors showed that the operating mechanisms of the photocatalytic processes generated by UV and visible lights are different. In the first case, the UV light excitation occurs on a TiO$_2$ semiconductor leading to the generation of electrons in the semiconductor conduction band and holes in the valence band. Electrons in the conduction band are then injected to the AuNPs acting as the electron buffers and catalytic sites for hydrogen generation. The holes are quenched by EDTA (figure 1(a)). In the second case, upon photoexcitation of AuNPs, electrons from Au are injected onto the TiO$_2$ conduction band leaving the holes in the AuNPs and leading to the generation of hydrogen at the surface of the TiO$_2$ NPs. Then the holes are quenched by the donors in the solution (figure 1(b)).

The proposed mechanism of the photocatalytic process in the second case can be justified by noting the accordance of the absorption spectrum of the localized plasmon resonance (LPR) of the AuNPs with that of the exciting light. Note that the above-mentioned mechanism is an oversimplification, because due to the Au/TiO$_2$ interfacial contact the conduction band of the TiO$_2$ undergoes a shift toward more negative potential and the charge redistribution causes a shift of the Fermi level toward more negative potential. The photo-generation of hydrogen by the Au/TiO$_2$ photocatalyst was also observed using visible light (cutoff filter, $\lambda > 400$ nm) and methanol as the sacrificial electron donor.

A similar charge transfer process, in which an excited electron from a plasmon in AuNPs is injected to the conduction band of a TiO$_2$ NP and the hole left behind in the AuNP is filled by a donor electron from the surrounding solution (figure 2), was demonstrated in the previous experimental work of Tian and Tatsuma [7]. In this work the authors prepared the Au/TiO$_2$ composite by deposition of gold in porous titania film and showed that the photoaction spectra for both the open-circuit potential and short-circuit current were in good agreement with the absorption spectrum of the AuNPs on the TiO$_2$ film. Thus the AuNPs were photoexcited due to the plasmon resonance, and the charge separation was accomplished by the transfer of photoexcited electrons from the AuNPs to the conduction band of TiO$_2$ and the simultaneous transfer of compensative electrons from the donors in the solution to the AuNPs. A series of donors were examined and it was shown that the incident photon-to-current conversion efficiency (IPCE) can be improved by a factor larger than 20. The prepared composite was potentially applicable to the visible-light-induced photocatalytic oxidation of ethanol and methanol as well as the reduction of oxygen. The above-mentioned plasmon resonance effect was reconfirmed in a subsequent work by the same authors [8].

The ultrafast plasmon-induced transfer of electrons from AuNPs into TiO$_2$NPs was then investigated by Furube et al [9]. These authors used femtosecond transient IR absorption spectroscopy to directly observe electrons injected from the plasmon band of AuNPs into TiO$_2$NPs. However, the plasmon band is due to the collective motion of conductive electrons induced by the electric field of incident light and the photon energy is shared by numerous electrons. Therefore each individual electron cannot have an energy sufficient enough to get over the $\sim 1.0$ eV Schottky barrier at the interface between Au and TiO$_2$. An electron can be injected...
from the AuNP into the TiO2NP only if the energy exchange takes place between the plasmon as a whole and the electron. Thus the observed electron transfer from AuNPs to TiO2NPs was a clear evidence of the involvement of plasmon as the whole complex quasiparticle in the interaction process. It is worth noting that the optical density spectra of the Au/TiO2 and original Au showed plasmon peaks at ~550 nm and 515 nm, respectively. The Au/TiO2 optical spectrum includes a strong scattering effect due to the presence of TiO2 film.

The above-presented demonstration of the plasmon-induced enhancement of the photocatalytic activity of a Au/TiO2 composite has promoted the rapid development of research on the physical processes and phenomena in which the contribution of plasmons induced a significant enhancement. The rapid development of research on plasmonic phenomena and processes resulted in the emergence of a new scientific discipline: plasmonics [10, 11]. The photocatalysts with enhanced catalytic activity due to the plasmonic effect were called plasmonic photocatalysts. The present article is a review of recent experimental works on plasmonic photocatalysts.

2. Two-component composite plasmonic photocatalysts

A simplest composite plasmonic photocatalyst consists of two components: metal and oxide semiconductors. In the experimental work of Awazu et al [12] the plasmonic photocatalytic nanocomposite consisting of silver nanoparticles (AgNPs) embedded in TiO2 was prepared and investigated. While TiO2 displayed photocatalytic behavior under near-UV irradiation, the excitation of localized plasmon polaritons (LPPs) on the surface of AgNPs caused a tremendous increase of near-field amplitude at the same wavelength region of the near-UV irradiation. In the fabrication of the composite from AgNPs and TiO2 there arose a problem to be solved: chemically very reactive AgNPs would be oxidized at direct contact with TiO2. For example, Ag could have been oxidized at the Ag–TiO2 interface to form eventually a 10 nm thick layer of silver oxide (Ag2O) at room temperature. To prevent this oxidation, the AgNPs have to be coated with a passive material, such as SiO2, to separate them from the TiO2. Since the near-field amplitude very rapidly decays with the increase of the distance to the NP surface, the protection layer has to be kept sufficiently thin. Furthermore, the peak wavelength of the plasmon resonance is sensitive to both the NP size and the properties of the medium surrounding the NP.

The authors have performed the formation of Ag/SiO2 core–shell structure by using the sputtering technique to coat AgNPs with SiO2. Then the photocatalytic TiO2 film of thickness ~90 nm was spin-coated onto the SiO2 layer, and the composite was heated at 500 °C for 30 min to produce the anatase phase. The photocatalytic decomposition of methylene blue (MB) on the TiO2 was examined by optical absorption spectroscopy. The rate of decomposition of MB on the composite of TiO2 and Ag/SiO2 core–shell structure was five times faster than that on the TiO2 alone. Since AgNPs were not found on the top surface of the TiO2, the accelerated decomposition of MB is not the result of AgNPs acting as the electron traps to aid the electron–hole separation. It must be the effect of localized surface plasmon (LSP) resonance.

The plasmon-assisted photoelectric light–current conversion in the visible and near-infrared wavelength regions was demonstrated by Misawa et al [13] using a photocathode consisting of gold nanorods (AuNRs) elaborately arrayed on the surface of TiO2 single crystals via a top-down nanostructuring process. It was known that NRs of noble metals exhibit characteristic bands of optical attenuation at visible and infrared wavelengths due to LSPs. These LSP bands are also associated with the enhancement of the electromagnetic field due to its localization within a few nanometers’ distance from the surface of the NRs. In the present experimental work the authors have fabricated AuNRs showing LSP resonance and deposited them on n-type TiO2 single crystals. The extinction spectra of the AuNRs/TiO2 composite were depicted. Two broad LSP bands were observed around the wavelengths of 650 and 1000 nm. The measured spectra indicated that the transverse mode (t-mode, λmax ≈ 1000 nm) of identical and parallel nanorod arrays can be selectively excited by controlling the orientation of the linear polarization of the incident light.

The measurement of the action spectrum of the photocurrent showed that the incident photon-to-photocurrent efficiency (IPCE) values of the photocurrent were 6.3% and 8.4%, corresponding to the LSP bands in the T-mode at 650 nm and the L-mode at 1000 nm. No photocurrent was observed at the TiO2 single crystal without AuNRs under the irradiation of light with a wavelength of 450 nm or longer.

In order to verify the relationship between the photocurrent generation and the plasmon excitation, the authors measured IPCE spectra as functions of the peak wavelength of the plasma resonance band and the density of gold nanoblocks. It was shown that the shape and peak wavelength of the IPCE spectra are almost in accordance with those of the plasmon resonance band and the IPCE value was highly dependent on the density of the AuNRs. Thus the injection of electrons from the AuNRs to the TiO2 single crystal substrate was induced by the LSP at the AuNRs.

In their interesting experimental work [14] Cronin et al firmly demonstrated the plasmonic enhancement of the photocatalytic activity of Au/TiO2 by investigating the photocatalytic splitting of water under visible light illumination. The measurement of photocatalytic reaction rates of TiO2 without and with AuNPs in a 1 M KOH solution was performed by using a three-terminal potentiostat with a pure TiO2 or Au/TiO2 working electrode, a Ag/AgCl reference electrode and a graphite counter electrode. The photocurrent was measured when the working electrode was irradiated by UV light or by visible lights with two different wavelengths. The authors received the following results.

Under the UV irradiation with λ = 254 nm the addition of AuNPs resulted in a four-fold decrease of the photocurrent. This reduction is due to the presence of AuNPs reducing the photon flux reaching both the TiO2 surface and the surface area of TiO2 in direct contact with the aqueous solution. On
the other hand, under the visible irradiations with
\( \lambda = 532 \text{ nm} \) and \( \lambda = 633 \text{ nm} \) the addition of AuNPs resulted
in a five-fold and 66-fold, respectively, increase of the photocurrent due to the large plasmonic enhancement of the local electromagnetic field. These reduction and enhancement factors were independent of the relative intensities of three light sources. Furthermore, the authors have also demonstrated that the photocurrent linearly increased with the light intensities, while the reduction and enhancement ratios remained constant.

Moskovits et al [15] demonstrated the significant photosensitization of TiO\(_2\) due to the direct injection by quantum tunneling of hot electrons from the decay of localized surface plasmon polaritons excited in AuNPs embedded in TiO\(_2\). Surface plasmon decay produces electron–hole pairs in AuNPs. A significant fraction of these electrons tunnel into the conduction band of TiO\(_2\) resulting in a significant electron current in TiO\(_2\) even when the device is illuminated by the light with photon energies well below the band gap of TiO\(_2\).

To carry out the experiment the authors fabricated a device in which the wide band gap semiconductor TiO\(_2\) is photosensitized by embedding AuNPs within this semiconductor, thereby significantly broadening its photoconversion ability beyond the UV region. The active element of the device is a composite solid film consisting of multiple dense two-dimensional arrays of AuNPs, each layer being well separated by TiO\(_2\). The ultraviolet/visible absorption/extinction spectrum ofAuNPs deposited on a quartz substrate showed a localized surface plasmon resonance (LSPR) maximum at 520 nm, indicative of well-separated AuNPs. When the AuNPs were capped by a TiO\(_2\) film of 200 nm (mass thickness), the LSPR red-shifted by 100 nm and became more intense, primarily due to the increase of the dielectric constant of the surrounding medium compared to that of air. A Schottky junction was also created at the metal–semiconductor interface, which resulted in charge transfer from the TiO\(_2\) to the AuNPs, charging the gold negatively and the TiO\(_2\) positively, and creating a Schottky barrier at \( \sim 0.9 \text{ eV} \).

In the experiment with the illumination at the wavelength of 600 nm the authors have observed a 1000-fold increase in the photocconductance of the device fabricated with multilayers of AuNPs embedded in TiO\(_2\) film compared to that of the device without AuNPs.

A particular type of heterogeneous photocatalytic composite consisting of AuNPs supported on semiconductor supports such as hydrotalcite (HT) \( \gamma\)-Al\(_2\)O\(_3\), n-Al\(_2\)O\(_3\) and ZnO was fabricated and investigated by Scaiano et al [16]. In the fabrication of the samples the authors used either the dry photochemical method [17] or the laser drop ablation method [18]. Five different AuNP-supported nanocomposites were prepared and the LED light was used for irradiating the samples in the experiments. Each nanocomposite was tested as a potential photocatalyst toward the oxidation of sec-phenethyl and benzyl alcohols over 40 min, and the conversions to acetoephone and benzaldehyde over 5 and 40 min, respectively, and the conversion to carbonyl products over 40 min.

It was shown that the support in the nanocomposite plays a very important role in the efficient alcohol oxidation. While 1\% Au@HT composites prepared by both methods were the most efficient heterogeneous photocatalysts for alcohol oxidation with near-complete conversion to acetophenone over 40 min, the Al\(_2\)O\(_3\) photocatalysts demonstrated much lower conversion yields. Control experiments have shown that in the absence of AuNPs and in the dark reactions the conversions were very low.

Park et al [19] prepared a nanodiode composed of a silver thin film on a titania layer, verified the formation of a Schottky barrier and investigated the enhanced surface plasmon effect of the Ag/TiO\(_2\) nanodiode on the internal photoemission. They observed the influence of localized surface plasmon resonance on hot electron flow at the metal–semiconductor surface: the photocurrent could be enhanced by optically excited surface plasmons. When the surface plasmons are excited on the corrugated Ag metal surface, they decay into energetic hot electron–hole pairs, contributing to the total photocurrent. The abnormal resonance peaks observed in the IPCE can be attributed to the effect of the surface plasmons. It was observed that the photocurrent enhancement due to surface plasmons was closely related to the corrugation (or roughness) of the metal surface. The photocurrent and internal photoemission efficiencies of the nanodiodes depend on the thickness and morphology of the Ag layer, which also affect the generation of hot electron flow and surface plasmon effects.

The mechanism of singlet oxygen generation in visible-light-induced photocatalysis of gold-nanoparticle-deposited titania (AuNP/TiO\(_2\)) was investigated by Saito and Nosaka [20]. These authors observed the generation of superoxide radical (\( \text{O}_2^- \)) and singlet molecular oxygen (\( \text{O}_2^* \)) in a AuNP/TiO\(_2\) aqueous suspension by chemiluminescence photometry and near-infrared emission, respectively. It was shown that under the plasmon resonance excitation, an electron in the AuNP transferred to the conduction band of TiO\(_2\) reducing \( \text{O}_2^- \) at the TiO\(_2\) surface. The produced \( \text{O}_2^- \) was oxidized by the hole remained in AuNP to generate \( \text{O}_2^* \).

Thus the generation of \( \text{O}_2^- \) and \( \text{O}_2^* \) on AuNP/TiO\(_2\) under visible-light irradiation was observed for the first time. The generation mechanism consists of three steps:

- **Step 1:** Visible-light absorption of AuNP/TiO\(_2\) caused the surface plasmon resonance of the AuNP and an electron transferred from the AuNP to TiO\(_2\) (figure 3(a)).
- **Step 2:** The transferred electron reduced \( \text{O}_2 \) to generate \( \text{O}_2^- \) (figure 3(b)).
- **Step 3:** The \( \text{O}_2^- \) was oxidized by the hole remaining in the AuNP (figure 3(c)).

It is worth noting that AuNP/TiO\(_2\) with a larger TiO\(_2\) particle size can generate a larger amount of \( \text{O}_2^- \) because of the delay of the recombination of the generated electron–hole pairs. Then the remaining hole in the AuNP oxidized \( \text{O}_2^- \) to generate more \( \text{O}_2^* \). The above-mentioned \( \text{O}_2^- \) and \( \text{O}_2^* \) generation is presented in figure 3.
Kim, Huber et al. [21] observed the plasmonic enhancement of Au nanodot arrays by investigating photochemical water splitting. The authors have fabricated printable metal nanostructures by direct contact printing. Size-controllable Au nanodot arrays were directly printed onto indium tin oxide (ITO) glasses by stamps of vertically aligned carbon nanopost (CNP) arrays that were supported within porous channels of anodic aluminum oxide (AAO) templates. The size of the printed Au nanodots was precisely adjusted by controlling the geometry of the stamp tips. As a result Au nanodots with narrow size distribution (±5%) were prepared. It was shown that the quality factor, defined as the ratio of LSPR peak energy on LSPR line width, increased as contact-printed Au nanodot size decreased from 83 nm to 50 nm. This quality factor is proportional to the rate enhancement for photoelectrochemical water splitting.

The stamping platforms consisted of vertical one-dimensional carbon nanopost arrays with circular tips supported by hexagonally aligned pore channels of the AAO matrices. The tip size and interval of the stamps were precisely adjusted by controlling the pore dimension of the mother AAO molds. The diameter of the printed plasmonic Au nanodot arrays was systematically tuned in tight correspondence with the stamp geometries. The metallic Au layers to be printed were then deposited on the tips of the CNP stamps by an electron-beam (e-beam) or thermal evaporation process. Transfer of metal layers from the stamp tips to the substrate surfaces was related to the different adhesion strengths of the metal between the stamps and the substrate surfaces. After lifting the stamps from the substrates, plasmonic Au nanodot arrays were formed on the ITO substrates. TiO$_2$ layers were coated on these nanostructures by dip-coating them into a TiO$_2$ sol solution. The TiO$_2$-coated Au nanodot arrays were directly used as working electrode in the photoelectrochemical water splitting reaction in which a Pt wire and a Ag/AgCl electrode were used as counter and reference electrodes, respectively.

The UV–Vis absorption spectra of Au nanodots with diameters of 50, 63 and 83 nm on ITO glass were recorded, and the plasmon absorption peaks were clearly seen in the visible region. The plasmon resonance wavelength experienced a red-shift as the Au nanodot size increased from 50 to 83 nm and also as the interdistance of nanodots decreased.

The fabricated TiO$_2$-coated Au nanodot electrodes were used for the study of photoelectrochemical water splitting under irradiation by visible light. For all these electrodes the photocurrent response with light on/off increased by about 6 times compared to those with the Au nanodot alone. This enhancement was probably related to the increased Au/TiO$_2$ interfacial area, resulting in the increased amount of photoinduced charge carrier (electron–hole pairs) driving the water splitting reaction locally generated at the metal/semiconductor interface due to the local field enhancement near the surface of the plasmonic nanoparticles. The current generated by visible light also increased from 10 to 25 times compared to that generated without the visible light, as the Au nanodot size decreased from 83 nm to 50 nm, similar to the water splitting.

![Figure 3. Generation of O$_2$ and $^{18}$O$_2$ on Au/TiO$_2$: (a) step 1, (b) step 2 and (c) step 3.](image-url)
A novel particular Au/TiO₂ nanocomposite with AuNPs highly dispersed onto rutile TiO₂ nanorod bundles was fabricated by Zhang, Li et al [22]. The AuNPs induced the visible-light-driven photocatalytic NO oxidation due to the LSPR effect as well as promoted the electron transfer to reduce the recombination of photoexcited electrons and holes. Besides its role as a semiconductor photocatalyst, TiO₂ also played the role of the support to deposit and stabilize the AuNPs. In addition, the special nanorod bundle structure promoted light harvest by multiple reflections. The cooperative promoting effects resulted in the high activity of Au/TiO₂ in photocatalytic oxidation of NO under solar and even visible light irradiation.

Photoelectrochemical measurements were carried out in a conventional three-electrode, single-compartment quartz cell on an electrochemical station. The Au/TiO₂ nanorod bundle structure was used as the material of the working electrode, while the counter and reference electrodes were a platinum sheet and a saturated calomel electrode (SCE). Although pure TiO₂ displays very little visible light absorbance, the Au/TiO₂ nanorod bundle structure exhibited significant spectral response in the visible light area centered at 550 nm, obviously owing to the LSPR effect. This could possibly be attributed to the enhanced light harvest via multiple reflections. The photoluminescence (PL) spectra clearly demonstrated that the Au/TiO₂ nanorod bundle structure displayed much lower intensity of the peak around 560 nm meaning the lower electron–hole recombination rate was due to the electron–hole separation. The photocatalytic NO oxidation in gas phase was carried out at ambient temperature in a continuous flow reactor under irradiation of either solar light or visible light. Experiments showed that no significant decrease of NO content was observed in the absence of either light irradiation or photocatalyst, meaning that the NO oxidation was mainly driven by photocatalysis.

Recently a new plasmonic photocatalyst with a metal nanocrystal core–CeO₂ shell nanostructure was fabricated and investigated by Wang and Yu [23]. The photocatalytic activity of this nanocomposite was enhanced due to the following two physical effects: the LSPR-induced light focusing for enhancing the light absorption and the electron transfer from the metal core to the oxide shell similar to that in the Au@Cu₂O core–shell structure performed in previous works [24, 25]. Besides the charge transfer, the oxide shell also protected the metal nanocrystal core from chemical etching, reshaping and aggregation. Moreover, the size, shape and composition of the metal nanocrystal core can be finely adjusted to tailor the LSPR properties for efficiently harvesting the light. The authors have performed a uniform coating of CeO₂ on Au nanospheres, Au nanorods, bimetallic Au@Pd and Au@Pt nanorods to fabricate a nearly monodisperse core–shell nanostructure. Their plasmon wavelengths can be varied from visible to near-infrared regions.

The fabricated photocatalytic nanostructures were used for the selective oxidation of benzyl alcohol to benzaldehyde with O₂ under both broad-band and monochromatic visible lights. The conversion rates of these plasmonic photocatalysts are superior to those prepared in most of the previous studies for the same reaction. The enhanced photocatalytic activities are attributed to the synergistic effect between the Au nanocrystal core acting as the plasmonic component for efficiently harvesting the light and the CeO₂ shell providing catalytically active sites for the oxidation reaction: the Au@CeO₂ core–shell nanostructure allows the light energy harvested by the Au nanocrystal core to be effectively transferred to the catalytic CeO₂ shell. The authors also expected that the Au@CeO₂ core–shell nanostructures would be used for gas sensing, solar energy harvesting and biomedical antioxidant therapy.

3. Three-component composite plasmonic photocatalysts

A photocatalytic composite nanostructure Au/TiO₂ with metal co-catalysts exhibiting strong LSPR effective for photoinduced hydrogen generation under irradiation of visible light was fabricated and investigated by Kominami et al [26]. These authors combined the traditional photodeposition of Pt in the presence of a hole scavenger (PH) with the subsequent Au colloid photodeposition in the presence of a hole scavenger (CPH) onto TiO₂@Pt. The sample having X wt% of metal co-catalyst and Y wt% of Au will be denoted Au(Y)/TiO₂@M(X). The absorption spectra of TiO₂, TiO₂@Pt(0.5), Au(1.0)/TiO₂ and Au(1.0)/TiO₂@Pt(0.5) were recorded. The bare TiO₂ sample exhibited absorption only at λ < 400 nm due to the band gap excitation. Loading PtNPs onto the TiO₂ resulted in an increase of the baseline of the extinction spectrum. In the spectra of the Au(1.0)/TiO₂ and Au(1.0)/TiO₂@Pt(0.5) samples, strong photoabsorption was observed at around 550 nm, which was attributed to the LSPR of the supported AuNPs. Since the photoabsorption due to Pt particles was also included, the Au(1.0)/TiO₂@Pt(0.5) sample exhibited stronger photoabsorption.

The TiO₂, TiO₂@Pt(0.5), Au(1.0)/TiO₂ and Au(1.0)/TiO₂@Pt(0.5) samples were used for generating H₂ from 2-propanol in their aqueous suspensions under visible light irradiation. No H₂ was evolved in the case of either TiO₂ or TiO₂@Pt(0.5). On the other hand, the Au(1.0)/TiO₂ sample was active in H₂ formation and showed an H₂ evolution rate of 0.87 μmol h⁻¹. Moreover, the Au(1.0)/TiO₂@Pt(0.5) sample exhibited a much larger H₂ generation rate of 6.5 μmol h⁻¹, indicating that the Pt particles loaded onto the TiO₂ effectively acted as reduction sites for H₂ generation. Among all samples of the form Au(1.0)/TiO₂@Pt(X), that with X = 0.5 exhibited maximum H₂ generation rate of the samples Au(Y)/TiO₂@Pt(0.5) versus Y was investigated. The authors observed that it most linearly increased with increasing Y until Y = 1.0 wt% and then gradually increased after Y = 1.0 wt%. It is worth noting that the activities of the Au(1.0)/TiO₂@Pt(0.5) sample were 5–9 times higher than those of the Pt-free sample, indicating the important role of Pt particles as the reduction sites.

By means of femtosecond transient absorption spectroscopy the authors studied the working mechanism of the H₂ generation from aqueous solutions of 2-propanol over
Au/TiO2 @M under visible light irradiation, with M denoting some noble metal (Pt for example). It was shown that it consisted of four processes: i) the incident photons were absorbed by Au through LSPR excitation; ii) electrons were injected from Au into the conduction band of TiO2; iii) the resultant electron-deficient Au particles oxidized 2-propanol to acetone and returned to their original metallic state; and iv) electrons in the conduction band of TiO2 transferred to the metal co-catalyst M at which the reduction of H+ to H2 occurred. The linear correlation between the light absorption and the H2 generation rate has been observed.

Subsequently to the above-presented study of composite nanostructure consisting of a TiO2NP separately deposited by a AuNP for enhancing the light absorption due to LSPR and a Pt or Ag particle as a co-catalyst playing the role of the site for reduction reactions, Kominami et al. [27, 28] fabricated another composite nanostructure Au@Pd/TiO2 consisting of a core–shell Au@Pd nanostructure, and employed this new plasmonically enhanced photocatalyst for photo-induced dechlorination of chlorobenzene under irradiation by visible light. The core–shell Au@Pd nanostructure was prepared by means of a simple two-step photodeposition method. The Au content was fixed at 0.8 wt%, the Pd content of X wt% was changed and the Au(0.8)@Pd(X) core–shell nanostructure was deposited on a TiO2NP. The resultant photocatalyst was denoted as Au(0.8)@Pd(X)/ TiO2.

The prepared Au(0.8)@Pd(X)/TiO2 samples were used for photocatalytic dechlorination of chlorobenzene in aqueous 2-propanol solutions under the irradiation of visible light. The authors examined the reaction by using strictly limited visible light (460–800 nm) in order to rule out the contribution of the original photocatalytic activity of TiO2 which can be excited with UV light. Benzene as the product of chlorobenzene dechlorination and acetone as the product of 2-propanol oxidation were generated. When the sample Au(0.8)@Pd(0.2)/TiO2 was used, the chlorobenzene was completely consumed after irradiation for 20 h. It was shown that benzene was formed with quite high selectivity (>99%) at >99% conversion of chlorobenzene.

Besides the plasmonic photocatalyst Au/TiO2, Wu et al. [29] fabricated and investigated the improved plasmonic photocatalyst Au@SiO2/TiO2 by using core–shell structure Au@SiO2 instead of AuNPs. The 300 nm TiO2 film was prepared by the thermal hydrolysis method and AuNPs were synthesized by the sodium citrate reduced method. The Au@SiO2 core–shell structures were fabricated by mixing the aqueous solution of 3-aminopropyltrimethoxyxilane (APS) with the gold dispersion. The photocatalytic activities of prepared photocatalysts Au@SiO2/TiO2, Au@TiO2 and TiO2 film were evaluated by the degree of methylene blue (MB) photocatalytic degradation under similar conditions with simultaneous UV (365 nm) and visible (400 nm < λ < 700 nm) light irradiation for 5 h. UV–visible spectroscopy was used to measure the concentration of the MB aqueous solution based on the intensity of the absorption peak at 664.3 nm.

The control experiment with only UV + visible light irradiation without the photocatalyst achieved MB degradation efficiency of near 15% after 5 h, whereas in the presence of the three photocatalysts TiO2, Au@TiO2 and Au@SiO2/TiO2 the MB degradation efficiency reached the values 44%, 80% and 95%, respectively, after 5 h of UV + visible light irradiation. The increase of the MB degradation efficiency of Au/TiO2 was due to following: i) the separation of photogenerated electrons and holes; ii) the LSPR effect from the AuNPs when they were irradiated by visible light. Although the coating of AuNPs by SiO2 shells prevented the charge separation, the MB photodegradation efficiency of Au@SiO2/TiO2 was still the highest. The simulation calculations using COMSOL multiphysics software based on the finite element method (FEM) showed the ~9-fold increase of the EM field at the SiO2-coated AuNP compared to the bare AuNP. Thus we can firmly deduce that the SiO2 coating further significantly promoted the LSPR of the AuNPs compared with the bare AuNPs.

The surface plasmon-induced visible light active composite photocatalyst consisting of a silica–titania (SiO2@TiO2) core–shell nanostructure decorated with AuNPs was fabricated and investigated by Kim et al. [30]. The silica bead was coated by a thin layer of TiO2 with a thickness of 15–20 nm, and then the SiO2@TiO2 surface was decorated with AuNPs of 5, 15 and 30 nm size. This design allowed the authors to investigate the evolution of visible light activity in terms of the size and distribution of AuNPs which were crucially important in dictating the LSPR Coupling effect in densely packed metal NP arrays, and then to develop an optimized system for the best photocatalytic efficiency. The photocatalytic activities of the samples were investigated by using UV–visible absorption spectroscopy to measure the absorbance maxima of methylene blue (MB), methyl orange (MO) and p-nitrophenol (PNP).

Three samples decorated by AuNPs with the size of 5, 15 and 30 nm and denoted SiO2@TiO2/Au(5), SiO2@TiO2/Au (15) and SiO2@TiO2/Au(30) were prepared. Since SiO2@TiO2/Au(15) showed a better and uniform distribution of the AuNPs, it was used as the reference system by which to study the effect of the areal density of AuNPs in the photocatalysis efficiency. The UV–visible spectra of the prepared nanostructures were recorded. They contained a peak at 325 nm attributed to the characteristic absorption of TiO2, and a broad peak between 500 and 600 nm due to the surface plasmon absorption of the AuNPs.

The efficiency of the photocatalytic degradation of MB, MO and PNP as three target toxic solutions by using prepared samples with different AuNP densities was determined. It was shown that the samples with the density of 700 μm−2 exhibited the best catalytic performance. The complete degradation of MB and MO was achieved within 2 and 3 h, respectively, whereas 90% degradation of PNP was achieved within 3 h.

There are two crucial factors that can assist TiO2 to work as a visible light active photocatalyst. The first one is the surface plasmon absorption of AuNPs in the visible region, which can be utilized for absorbing visible light. The second one is the position of the LSPR band which is located above the conduction band of TiO2. Under visible light absorption,
the plasmon-induced photoexcited electrons in the AuNPs of SiO₂@TiO₂/Au moved through the Au/TiO₂ interface into the conduction band of TiO₂. Then electrons in the conduction band of TiO₂ generated superoxide radicals, which can be used for the degradation of organic dyes.

Several highly active plasmonic photocatalytic nanostructures were fabricated and investigated by Tada et al. [31]. These nanostructures consisted of AuNP-loaded mesoporous (mp) titania thin films (Au/mp-TiO₂) coated on various conducting substrates. The material of a conducting substrate may be fluorine-doped tin oxide (FTO), indium tin oxide (ITO), Ti, Au and Pt. A similar nanostructure using a glass plate instead of conducting substrate was also used for comparison.

The UV–visible absorption spectra of Au/TiO₂ NPs, Au/mp-TiO₂/FTO and Au/mp-TiO₂/glass nanostructures were measured. Au/TiO₂ has a broad absorption peak around 570 nm due to the LSPR of the AuNPs. The electrochemical measurements were performed for obtaining information on the Au/mp-TiO₂/FTO–solution interface. A glassy carbon electrode and a Ag/AgCl electrode were used as counter electrode and reference electrode. As a test reaction, amine oxidation was carried out to evaluate the catalytic activities of three photocatalysts. It was observed that after 16 h irradiation were determined to compare the visible-light activities of three photocatalysts. It was observed that Au/mp-TiO₂/FTO exhibits a higher photocatalytic activity than Au/mp-TiO₂/glass and even Au/TiO₂ NPs. The yield after 16 h reaches ~100% in the case of the Au/mp-TiO₂/FTO nanostructure.

In order to clarify the origin of the high visible-light activity of Au/mp-TiO₂/FTO the authors studied the charge separation process by labeling and visualizing the reduction sites with Ag particles. They demonstrated that the electrons injected from AuNPs to the conduction band of TiO₂ by LSPR excitation were subsequently transferred to the FTO underlayer. The high conductivity of FTO enables the long-distance charge separation enhancing the Au/mp-TiO₂ photocatalytic activity.

As another test reaction, the visible-light activities of two different samples, Au/mp-TiO₂/FTO and Au/mp-TiO₂/glass under the irradiation at wavelength λ > 430 nm for selectively oxidizing cinnamyl alcohol to cinnamaldehyde were determined. It was shown that the photocatalytic activity of Au/mp-TiO₂/FTO is larger than that of Au/mp-TiO₂/glass by a factor of 2. It was also shown that the photocatalytic activity increases with the decrease of the TiO₂ particle size.

The effect of substrates on the activity for cinnamyl alcohol oxidation was investigated by using FTO, ITO, Ti, Au, Pt and glass as substrates for Au/mp-TiO₂. For comparison this oxidation process was also investigated on Au/mp-TiO₂ without a substrate. It was shown that the activity strongly depends on the kind of substrate, and the order is

\[ Pt > Au > Ti > IOT \approx \text{without substrate} > \text{FTO} > \text{glass}. \]

The most important structural feature of the present Au/mp-TiO₂-conducting substrate photocatalysts is the mesoporosity of the overlayer enabling the permeation of the reaction solution to the interface between the Au/mp-TiO₂ and substrate. At the interface of three phases (Au/mp-TiO₂–conducting substrate–solution) the electrons transferred from AuNPs to the conducting substrate through the conduction band of TiO₂ can reduce O₂ in the reaction solution, which is the rate-determining step in most photocatalytic reactions.

On the basis of the above-presented results the authors formulated the essential action mechanism of the fabricated plasmonic photocatalysts as follows. The LSPR excitation of Au/mp-TiO₂ caused the interfacial electron transfer from the AuNPs to the conduction band of mp-TiO₂. As a result of the lowering in the Fermi energy, the oxidation of amine and alcohol was induced on the Au surface. On the other hand, the electrons were subsequently transferred to the conducting substrate, and O₂ reduction occurred on the surface to complete the photocatalytic cycle.

In some earlier works [32–34] it was shown that the absorption of visible light by nanocomposites of the form Ag@AgX (X = Cl, Br, I) is significantly enhanced compared to that of AgX due to LSPR in metallic Ag. Exploiting this enhancement effect An, Wong et al. [35] fabricated the plasmonic nanocomposites of the form Ag@AgX@CNTs and for the first time observed the visible-light-driven photocatalytic inactivation of E. coli. The crystal phase composition, surface chemistry properties as well as surface structure of photocatalysts before and after use were characterized by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy. Photoluminescence (PL) spectra of samples were recorded by using a combined fluorescence lifetime and steady state spectrometer. As a comparison, light control was carried out in the absence of photocatalysts under visible light irradiation, and the bacterial population remained essentially unchanged after 60 min, meaning that there was no photolysis for the E. coli. As another comparison, in the dark control (with the presence of photocatalysts and without the light) the bacterial population also remained essentially unchanged after 60 min, indicating that there was no toxic effect caused to E. coli by the photocatalysts alone. There is a difference in disinfection performance of the different prepared nanocomposites: about 1.5 × 10⁷ cfu mL⁻¹ of E. coli could be completely inactivated within 40 min by Ag@AgBr@CNTs, 50 min by Ag@AgCl@CNTs and 60 min by Ag@AgI@CNTs.

The authors also studied the bacterial inactivation mechanism. The photocatalysis generates various reactive species (RSs) such as H₂O₂, O₂, OH, h⁺ and e⁻, which are potentially involved in the photocatalytic bacterial inactivation process. It was shown that the photocatalytic reaction was initiated by the absorption of visible light photons, leading to the generation of electron–hole pairs derived from both photoexcited AgX and plasmon-excited Ag nanoparticles:

\[ hv + AgBr \rightarrow e^- + h^+ + AgBr, \]
\[ hv + Ag \rightarrow Ag^+. \]

Then charge carriers transferred to the surface of CNTs. The effective charge separation was promoted, and a relatively high electron concentration was generated on the surface of the CNTs. The electrons could be trapped by \( O_2 \) and \( H_2O \) to form \( H_2O_2 \):

\[ O_2 + e^- \rightarrow *O^{2-}, \]

\[ *O^{2-} + H_2O \rightarrow *OOH + OH^-. \]

\[ 2*OOH \rightarrow O_2 + H_2O_2. \]

The RSs such as \( e^- \), \( h^+ \) and \( H_2O_2 \) could attack the \( E. coli \), disrupt the cell membrane and result in ultimate cell death:

\[ h^+, e^- + H_2O_2 + E. coli \rightarrow \text{organic debris of bacterial cells}. \]

### 4. Variety of plasmonic enhancement phenomena

In the preceding sections we have presented the plasmonic enhancement generated by the plasmon resonance in metal NPs and bimetallic composite NPs. Besides this basic effect, the coupling between different parts of certain assemblies can also generate complementary enhancement effects.

The plasmonic enhancement of the photoluminescence (PL) of quantum dots (QDs) coupled to Au microplates was investigated by Wu et al. [36]. These authors engineered the coupling between single CdSeTe/ZnS QDs and single Au microplates and studied the dependence of the PL properties of QDs on the separation distance between the surface of Au microplates and the center of QDs. By precisely controlling the thickness of the poly(methyl methacrylate) (PMMA) separating layer, the authors observed the gradual changes of the QD PL intensity and lifetime. Up to \( \sim 16 \)-fold PL enhancement was experimentally achieved when the separation distance was \( 18 \pm 1.9 \) nm and accordingly, the shortest PL was observed. In the investigation of the PL of QDs, a scanning confocal microscope system was used. The excitation source was a 532 nm solid state continuous wave laser. The PL light was collected by the microscope objective, and after special and spectral filtering was sent to a silicon avalanche photodiode single-photon detector for monitoring the intensity or to a spectrometer for spectrum analysis. The spontaneous emission decay lifetime of a single QD was measured using a time-correlated single-photon counter (TCSPT) when the excitation laser source was replaced by a frequency-double mode-locked pulsed Yb-doped fiber laser. It is worth noting that the QD PL was completely quenched when the QD was directly placed on the surface of the microplate.

In their interesting work Zhao et al [37] used the polarization-dependent dark-field technique to study the plasmon coupling in AgNP assemblies such as dimers and trimers. The Ag nanocubes were synthesized through a polylol method and high-quality Ag nanospheres were fabricated by etching the precursor of Ag nanocubes using ferric nitrate as the etchant. The uniform Ag nanocubes were perfect precursors for the fabrication of single crystalline and uniform Ag nanospheres. The Ag nanospheres were close to perfectly spherical in shape with a diameter of 85 (\( \pm 5.9\% \)) nm. More than 50% of Ag nanospheres were assembled into clusters, forming dimers, trimers, tetramers etc.

The scattering spectra of individual Ag nanospheres were recorded. The resonance wavelengths of the major peak at 453 \( \pm 6 \) nm originating from the light–plasmon interaction in Ag nanospheres were distributed in a narrow range, indicating that the Ag nanospheres were highly uniform. The charge of Ag nanospheres induced a charge distribution called image charge on the substrate and the interaction between each Ag nanosphere with its image charge gave rise to a side peak at 625 nm. Besides the major peak and the side peak, two scattering peaks located at \( \sim 460 \) and \( \sim 644 \) nm were observed in the scattering spectra. Besides the measurement of the intensities of the scattered lights, the authors also investigated their polarization dependence. In order to understand the physical mechanism of the observed phenomena the authors performed the theoretical calculation using the T-matrix [38] and discrete dipole approximation (DDA) [39] methods. It was shown that for the Ag nanosphere dimers, the maximal scattering intensity can be reached only when the polarization direction is aligned with the long dimer axis. For the Ag nanosphere trimers, three peaks were observed in the scattering spectra. Although the wavelengths of the two major peaks were very similar to those of the dimers, the profiles of scattering intensity for the trimers and dimers were different. Theoretical calculation using the T-matrix method demonstrated that only the assemblies with \( C_{2v} \) symmetry strongly coupled with the polarization of the electron field of incident light, while the assemblies with \( D_{3h}, D_{5h}, D_{4h} \) and \( D_{5h} \) symmetries did not. Calculations using the DDA method showed that slight deviations of NP shape away from perfect spheres resulted in extra peaks and polarization-dependence of scattering spectra, in good agreement with the experimental results.

In a subsequent work [40] Zhao et al fabricated uniform film of 120 nm AuNPs on a 3-aminopropyltriethoxysilane (APS)-coated glass substrate by means of a simple and reproducible method based on electrostatic interaction. The AuNP random arrays exhibited a blue-shifted narrow LSPR band compared to the LSPR of AuNPs in water as well as to that of single AuNPs on glass, in agreement with the results of theoretical studies using the T-matrix method [38]. The authors also demonstrated that not only the LSPR \( \lambda_{\text{max}} \), but also the LSPR width of the AuNP arrays, were sensitive to the changes in the dielectric media. The LSPR substrates were reproducible, uniform and robust against high electrolyte concentration and, therefore, may be used for LSPR width-based sensing and imaging applications.

The extinction spectra of the AuNPs in solution as well as the AuNPs immobilized on a glass substrate were measured by UV–visible spectroscopy. For comparison with AuNP random arrays on glass, scattering spectra of a single
AuNP was determined using a dark-field scattering microscope. Scattering spectra were corrected by signals collected from a nearby region without AuNPs and normalized by the lamp intensity profile. In the extinction spectrum of 120 nm AuNPs in solution the LSPR band is broad with a peak at the wavelength of 600 nm and the full width at half-maximum (FWHM) of 174 nm (0.61 eV). Then the AuNPs are immobilized on APS-treated glass, a narrow blue-shifted LSPR band spectrum was observed with a peak at 530 nm, and the FWHM of LSPR band is 84 ± 4 nm (0.36 ± 0.02 eV), a 52% decrease from that in the LSPR band of the AuNPs in solution.

The physical origin of the formation of narrow and blue-shifted LSPR bands of AuNP arrays, ordered as well as random, can be explained by means of theoretical calculations using the T-matrix method [38]. In previous works [41–43] it was shown that the long-range plasmon coupling in ordered NP arrays resulted in narrow and interparticle-distance-dependent plasmon resonance. Similar calculations have been performed in the present work to understand the origin of the narrow and blue-shifted LSPR band of the AuNP random arrays.

It is worth remarking that between the ordered and random AuNP arrays there is a major difference: the range of plasmon coupling between AuNPs is much longer in the ordered array than in the random array. The extinction of the ordered and random AuNP array depends on the interparticle distance (d). When d = 226 nm, i.e. twice the AuNP diameter, the plasmon coupling is dominated by neighboring AuNPs in both the ordered and random arrays and no difference exists in their extinction spectra. However, when d increases to 400 nm, the periodic plasmon coupling in the ordered array has a much longer range compared to the case with d = 226 nm. This long-range coupling is caused by the constructive interference between the scattered light from the AuNPs in the array. However, in the random array this long-range coupling is canceled due to the randomness of the AuNPs. The randomness shifts the AuNPs from their lattice position, changes the interparticle distance, and reduces the constructive interference of the scattered light. Therefore a slightly broadened extinction spectrum with lower peak intensity of the random array compared to that of the ordered array with d = 400 nm was observed. The difference becomes more prominent when d is further increased.

In the framework of classical electrodynamics Nguyen and Ngo [44] presented a clear and simple demonstration of the plasmonic enhancement near each individual NP as well as in some ordered networks of NPs.

First the authors considered a metallic spherical nanoparticle with the radius ρ and denoted by ε(ω), the effective dielectric constant or electric permittivity of the metallic material with respect to the electrical field in the monochromatic electromagnetic radiation with the angular frequency ω, by ε_m, that of the dielectric medium surrounding the metallic nanoparticle. It is known that the electrical field

\[ E^{(0)}(r, t) = e^{i(kr - ωt)}E^{(0)}, \]

\[ k = \frac{2π}{λ}, \]  

(7)

of the linearly polarized monochromatic incident light induces following electrical dipole moment \( p(R, t) \) inside the metallic spherical nanoparticle with the center located at some point \( R \) in the space

\[ p(R, t) = 4πε_m ρ^3 L(ω)E^{(0)}(R, t), \]

(8)

where

\[ L(ω) = \frac{ε(ω) - ε_m}{ε(ω) + 2ε_m}. \]

(9)

The induced electrical dipole moment located at some point \( R \) emits into the surrounding space the electromagnetic radiation

\[ A_{ind}(r, t) = -\frac{ik}{4πε_m}e^{ik|r - R|}p(R, t). \]

(10)

It follows that the induced electrical field \( E_{ind}(r, t) \) equals

\[ E_{ind}(r, t) = \frac{1}{4πε_m}e^{-iωt}e^{ikR}e^{ik|r - R|}\left\{ \left[ n \wedge p \wedge n \right] \frac{k^2}{|r - R|} + [3(np)n - p]\left( \frac{1}{|r - R|} - \frac{ik}{|r - R|} \right) \right\}, \]

(11)

where

\[ n = \frac{r - R}{|r - R|}. \]

(12)

At a point \( r \) very near to the metallic spherical nanoparticle, \( k|r - R| \ll 1 \), formula (11) has the following approximate form

\[ E_{ind}(r, t) = e^{-iωt}e^{ikR}3(np)n - p\frac{1}{|r - R|}. \]

(13)

In terms of the components \( E_{ind}(r, t)_α \) of \( E_{ind}(r, t) \) and the components \( p_α \) of the induced electrical dipole moment \( p \), formula (11) can be rewritten in the form

\[ E_{ind}(r, t)_α = \frac{1}{4πε_m}e^{-iωt}e^{ikR}\sum_β C_{αβ}(r - R)p_β, \]

(14)

where

\[ C_{αβ}(r - R) = δ_{αβ}\left[ \frac{k^2}{(|r - R|)^3} + \frac{ik}{(|r - R|)^2} - \frac{1}{|r - R|^2} \right] \]

\[ - n_α n_β \left[ \frac{k^2}{(|r - R|)^3} + \frac{3ik}{(|r - R|)^2} - \frac{3}{|r - R|^2} \right]. \]

(15)
Formulas (8), (9) and (11) show that the enhancement effect due to the presence of a metallic spherical nanoparticle with the diameter \( \rho \) depends on the value of the function \( L(\omega) \) expressed in terms of the electrical permittivity \( \varepsilon(\omega) \) of the metal at the photon energy \( h\omega \). From the experimental data on the \( \varepsilon(\omega) \) of gold we obtain the values of the real and imaginary parts of \( L(\omega) \) presented in figure 4.

For the evident expression of the relationship between the induced electric field \( \mathbf{E}_{\text{ind}}(\mathbf{r}, t) \) at a point \( \mathbf{r} \) outside the metallic spherical nanoparticle and the electric field \( \mathbf{E}^{(0)}(\mathbf{R}, t) \) of the incident light at the point \( \mathbf{R} \) coinciding with the center of the metallic spherical nanoparticle (when it is absent) we chose this center to be the origin of the coordinate system \( (\mathbf{R} = 0) \) and the vector \( \mathbf{r} \) to be parallel to \( \mathbf{E}^{(0)} \). Then from formulas (11), (12) and (14) we have

\[
E_{\text{ind}}(\mathbf{r}, t) = \chi(\omega, d) E^{(0)}(0, t),
\]

where \( d = r - \rho \). The values of real and imaginary parts of \( \chi(\omega, d) \) versus \( \omega \) for the metallic spherical nanoparticles with different radii at \( d = 0 \) and their maxima versus distances \( d \) for the sphere with \( \rho = 10 \) nm are shown in figure 5.

Then the authors studied the system of equations determining the enhanced electrical field in the spatial region surrounding a network of identical metallic spherical nanoparticles when this network is illuminated by a linearly polarized monochromatic light beam. Being induced by the electric field of the incident light, each metallic nanoparticle as a dipole moment itself emits electromagnetic radiation into the surrounding space. Therefore the total electric field at any point \( \mathbf{r} \) nearby but outside the metallic nanoparticles must be the superposition of the electric fields \( E_{\text{ind}}^{(i)}(\mathbf{r}, t) \) of the electromagnetic radiations emitted by other induced electrical dipole moments \( \mathbf{p}(\mathbf{R}_i, t) \), \( j \neq i \):

\[
\mathbf{E}^{(\text{tot})}(\mathbf{r}, t) = \mathbf{E}^{(0)}(\mathbf{r}, t) + \sum_{j=1}^{N} \mathbf{E}_{\text{ind}}^{(i)}(\mathbf{r}, t).
\]

This total electric field induces the electrical dipole moment

\[
\mathbf{p}(\mathbf{R}_i, t) = 4\pi\varepsilon_m\rho^3 L(\omega) \mathbf{E}^{(\text{tot})}(\mathbf{R}_i, t).
\]

The induced dipole moment (17) can be represented in the form

\[
\mathbf{p}(\mathbf{R}_i, t) = e^{i(k\mathbf{R}_i - \omega t)} \mathbf{p}^{(i)},
\]

with following components \( p_\alpha^{(i)} \) of the induced electrical dipole moments \( \mathbf{p}_\alpha \):

\[
p_\alpha^{(i)} = 4\pi\varepsilon_m\rho^3 L(\omega) E_\alpha^{(0)} + \rho^3 L(\omega) \sum_{j=1}^{N} e^{ik(\mathbf{R}_i - \mathbf{R}_j)} e^{i\mathbf{R}_i \cdot \mathbf{R}_j} \chi(\omega, \rho, \mathbf{R}_j, t) \chi(\omega, \rho, \mathbf{R}_j, t) \]

\[
\times \sum_{\beta} C_{\alpha\beta}(\mathbf{R}_i - \mathbf{R}_j) p_\beta^{(j)}.
\]

By solving the system of equation (21), one can find the functions \( p_\alpha^{(i)}(t) \) determining the components of the induced electrical dipole moments of all metallic spherical nanoparticles in the network.

Consider now some examples. The simplest case is a system of two identical metallic spherical nanoparticles with the radius \( \rho \) located at the distance \( l \) \((l \geq 2\rho)\). This system is called a dimer. We choose to work in such a Cartesian coordinate system that the centers \( \mathbf{R}_1 \) and \( \mathbf{R}_2 \) of two metallic spherical nanoparticles are located at two points with the coordinates \(-l/2 \) and \( l/2 \), respectively, in the axis \( \text{Oy} \) (figure 6), and consider the behavior of the dimer in the presence of a monochromatic incident electromagnetic field with the wave vector \( \mathbf{k} \) parallel to the axis \( \text{Oz} \). \( \mathbf{k}/\text{Oz} \).

It is straightforward to derive the system of equations for two induced electrical dipole moments \( \mathbf{p}^{(1)} \) and \( \mathbf{p}^{(2)} \) of two metallic spherical nanoparticles. If the incident electromagnetic wave is linearly polarized along the axis \( \text{Ox} \), then we have following system of equations

\[
\mathbf{p}^{(1)} = 4\pi\varepsilon_m\rho^3 L(\omega) E^{(0)} + \xi \mathbf{p}^{(2)},
\]

\[
\mathbf{p}^{(2)} = 4\pi\varepsilon_m\rho^3 L(\omega) E^{(0)} + \xi \mathbf{p}^{(1)},
\]

where

\[
\xi = 2\rho^3 L(\omega) e^{ikl}(1 - ikl).
\]

Its solution is

\[
\mathbf{p}^{(1)} = \mathbf{p}^{(2)} = \frac{1}{1 - \xi} 4\pi\varepsilon_m\rho^3 L(\omega) E^{(0)}.
\]

In comparison with formula (8) for the induced electrical dipole moment of a single metallic spherical nanoparticle there arises the factor \( 1/(1 - \xi) \). Similarly, if the incident electromagnetic wave is linearly polarized along the axis \( \text{Ox} \), then the induced electrical dipole moments \( \mathbf{p}^{(1)} \) and \( \mathbf{p}^{(2)} \) of two metallic spherical nanoparticles must satisfy following
system of equations

\[ p^{(1)} = 4\pi \varepsilon_0 \rho^3 L(\omega) E^{(0)} - \eta p^{(2)}, \]

\[ p^{(2)} = 4\pi \varepsilon_0 \rho^3 L(\omega) E^{(0)} - \eta p^{(1)}, \] (25)

where

\[ \eta = \frac{\rho^3}{l} L(\omega)e^{ikl} \left( 1 - ikl - k^2 \rho^2 \right). \] (26)

Its solution is

\[ p^{(1)} = p^{(2)} = \frac{1}{1 + \eta} 4\pi \varepsilon_0 \rho^3 L(\omega) E^{(0)}. \] (27)

In comparison with formula (8) now there arises the factor \(1/(1 + \eta)\).

The enhancement of the electrical dipole moment of each spherical nanoparticle due to the mutual influence of the other is characterized by the so-called enhancement factor \(F\) which is equal to \(1/(1 - \xi)\) in the case when their polarization direction (that of the electrical field \(E^{(0)}\)) is parallel to the \(Oy\) axis and is equal to \(1/(1 + \eta)\) in the case of polarization perpendicular to the \(Oy\) axis. The values of the complex values of the enhancement factor \(F\) for a dimer consisting of two identical metallic nanospheres with the radius \(\rho = 10\) nm and placed at the distance \(l = 25\) nm of their centers have been calculated on the basis of formulas (23) and (26). They depend on the photon energy \(h\omega\) and are plotted in figure 7(a) for both configurations of the arrangement of the polarization of the electrical field and the \(Oy\) axis. The picture of the dimer is presented in the inset of this figure. The dependence of the maximum values of the real and imaginary parts of the
enhancement factor $F$ for both configurations on the distance between the two centers of two metallic spherical nanoparticles is presented in figure 7(b).

The second simple example of a network of identical metallic sphere nanoparticles is a linear chain of equidistant ones with the centers located at the points $R_i = i\mathbf{l}$, $i$ being integers and $\mathbf{l}$ being some vector (figure 8). The center $R_0$ of one spherical nanoparticle is the origin of the coordinate system. Suppose that the wave vector $\mathbf{k}$ is perpendicular to the direction of the chain: $\mathbf{k}\cdot\mathbf{l} = 0$. In the case of the linearly polarized incident electromagnetic wave with the electrical field $E^{(0)}(\mathbf{r},t)$ parallel to the direction of the chain, the values $p^{(i)}$ of the induced electrical dipole moments are determined by the following system of equations

$$p^{(i)} = 4\pi\varepsilon_0\rho^3L(\omega)E^{(0)} + 2\rho^3L(\omega)\sum_{j=0}^{l-1} e^{ikl|\\mathbf{l}|}$$

$$\times \left( \frac{1}{|\\mathbf{l}|} - \frac{i k}{|\\mathbf{l}|^2} \right) p^{(j)}.$$  

For the infinite linear chain, due to the translational invariance of this chain, the solution of equation (28) is

$$p^{(i)} = p = \frac{1}{1 - \alpha} 4\pi\varepsilon_0\rho^3L(\omega)E^{(0)}.$$  

(29)

with

$$\alpha = 2\frac{\rho^3}{l^2}L(\omega)\sum_{j=0}^{l-1} e^{ikl|\\mathbf{l}|}(1 - ik|\\mathbf{l}|).$$

(30)

Similarly, in the case of the linearly polarized incident electromagnetic wave with the electrical field $E^{(0)}(\mathbf{r},t)$ perpendicular to the direction of the chain, $E^{(0)}(\mathbf{r},t) \perp \mathbf{l}$, we have the following system of equations

$$p^{(i)} = 4\pi\varepsilon_0\rho^3L(\omega)E^{(0)} - \rho^3L(\omega)\sum_{j=0}^{l-1} e^{ikl|\\mathbf{l}|}$$

$$\times \left( \frac{1}{|\\mathbf{l}|^2} - \frac{i k}{|\\mathbf{l}|} - \frac{k^2l^2}{|\\mathbf{l}|^2} \right) p^{(j)}.$$  

(31)

For the infinite linear chain its solution is

$$p^{(i)} = p = \frac{1}{1 + \beta} 4\pi\varepsilon_0\rho^3L(\omega)E^{(0)}.$$  

(32)

with

$$\beta = \frac{\rho^3}{l^2}L(\omega)\sum_{j=0}^{l-1} e^{ikl|\\mathbf{l}|} \left( \frac{1}{|\\mathbf{l}|^2} - \frac{i k}{|\\mathbf{l}|} - \frac{k^2l^2}{|\\mathbf{l}|^2} \right).$$

(33)

According to formulas (29) and (32) the enhancement factor $F$ is equal to $1/(1 - \alpha)$ in the case of the electrical field $E^{(0)}(\mathbf{r},t)$ parallel to the direction of the chain and is equal to $1/(1 + \beta)$ in the case of the electrical field perpendicular to the direction of the chain. The numerical calculations have been done for the chain consisting of 3, 7, 11 and 15 identical metallic spherical nanoparticles with the radius $\rho = 10$ nm and with the distance of the two nearest ones $l = 25$ nm. The photon energy $\hbar\omega$ dependent real (black) and imaginary (red) parts of the enhancement factor $F$ for both polarization configurations are plotted in figure 9.

The third network, which would be more often used, is that of a two-dimensional square lattice of identical metallic spherical nanoparticles with their centers located at the points $\mathbf{R}_{(i,j)} = (ie_x + je_y)\mathbf{l}$, $i$ and $j$ being integers, $\mathbf{e}_x$ and $\mathbf{e}_y$ being the
unit vectors along the coordinate axes $Ox$ and $Oy$, respectively, $l$ being the nearest distance between two spherical nanoparticles (figure 10). We write the dipole moment induced on the spherical metallic nanoparticle with the center located at the point $\mathbf{R}_{ij}$ in the form similar to the expression (20):

$$
\mathbf{p}(\mathbf{R}_{ij}, t) = e^{i(k\mathbf{R}_{ij} - \omega t)}\mathbf{p}_{ij}.
$$

(34)

For the definiteness we choose the center $\mathbf{R}_{(0,0)}$ of one spherical nanoparticle to be the origin of the coordinate system. Suppose that the wave vector $\mathbf{k}$ of the incident light is perpendicular to the plane of the network: $\mathbf{k}\mathbf{R}_{(0,0)} = 0$, and consider the case when the incident electromagnetic wave is linearly polarized and has the electrical field $\mathbf{E}^{(0)}(\mathbf{r}, t)$ parallel to the direction of the axis $Ox$. It is straightforward to derive following system of algebraic equations determining the
induced electrical dipole moments $p^{(ij)}$:  
\[ p^{(ij)} = 4\pi\varepsilon_0 L(\omega)E^{(0)} + \rho L(\omega) \sum_{\langle i',j' \rangle \neq \langle i,j \rangle} e^{i\mathbf{k} \cdot (\mathbf{R}_{i',j'} - \mathbf{R}_{i,j})} \]
\[ \times \left\{ \frac{n_{i,j}(i',j')p^{(ij)}(i',j')} - \frac{1}{\mathbf{R}_{i',j'} - \mathbf{R}_{i,j}} \right\} \]
\[ \times \left[ \frac{k^2}{\mathbf{R}_{i',j'} - \mathbf{R}_{i,j}} + 3 \left( n_{i,j}(i',j')k^2 \right) \right] \]
\[ \times n_{i,j}(i',j') \left( \frac{ik}{\mathbf{R}_{i',j'} - \mathbf{R}_{i,j}} \right)^2 \]
\[ \times \left\{ \frac{k^2}{\mathbf{R}_{i',j'} - \mathbf{R}_{i,j}} \right\} \]
\[ \text{where} \quad n_{i,j}(i',j') = \frac{\mathbf{R}_{i',j'} - \mathbf{R}_{i,j}}{\mathbf{R}_{i',j'} - \mathbf{R}_{i,j}} \]
\[ \text{(35)} \]

Due to the translational invariance of the infinite square lattice, the solution of the system of equation (35) for the network of infinite square lattice of identical metallic spherical nanoparticles becomes \[ p^{(ij)} = p = \frac{1}{\zeta - 1} 4\pi\varepsilon_0 \rho L(\omega)E^{(0)} \]
\[ \text{(37)} \]

The first term on the rhs of equation (38) is expression (30) of the constant $\alpha$ in formula (29) for the induced electrical dipole moment in the infinite linear chain of identical metallic spherical equidistant nanoparticles located in the real axis Ox, while the remaining terms are the contributions of all other linear chains different from that in the real axis Ox.

The photon energy $\hbar\omega$ dependent values of the real (black) and imaginary (red) parts of the enhancement factor $F$ (equal to $1/(1 - \xi)\omega$) of the square networks of $n \times n$ metallic spherical nanoparticles with $n = 3, 7, 11$ and 15 are presented in figure 11.

5. Discussions and conclusion

Besides the preparation of plasmonic photocatalysts by conventional methods, there have been attempts to improve the preparation method as well as increase interest in studying the correlation between physical characterizations and photocatalytic activities of Au/TiO$_2$ nanocomposite.

As an improvement to the conventional single-step (SS) photodeposition method, Kominami et al [45, 46] proposed the multistep (MS) photodeposition procedure in which the addition of metal sources and the photodeposition of metals on the semiconductor particles were repeated several times in order to obtain the desired loading. Kominami et al [47] applied this MS photodeposition method to prepare Au/CeO$_2$ nanocomposite exhibiting LSPR absorption stronger than that of a Au/CeO$_2$ nanocomposite prepared by the conventional SS method. The physical and photocatalytic properties of Au/CeO$_2$ nanocomposite prepared by both photodeposition methods were simultaneously determined for comparison.

It was shown that the average sizes of Au(1.0)/CeO$_2$ NPs prepared by the SS and MS photodeposition methods were 59 ± 4.9 nm and 92 ± 8 nm, respectively. These results indicated that the size of NPs of the above composite was strongly affected by the type of photodeposition method, and there was the tendency towards the formation of larger NPs by the MS photodeposition method. Au(X)/CeO$_2$ samples with various Au contents (X) were prepared for the study.

The authors have determined the average size $D_{Au}$, the number density $N_{Au}$ and the (calculated) external surface area $S_{Au}$ of AuNPs, and obtained following results:

- The $D_{Au}$ values of AuNPs in the samples prepared by both SS and MS methods increased with the increase of X and $D_{Au}$ values in the case of the MS method were always larger than those in the case of the SS method.
- The $N_{Au}$ values of the samples prepared by the SS method decreased with the increase of X until reaching the minimum at $X = 1.0$ and then further slightly increased, while those of the samples prepared by MS method were almost constant.
- The $S_{Au}$ values of the samples prepared by the MS method were always smaller than those of the samples prepared by the SS method, and they both increased with increasing X.

The photoabsorption spectra of the Au(1.0)/CeO$_2$ samples prepared by the SS and MS methods were recorded. A strong photoabsorption peak was observed around 550 nm in both spectra. This was attributed to LSPR of the supported AuNPs. It is worth noting that the samples prepared by the MS method exhibited photoabsorption much stronger than those prepared by the SS method. This result indicated that the intensity of the photoabsorption due to the LSPR of Au was affected by the size of the AuNPs. Similar results have been obtained in plasmonic Au/TiO$_2$ photocatalysts and AuNPs. It was interesting also to note that the photoabsorption property of the Au/CeO$_2$ samples matched with the wavelength of the light emitted from a green LED.

Photocatalytic oxidation of benzyl alcohol in aqueous suspensions of Au(1.0)/CeO$_2$ samples prepared by SS and MS methods under irradiation by green light from an LED was investigated. The authors have shown that the benzyl alcohol was completely consumed after 20 h for the case of the SS method and 15 h for the case of the MS method, and no CO$_2$ was detected in both cases during the photoirradiation. Moreover, benzaldehyde was formed with a quite high
selectivity (>99%) at >99% of benzyl alcohol, indicating that the benzyl alcohol was almost completely converted to benzaldehyde. The rates of benzaldehyde formation were determined to be 1.9 and 3.0 μmol h\(^{-1}\) for the samples prepared by the SS and MS methods, respectively. It was interesting to note that the samples prepared by the MS method exhibited relatively strong photoabsorption as well as photocatalysis even at around 600–700 nm.

The correlation between physical characterizations and photocatalytic activities of Au/TiO\(_2\) plasmonic photocatalysts was studied by Kominami et al.\[^{[48]}\]. For loading colloidal AuNPs on TiO\(_2\) supports the authors have applied four different methods: colloid impregnation (CI), colloid salting-out (CS), colloid photodeposition (CP) and colloid photodeposition with a hole scavenger (CPH). The conventional photodeposition with a hole scavenger (PH) was also used for comparing with the result of the CPH method. The amounts of Au loaded on TiO\(_2\) were determined by atomic absorption spectrometry after dissolving Au-loaded TiO\(_2\) samples with aqua regia. The composite Au/TiO\(_2\) having X wt% of Au was denoted Au(X)/TiO\(_2\). The diffuse reflectance spectra of the Au/TiO\(_2\) samples were recorded and their morphology was also observed. After a comprehensive study of the prepared samples, the authors have achieved interesting results:

- The size of the AuNPs was changed after Au loading on TiO\(_2\) by CI and CS methods, Au loading was insufficient when the CP method was used, fine AuNPs with the size of ca. 10–30 nm were observed by the PH method and colloidal AuNPs were quantitatively loaded without change in particle size only by using the CPH method. The absorption spectra of the Au(X)/TiO\(_2\) samples prepared by the CPH method with X changing up to 7 w% were attributed to LSPR of the AuNPs. The photoabsorption increased with increasing X. No clear changes in other physical properties such as crystalline phase and specific surface area were observed.
- The study of mineralization of formic, oxalic and acetic acids in an aqueous suspension of Au/TiO\(_2\) prepared by the CPH method showed that after irradiation by visible light, CO\(_2\) was evolved and the formation of CO\(_2\) continued almost linearly with irradiation time. On the other hand, no CO\(_2\) was formed in the control experiments, indicating that neither the photochemical reaction of organic acids in the absence of Au/TiO\(_2\) nor

Figure 11. Photon energy dependence of the complex enhancement factor \(F\) of the square networks of (a) \(3 \times 3\), (b) \(7 \times 7\), (c) \(11 \times 11\) and (d) \(15 \times 15\) metallic spherical nanoparticles with \(ρ = 10\) nm and distance of the two nearest ones \(l = 25\) nm \[^{[44]}\].
the dark reaction by Au/TiO₂ occurred. The rate of CO₂ evolution increased almost linearly with the amount of Au loading up to X = 3.5. Very large reaction rates were obtained when X > 5, then the rate tended to be saturated. Thus the activity of Au/TiO₂ plasmonic photocatalysts prepared by the CPH method can be controlled simply by the amount of Au loading.

From these scientific results we can conclude that during recent years the research on plasmonic photocatalysis has rapidly developed and has been highly successful. Various two-component as well as three-component nanocomposite plasmonic photocatalysts have been fabricated and effectively used for enhancing photocatalytic processes. Besides the plasmonic enhancement near the individual NPs, the plasmonic coupling between different parts of the assemblies can also generate complementary enhancement effects. It has also been shown that the improvement of the preparation method can result in the successful fabrication of photocatalysts with a higher quality.

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