Recent Advances on Plasmon-enhanced Titania Nanocatalysts for Photocatalytic Degradation of Organic Dyes

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Abstract

In the past several years, solar-driven photocatalytic degradation of organic dyes has been considered as one of the most promising and effective ways to address water pollution issues. Nevertheless, the implementation of such technology for large scale industrial wastewater application is still hampered by the limitation in currently used photocatalysts. Recently, plasmon-enhanced titania-based nanocatalyst has emerged as one of the promising photocatalytic materials for solar-driven wastewater treatment due to its excellent activity and ability to absorb a large portion of solar radiation. Therefore, this review highlights recent progress on applying such material for the photodegradation of organic dyes. In this review, the focus is placed on several mechanisms on how the surface plasmon resonance (SPR) phenomenon could enhance the photocatalytic activity of semiconductors, such as TiO\textsubscript{2}. Furthermore, the performance of several types of plasmon-enhanced titania nanocatalyst with different kinds of metal plasmonic nanoparticles, i.e., Au-TiO\textsubscript{2}, Ag-TiO\textsubscript{2}, and Pd-TiO\textsubscript{2}, is also compared and comprehensively discussed. Finally, a particular emphasis is also given to highlight the nanocatalysts’ kinetics in facilitating the photocatalytic degradation of different types of organic dyes.

Article History:
Received: 4 November 2020, Revised 6 December 2020, Accepted 8 December 2020, Available Online 30 December 2020
https://dx.doi.org/10.34311/jics.2020.03.3.117

Keywords: Metal nanoparticles, Photocatalyst, Photodegradation, Surface plasmon resonance, Titania

Acknowledgment
MK would like to gratefully acknowledge the financial support provided by the Directorate of Research and Development, Universitas Indonesia, under Hibah PUTI Saintekes 2020 (No. NKB-2420/UN2.RST/HKP.05.00/2020). GTMK acknowledges the financial support from the Asahi Glass Foundation 2020.
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Introduction

The scarcity of clean water supply has been considered as one of the main negative impacts resulting from fast growth in the human population and rapid industrialization advancement. In most cases, irresponsible discharges of organic and inorganic toxic materials into water bodies such as lakes, rivers, and oceans, are responsible for the severe environmental and water pollution problems [1]. In the last several decades, it is reported that the majority of water pollution in the various suburb and industrial areas was predominately caused by the presence of persistent organic pollutants (POPs), which could substantially harm aquatic ecosystems [2,3]. Recently, a great deal of effort has been made to solve these water pollution problems, such as using adsorption, filtration, coagulation, or biological approaches such as biological oxidation [4–6].
However, most of these techniques could not entirely remove certain types of POPs, such as azo-based dyes, due to their high chemical and thermal stabilities. Consequently, a more advanced technology that can thoroughly remove various kinds of organic pollutants still needs to be developed to provide a better solution for such water pollution issues.

During the past several years, treating wastewater via photocatalytic degradation has attracted much attention due to its efficiency for the complete removal of organic and inorganic water pollutants. Additionally, such technology could potentially be applied for large scale industrial wastewater treatment since it utilizes inexpensive and nontoxic metal oxides-based semiconductors as the catalyst. Among different types of these semiconductors, titanium dioxide (TiO$_2$) nanoparticles have been widely used as photocatalytic material for wastewater treatment [1,2,7]. This is not only because TiO$_2$ is widely known as cheap and nontoxic material but also has been proven to exhibit good photocatalytic ability to facilitate degradation of various organic pollutants and its excellent thermal dan chemical stability [8,9]. Nevertheless, TiO$_2$'s wide energy gap (~3.2 eV) and its fast electron-hole recombination process have been considered as one of the significant challenges for its potential application in large scale solar-driven wastewater treatment [10,11]. Besides, it is also reported the photoactivity of TiO$_2$ could often be further reduced due to the low dye absorption and the competition of light absorption with dye, especially at highly concentrated dye mixtures [12,13].

In literature, various strategies such as doping TiO$_2$ with both metal and nonmetal atoms to narrow its bandgap or integrating them with photosensitizers like organic dyes or metal complexes have been carried out to address the issues as mentioned earlier [14-16]. However, improving TiO$_2$'s photocatalytic activity by combining it with plasmonic particles has recently received plenty of attention due to its ability to significantly enhance TiO$_2$'s solar light-harvesting capacity efficiently reduce the rate of the electron-hole recombination process [17]. Therefore, this review aims to provide a comprehensive discussion on the recent advances in the application of plasmon-enhanced titania-based nanocatalysts for photocatalytic degradation of organic dyes. In this review, the mechanisms on how the surface plasmon resonance (SPR) phenomenon could enhance the photocatalytic activity of TiO$_2$ are firstly discussed. Furthermore, the performance of several types of heterostructured hybrid nanocatalysts, such as Au-TiO$_2$, Ag-TiO$_2$, and Pd-TiO$_2$, in both wastewater treatment and photodegradation of organic pollutants are also briefly highlighted. Here, the catalytic mechanism for each type of nanocatalysts is also provided. Finally, this review also provides a comprehensive comparison of the ability of this plasmon-enhanced catalytic system for the degradation of different types of organic dyes that are often found in various industrial wastes, such as methylene blue (MB), rhodamine B (RhB), and methyl orange (MO).

**Mechanism of Surface Plasmon Resonance (SPR)-enhanced Photocatalysis**

As mentioned earlier, the integration of plasmonic metal nanoparticles could be used to improve the photocatalytic activity of semiconductors due to the unique presence of the surface plasmon resonance (SPR) phenomenon. In general, the SPR phenomenon can be viewed as a collective and coherent oscillation of the conduction band electrons, which is induced due to the electromagnetic interaction field when the size of metal nanoparticles is much smaller than the wavelength of light [18,19]. Consequently, the metal nanoparticles can generate intense electric fields when irradiated with light that has a suitable plasmon frequency. Interestingly, this frequency can easily be tuned by simply synthesizing nanoparticles with different sizes, shapes, types of metals, and proximity to other nanoparticles in the system [18,20,21]. Among different types of metal plasmonic nanoparticles, Au, Ag, and Pd nanoparticles have been widely considered as one of the most common nanoparticles to be used to enhance the photocatalytic activity of TiO$_2$. In general, there are three major mechanisms on how the SPR phenomenon could help improve the photocatalytic activity of semiconductors, i.e., photo-induced charge transfer, near-field enhancement, and far-field enhancement (scattering) [17].

**Photo-induced charge transfer**

The enhancement of photocatalytic activity due to the plasmonic phenomenon via photo-induced charge transfer was first realized experimentally by Tian and Tatsuma after observing a significant enhancement in photon-to-current conversion efficiency (IPCE) of Au loaded TiO$_2$ under the
illumination of visible light [22,23]. Here, it is believed that the plasmon resonance phenomenon was able to excite electrons on Au nanoparticles, which could then be transferred to the conduction band of TiO$_2$. As a result, this electron transfer would cause the Fermi level equilibrium between the two materials. This is very similar to the mechanism of charge transfer in the Z-type heterojunction of semiconductors. Figure 1 shows the schematic illustration of the photo-induced charge transfer in Au-TiO$_2$ nanocomposites.

![Figure 1](image.png)

**Figure 1.** Schematic illustration of the proposed photo-induced charge transfer mechanism for the plasmon-enhanced photocatalytic activity of Au-TiO$_2$. Reproduced with permission from ref. [23], copyright 2005, American Chemical Society.

Nevertheless, it is also important to note that the plasmonic metal nanoparticles are not associated with a distinct energy separation such as HOMO-LUMO or analogous valence and conduction bands. This is primarily because the surface plasmon is made of a collection of charge density waves at the metal's surface. Therefore, all of the plasmonic charges are located at the metal's Fermi energy and unable to be used to drive any reduction or oxidation half-reactions [24]. However, a recent study suggested that the photochemical activity of plasmonic metal nanoparticles could be achieved by reducing their size into a few atom-metal clusters. For instance, Ag$_x$ and Au$_x$ clusters were experimentally proven to be photochemically active and exhibit well-defined light absorption and emission features with molecular-like excited-state properties [25–27]. At these very small plasmonic metal sizes, it is believed that the optical absorption cross-section of the metals becomes very limited, which causes their band structures to become discontinue and split into discrete energy levels [28].

**Near-field enhancement**

Another type of proposed mechanism on how plasmonic metal nanoparticles to enhance the photocatalytic activity of semiconductors is via near-field enhancement. In general, near-field enhancement can be viewed as the generation of an intense electric field called a “hot spot” near semiconductors’ surface due to the excitation of localized SPR of metal nanoparticles [17,29]. According to a recent electromagnetic simulation using a finite-difference time-domain (FDTD) method, it is found that electric field intensity at this “hot spot” region could reach up to 1000 times more than that of the incident electric field [30,31]. As a result, this would significantly increase the rate for the photogeneration of charge carriers in semiconductors since it is proportional to the local light intensity. Consequently, this would lead to the overall improvement of the semiconductors’ photocatalytic activity as more hot electrons and holes can be used to facilitate the reduction and oxidation half-reactions.

Additionally, the generation of this intense electric field due to the plasmonic phenomenon could also induce metal nanoparticles’ ability to act as a reservoir for the photogenerated electrons in the semiconductors [32,33]. As opposed to the previously discussed photo-induced charge transfer, it is believed that the photogenerated electrons at the conduction band of the semiconductors could also be transferred back into the metal nanoparticles. Hence, this would significantly reduce the rate of electron-hole recombination, ultimately enhancing the overall photocatalytic activity. The evidence for this electron storage ability by the plasmonic metal nanoparticles could experimentally be noticed by the blue-shift of the surface plasmonic frequency. For instance, Khalil and co-workers observed that the maximum wavelength due to SPR ($\lambda_{SPR}$) of Au-TiO$_2$ was shifted to 530 nm from the $\lambda_{SPR}$ of pristine Au nanoparticles, which was observed at 545 nm [1]. It is reported that such a phenomenon was believed primarily because the potential energy of TiO$_2$’s conduction band is less positive than the Fermi level of Au nanoparticles (0.75 V vs. NHE) [34].

**Far-field effect (scattering)**

Plasmonic nanoparticles could also enhance the photocatalytic activity of semiconductors due to their excellent scattering efficiency. This effect is also known as the far-field effect [17]. In general, the far-field effect is generated due to the increase in the average path length of photons as a result of the multiple reflections of light caused by the light scattering by plasmonic metal nanocrystals. Here,
plasmonic metal nanoparticles are believed to be able to scatter a portion of resonant photons that are not absorbed by the semiconductors and give rise to the enhancement in light absorption [35]. In other words, the plasmonic metal nanoparticles are essentially acting like a mirror that can reflect and scatter light. Therefore, unlike the previous two mechanisms, the far-field effect could only be observed at metal nanoparticles that are relatively large enough to produce intense light scattering [36].

Plasmon-enhanced Titania Nanocatalysts

Au-TiO:

Gold (Au) is a unique element that has vast coordination types and organometallic chemistry. Albeit gold exhibits a weak affinity towards molecules due to the high ionization potential, downsizing it into nanoscale could generate an active surface for the catalytic reaction of various organic molecules, including the photodegradation of dyes [37–39]. The dawn of the gold nanoparticles (Au NPs)-based catalysis was begun in the 1970s for the oxidation of carbon monoxide using supported Au NPs catalyst. The catalytic performance of Au NPs in various reactions could be dramatically increased when the size is reduced to less than 10 nm. Au NPs exhibit a broad spectrum of absorption in UV and visible regions, which could be utilized to drive the chemical reaction on the surface of Au NPs. Tsivadze and co-workers studied the fine structure of plasmon bands in Au NPs [40]. They revealed the presence of low energy plasmons of 1.14 eV, 2.7 eV, and 6.5 eV corresponding to 5δp6s3(ΔD(2s)), 5δp6s2(ΔD(2s)), and 5δs5p 6s1/2 6p1/2 electronic excitation of the gold element, respectively. Moreover, the bulk plasmon energy of 25.4 eV is originated from the combined oxidation states of gold ions within the core of Au NPs.

The crucial aspect of Au NPs is that it exhibits the surface plasmon resonance (SPR) at around 520 nm to 570 nm because of the collective coherent oscillation of the free- electron conduction band electrons confined within the single nanoparticle [11,29,41,42]. The electron oscillation induces a charge separation to generate a dipole oscillation along with the propagation of the electric field of light. The SPR causes a strong absorption of the incident light in the UV and visible light regions; thus, detectable by the UV-Vis spectrometer. In recent years, supported Au NPs have attracted significant attention as the heterogeneous catalyst for the photocatalytic decomposition of organic pollutants in the aqueous environment [43–47]. Among various supports, TiO2 has shown notable photocatalytic activity towards the degradation and mineralization of organic pollutants. The major issues of TiO2 are its wide band gap and intense recombination of photogenerated charge carriers, which prevent the maximum photocatalytic performance. Several methods have been attempted to reduce the bandgap within TiO2, such as ion doping, metal complexes, hybridization with a narrow bandgap semiconductor, and modification with noble metal nanoparticles [7].

The modification of TiO2 with Au NPs is attractive since it can facilitate the photocatalytic reaction under UV and visible light irradiation. Under UV light irradiation, the valence band’s electron could be excited to the conduction band producing holes and electrons pair. The recombination of holes and electrons is suppressed due to the electron transfer from the TiO2 conduction band to Au NPs via the Schottky barriers. This is possible since the Fermi energy level of Au and other noble metals is below the TiO2 conduction band’s energy level. The photoexcited electron can be captured by the Au NPs, whereas the holes are maintained in the TiO2 valence band. As a result, the production of superoxide and hydroxyl radicals could be enhanced, leading to increased photocatalytic performance. On the other hand, the SPR behavior is responsible for the photocatalytic enhancement under visible light irradiation. The excited SPR electron is injected into the TiO2 conduction band. It should be noted that holes are not formed so that the photogenerated charge carrier’s recombination is disallowed. The photoexcited electron is transferred to adsorbed O2 leading to the formation of superoxide and hydroxyl radicals. The schematic illustration of the role of Au NPs is depicted in Figure 2.

Generally, the UV light’s photocatalytic reaction is faster than that under visible light since the UV absorption generates more electron injections from Au NPs to the oxygen molecule than the visible light absorption does. The surface of Au NPs is highly electronegative and able to capture electrons corresponding to the positive charge in the electronic band of Au NPs. Under UV light irradiation, the positive charge of Au NPs is located in the lower 5d band and facilitating the oxidation of the hardly degraded molecules, such as phenol. Meanwhile, the visible light absorption leads to the positive charge in the 6sp band, which can capture electrons from the easily oxidized molecules, e.g., methanol and dyes.
To maximize the photocatalytic performance of Au/TiO$_2$, one should engineer the composite materials’ architecture. For example, the anatase/rutile phase junction of TiO$_2$ is preferred for the charge separation. Meanwhile, one-dimensional TiO$_2$ nanostructures (nanorods or nanowires) have shown remarkable photocatalytic performance with distinguished charge transport properties. Recently, Wu and co-workers reported nanorod TiO$_2$ structures with branched nanowire arrays leading to the formation of a distinct morphology, so-called nanoforest, with anatase/rutile phase junctions [49]. Decorating this unique TiO$_2$ with Au NPs considerably enhances the photocatalytic performance under UV and visible light irradiation. Au NPs are preferably located at the anatase/rutile phase junctions, which also play a crucial role in increasing the photocatalytic performance. Figure 2c shows the schematic illustration to synthesize the TiO$_2$ nanoforest decorated with Au NPs.

**Ag-TiO$_2$:**

Ag/TiO$_2$ nanostructures have been reported as highly active photocatalytic composite materials. Ag NPs could play a role as an electron capturing material, which restricts the electron-hole recombination due to the formation of the Schottky barrier at Ag-TiO$_2$ junctions. Moreover, there is an increasing interest in the utilization of Ag NPs because their notably high oxygen adsorption reactivity could enhance the photocatalytic performance. Kassiba and co-workers reported that the number of photo-induced charge carriers and electron-hole recombination lifetimes are the fundamental parameters that dictate the photocatalytic performance of TiO$_2$ [50]. A reduction of the bandgap was demonstrated due to the Ag NPs decoration on the surface of TiO$_2$ leading to improved visible light absorption and better photocatalytic activity. This positive impact of Ag NPs was generated by surface plasmon resonance of Ag NPs, which are strongly interacted with the semiconductor surface.

Barrientos et al. reported the growth of Ag NPs on TiO$_2$ using mercaptoacetic acid as a bridging agent, which allowed the chemical bond of Ag NPs and TiO$_2$ [51]. As a result, the heterojunction was substantially improved, and the transmission of photoexcited electrons was enhanced. Moreover, the presence of an organic linker helped the formation of spherical Ag NPs within the size of 10–50 nm exhibiting strong SPR behavior. The presence of Ag NPs significantly reduced the bandgap energy of TiO$_2$ from 3.20 eV (UV region) to 2.60 eV (visible region). Besides, there was an increment of the photoresponse properties of the Ag/TiO$_2$, which prevent the recombination of electron-hole pair leading to better photocatalytic performance.

Hoefelmeyer and co-workers reduced silver nitrate solution using oleylamine and 1,2-hexadecanediol in the presence of oleic acid-stabilized anatase TiO$_2$ nanorods resulting in the generation of Ag-TiO$_2$ hybrid nanocrystals (HCNs) [52]. The number and size distribution of Ag NPs could be tailored based on the Ag:TiO$_2$ ratio in the synthesis mixture and the choice of the reducing agent. This reported method resulted in ultrasmall Ag NPs having a size of around 1.5 nm to 4 nm with ca. 2 to 5.5 Ag NPs in a single TiO$_2$ nanorod. Vandarkhuzali et al. also reported the synthesis of ultrasmall Ag NPs decorated on hierarchical mesoporous TiO$_2$ [53]. The size of Ag NPs was around 3 nm, uniformly distributed on mesoporous
TiO₂ matrices (Figure 3). Upon UV-Vis light irradiation, the Fermi energy level of the ultrasmall Ag NPs and the TiO₂ begin to equilibrate the electron migration from the TiO₂ conduction band to Ag NPs due to their electron capturing nature. The Fermi energy level of ultrasmall Ag NPs is significantly shifted to a more negative potential, leading to enhancing the interfacial charge-transfer process. Thus, the number of the active holes in the photocatalytic system could be increased as a result of the reduction of the electron density in the TiO₂ conduction band. Furthermore, the injected electrons on the surface of Ag are transferred to the oxygen molecules to generate strong oxidative radicals, which are highly effective in the degradation of dyes.

Figure 3. Ag–TiO₂: HNCs synthesized from 4:1 oleylamine/1,2-hexadecanediol reducing agents. (a) TEM image and size distribution of Ag NPs, (b) X-ray diffraction patterns, (c) UV–visible spectra, and (d) photoluminescence emission spectra (λc = 300 nm) of TiO₂ nanorods and Ag–TiO₂: HNCs. Reproduced with permission from ref. [53], copyright 2019 American Chemical Society.

Pd-TiO₂

Similar to Au and Ag NPs, Pd NPs have been utilized to increase the photocatalytic performance on the TiO₂ surfaces by preventing the electron-hole recombination. The photoexcited electrons flow to the Pd NPs because of their relatively low Fermi energy level, which renders the holes stable by significantly prolonging the charge carriers’ lifetime. Hence, more hydroxyl and superoxide radicals are produced to increase the photocatalytic performance. Wu et al. reported that the TiO₂ bandgap could be reduced as a function of the Pd amount [54]. Pristine TiO₂, 0.05% Pd/TiO₂, and 0.1% Pd/TiO₂ possess a bandgap of 3.2 eV, 3.14 eV, and 3.12 eV, respectively. They found that the photocatalytic performance of Pd/TiO₂ was higher than that of pristine TiO₂ under white light irradiation because of, at least, two following reasons; (i) Pd addition reduces the TiO₂ band gap leading to the easy electron-hole pairs excitation on Pd/TiO₂ than TiO₂ surface. The active radicals are produced faster on Pd/TiO₂ to promote the degradation and mineralization reactions; (ii) Pd metal has been shown to enhance the ability of electron migration from valance band to Pd metal and suppress the electron-hole pair recombination. The large population of photogenerated holes might facilitate the generation of more active radicals and ultimately increase the degradation rate.

Photocatalytic Degradation of Organic Dyes

Methylene blue

In general, methylene blue (MB) is widely used in coloring fabrics in the garment industry. MB is a group of azo compounds that are difficult to degrade by microorganisms. Hence, the photocatalytic degradation process is a promising method that is expected to treat MB. For example, Harifi and Montazer used Fe³⁺:Ag-TiO₂ to degrade methylene blue compounds, but this study requires a long time for the degradation process [55]. The reaction time needed to degrade MB until 99% was 540 minutes. Then, Rather et al. modified titania with Ag and Cu as plasmonic materials. This result shows a significant difference from the previous study where -TiO₂ and Cu-TiO₂ managed to degrade MB reach up to 99 and 96%, respectively [56]. Furthermore, the crystal modification and morphology of TiO₂ were also developed by Khalil and co-workers to form unique morphology like nanospindles and nanocubes [1]. According to the report, the nanocatalysts were to degrade MB up to 100% with a fast reaction time of 60 minutes. The development of Au and Ag as plasmonic materials to the enhanced titania performance attracted many researchers to make several modifications with a different metal. In another report, Kallel et al. synthesized (Ag,Y)-TiO₂, which was able to degrade MB up to 93% for 120 minutes [57]. Table 1 shows the photocatalytic performance of nanocatalysts for MB photodegradation.
Plasmon Enhanced TiO₂ Photodegradation of MB Using Plasmonic Catalysis

Several researchers have also studied the kinetics model in the degradation of MB with plasmon-enhanced titania nanocatalysts. Table 2 summarizes several kinetic studies related to the comparison of different types of nanocatalysts in the photodegradation of MB. In general, the most suitable kinetics model for the degradation reaction of MB was pseudo-first-order. Additionally, it is also evident that the reaction rate for the photodegradation of MB using plasmon-enhanced titania-based nanocatalysts was superior to the reaction catalyzed by non-plasmonic metal-doped TiO₂.

### Table 2. Kinetic study of MB degradation over plasmon-enhanced titania nanocatalysts.

<table>
<thead>
<tr>
<th>Nanocatalysts</th>
<th>$k_{app}$ (h⁻¹)</th>
<th>$R^2$</th>
<th>Kinetic Model</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>0.021</td>
<td>0.99</td>
<td>Pseudo-first-order</td>
<td>[57]</td>
</tr>
<tr>
<td>Y-doped TiO₂</td>
<td>0.062</td>
<td>0.99</td>
<td>Pseudo-first-order</td>
<td>[57]</td>
</tr>
<tr>
<td>Ag-doped TiO₂</td>
<td>0.075</td>
<td>0.98</td>
<td>Pseudo-first-order</td>
<td>[57]</td>
</tr>
<tr>
<td>(Y,Ag)-doped TiO₂</td>
<td>0.348</td>
<td>0.97</td>
<td>Pseudo-first-order</td>
<td>[57]</td>
</tr>
<tr>
<td>Fe³⁺/TiO₂</td>
<td>1.014</td>
<td>0.94</td>
<td>Pseudo-first-order</td>
<td>[55]</td>
</tr>
<tr>
<td>Ag/TiO₂</td>
<td>0.876</td>
<td>0.95</td>
<td>Pseudo-first-order</td>
<td>[55]</td>
</tr>
<tr>
<td>Fe³⁺:Ag/TiO₂</td>
<td>2.124</td>
<td>0.93</td>
<td>Pseudo-first-order</td>
<td>[55]</td>
</tr>
</tbody>
</table>

### Rhodamine B

Rhodamine B (Rhb) is an organic dye that is also one of the most commonly used dyes in the garment industry. In literature, many previous studies have been carried out to develop plasmon-enhanced titania-based materials as a photocatalyst to degrade RhB. Table 3 presents the performance of several nanocatalysts that have been successfully utilized in the photodegradation of RhB. For example, Mahlambi and co-workers were able to efficiently degraded RhB with photodegradation efficiency up to 97% at considerably short reaction time using various types of plasmon-enhanced titania nanocatalysts [59]. According to the report, photocatalysts with thin-film structure showed slightly lower activity in removing RhB than the corresponding nanoparticles. This phenomenon is primarily due to the variation in the available active sites for facilitating the reaction.

### Table 3. Summary of the photocatalytic performance of plasmon-enhanced titania nanocatalyst for RhB degradation under visible light irradiation.

<table>
<thead>
<tr>
<th>Nanocatalysts</th>
<th>Bandgap (eV)</th>
<th>Efficiency (%)</th>
<th>Reaction Time (mins)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>n/a</td>
<td>20</td>
<td>300</td>
<td>[59]</td>
</tr>
<tr>
<td>Ag(1%)-TiO₂</td>
<td>2.98</td>
<td>96</td>
<td>300</td>
<td>[59]</td>
</tr>
<tr>
<td>Co(1%)-TiO₂</td>
<td>2.89</td>
<td>97</td>
<td>300</td>
<td>[59]</td>
</tr>
<tr>
<td>Ni(1%)-TiO₂</td>
<td>2.98</td>
<td>90</td>
<td>300</td>
<td>[59]</td>
</tr>
<tr>
<td>Pd(1%)-TiO₂</td>
<td>2.93</td>
<td>97</td>
<td>210</td>
<td>[59]</td>
</tr>
<tr>
<td>Ag-TiO₂ (thin film)</td>
<td>2.98</td>
<td>96</td>
<td>390</td>
<td>[60]</td>
</tr>
<tr>
<td>Co-TiO₂ (thin film)</td>
<td>2.89</td>
<td>97</td>
<td>390</td>
<td>[60]</td>
</tr>
<tr>
<td>Pd-TiO₂ (thin film)</td>
<td>2.98</td>
<td>94</td>
<td>390</td>
<td>[60]</td>
</tr>
<tr>
<td>Ni-TiO₂ (thin film)</td>
<td>2.93</td>
<td>85</td>
<td>390</td>
<td>[60]</td>
</tr>
<tr>
<td>Ag-TiO₂ (n/a)</td>
<td>95</td>
<td>300</td>
<td></td>
<td>[61]</td>
</tr>
</tbody>
</table>

Furthermore, kinetics studies also revealed that most of the photocatalytic degradation of RhB
follows a pseudo-first-order due to a physisorption mechanism that indicates an adsorption process on the surface of the nanocatalyst. Here, RhB degradation is believed to be initiated by its physical adsorption on nanocatalysts, where it would then react with the available photogenerated holes from the TiO$_2$ valence band or reactive oxygen species (ROS) such as hydroxyl radical (•OH) produced from the water oxidation. Table 4 shows the kinetic parameters obtained from the kinetic studies on the application of plasmon-enhanced titania nanocatalysts in the photodegradation of RhB.

**Table 4.** Kinetic study of RhB degradation over plasmon-enhanced titania nanocatalysts under visible light irradiation.

<table>
<thead>
<tr>
<th>Nanocatalysts</th>
<th>$k_{app}$ (h$^{-1}$)</th>
<th>Kinetic Model</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.049</td>
<td>Pseudo-first-order</td>
<td>[59]</td>
</tr>
<tr>
<td>Ag (1%)-TiO$_2$</td>
<td>0.732</td>
<td>Pseudo-first-order</td>
<td>[59]</td>
</tr>
<tr>
<td>Co (1%)-TiO$_2$</td>
<td>0.732</td>
<td>Pseudo-first-order</td>
<td>[59]</td>
</tr>
<tr>
<td>Ni (1%)-TiO$_2$</td>
<td>0.930</td>
<td>Pseudo-first-order</td>
<td>[59]</td>
</tr>
<tr>
<td>Pd (1%)-TiO$_2$</td>
<td>1.080</td>
<td>Pseudo-first-order</td>
<td>[59]</td>
</tr>
<tr>
<td>Ag-TiO$_2$ thin film</td>
<td>0.552</td>
<td>Pseudo-first-order</td>
<td>[60]</td>
</tr>
<tr>
<td>Co-TiO$_2$ thin film</td>
<td>0.612</td>
<td>Pseudo-first-order</td>
<td>[60]</td>
</tr>
<tr>
<td>Ni-TiO$_2$ thin film</td>
<td>0.354</td>
<td>Pseudo-first-order</td>
<td>[60]</td>
</tr>
<tr>
<td>Pd-TiO$_2$ thin film</td>
<td>0.498</td>
<td>Pseudo-first-order</td>
<td>[60]</td>
</tr>
</tbody>
</table>

Methyl orange

Methyl orange (MO) is a chemically and thermally stable azo compound, which is often widely used as a synthetic dye in the garment industry. Recently, MO’s photodegradation is commonly done via the advanced oxidative process (AOP), where plasmon-enhanced titania nanocatalysts are used as the catalytic materials. For instance, Vandarkuzhali et al. synthesized mesoporous TiO$_2$-based materials combined with Ag and Au for efficient photodegradation of MO [52]. According to the report, Ag-TiO$_2$ and Au-TiO$_2$ with mesopores structure have a higher photodegradation efficiency with shorter reaction times. It is believed that this superiority was mainly due to the suitability of the size of the methyl orange molecule with the pore size of TiO$_2$. Meanwhile, Bathla and co-workers also utilized CuO-TiO$_2$ material with several morphological forms of TiO$_2$ such as stars, needles, and crumbles [62]. Based on the result, it was found that CuO-TiO$_2$ nanostars have the highest photodegradation efficiency with a reaction time of 480 minutes. Table 5 summarizes the performance of some plasmon-enhanced titania nanocatalysts for the degradation of MO.

**Table 5.** Performances of plasmon-enhanced titania nanocatalysts for MO degradation under visible light irradiation.

<table>
<thead>
<tr>
<th>Nanocatalysts</th>
<th>Bandgap (eV)</th>
<th>Efficiency (%)</th>
<th>Reaction Time (mins)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>3.16</td>
<td>54</td>
<td>60</td>
<td>[53]</td>
</tr>
<tr>
<td>Au-mesoporous TiO$_2$</td>
<td>2.99</td>
<td>91</td>
<td>60</td>
<td>[52]</td>
</tr>
<tr>
<td>Ag-mesoporous TiO$_2$</td>
<td>3.05</td>
<td>80</td>
<td>60</td>
<td>[52]</td>
</tr>
<tr>
<td>CuO-TiO$_2$ nanostars</td>
<td>n/a</td>
<td>99</td>
<td>480</td>
<td>[62]</td>
</tr>
<tr>
<td>CuO-TiO$_2$ nanoneedles</td>
<td>n/a</td>
<td>83</td>
<td>480</td>
<td>[62]</td>
</tr>
<tr>
<td>CuO-TiO$_2$ nanocrumbles</td>
<td>n/a</td>
<td>65</td>
<td>480</td>
<td>[62]</td>
</tr>
</tbody>
</table>

Besides, Vandarkuzhali et al. also performed kinetics studies to further evaluate the performance of both Ag-TiO$_2$ and Au-TiO$_2$ for photodegradation of MO in various photocatalytic conditions, i.e., under sunlight and UV irradiation. Based on the result, it is revealed that the synergistic effect between the surface plasmon resonance from metal plasmonic nanoparticles and the mesoporous structures was responsible for the enhancement of TiO$_2$’s photocatalytic activity. This is mainly due to the ability of metal plasmonic nanoparticles (Au and Ag nanoparticles) to facilitate an additional absorption of light energy at the visible range. At the same time, the mesoporous structure of titania was believed to be responsible for the increment of methyl orange adsorption and facilitates methyl orange by providing a larger active surface area. Based on the
surface area analysis, it was reported that the surface area of TiO$_2$. Au-mesoporous TiO$_2$. Ag-mesoporous TiO$_2$ were found to be 173, 160, 153 cm$^2$/g, respectively. Furthermore, the result also demonstrated that the apparent reaction rate ($k_{app}$) under the illumination of solar radiation for both photocatalysts was found to be higher than that of under UV irradiation. Table 6 shows the kinetic parameters of both Ag-TiO$_2$ and Au-TiO$_2$ for MO removal under different photocatalytic conditions.

**Table 6.** Kinetic parameters of both Ag-TiO$_2$ and Au-TiO$_2$ photocatalysts for MO removal under different photocatalytic conditions.

<table>
<thead>
<tr>
<th>Nanocatalysts</th>
<th>$k_{app}$ (h$^{-1}$)</th>
<th>Kinetic model</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>1.072</td>
<td>Pseudo-first-order</td>
<td>[53]</td>
</tr>
<tr>
<td>Ag-TiO$_2$ (solar irradiation)</td>
<td>2.278</td>
<td>Pseudo-first-order</td>
<td>[52]</td>
</tr>
<tr>
<td>Au-TiO$_2$ (solar irradiation)</td>
<td>3.178</td>
<td>Pseudo-first-order</td>
<td>[52]</td>
</tr>
<tr>
<td>Ag-TiO$_2$ (UV irradiation)</td>
<td>1.198</td>
<td>Pseudo-first-order</td>
<td>[52]</td>
</tr>
<tr>
<td>Au-TiO$_2$ (UV irradiation)</td>
<td>1.620</td>
<td>Pseudo-first-order</td>
<td>[52]</td>
</tr>
</tbody>
</table>

**Conclusion and Future Directions**

In summary, a review for the recent progress on the enhancement of the photocatalytic activity of titania nanocatalysts for the degradation of organic pollutants via surface plasmon resonance phenomenon has been presented in this article. This review highlighted the three most essential mechanisms on how metal plasmonic nanoparticles are responsible for enhancing semiconductor’s photocatalytic activity, *i.e.*, photo-induced charge transfer near-field enhancement and far-field effect due to scattering. In general, the integration of plasmonic nanoparticles into the surface of TiO$_2$ could serve not only to broaden its light absorption ability to the visible region but also to prevent the fast recombination of photogenerated electrons and holes. Moreover, several plasmon-enhanced titania nanocatalysts’ performance in photocatalytic degradation of organic dyes has also been discussed in this article. In most cases, Au, Ag, and Pd nanoparticles have been considered as the most common plasmonic nanoparticles to be used in this regard. This is primarily due to their high thermal and photostability, excellent photoactivity, and ability to be produced in various sizes and shapes in a controlled manner. Finally, it is also found that the kinetics of most of these plasmon-enhanced titania nanocatalysts for photodegradation of different organic dyes such as MB, RbB, and MO follows a pseudo-first-order model.

**Conflict of interest**

The authors declare no conflict of interest in this study.

**References**


