Research Article

Efficient Degradation of Methylene Blue over Two-Dimensional Au/TiO₂ Nanosheet Films with Overlapped Light Harvesting Nanostructures

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Two-dimensional TiO₂ nanosheet films with visible light trapping nanostructures were successfully fabricated by alkali hydrothermal reaction using Ti sheet as precursor. Metallic Au nanoparticles (NPs) were then deposited on the surface of TiO₂ film through a microwave-assisted reduction process. The investigations reveal that the localized surface plasmon resonance (LSPR) of Au NPs is greatly enhanced by the overlapped light harvesting nanostructures between TiO₂ film and Au NPs, resulting in an enhanced LSPR-absorption with two peaks at 389 nm and 540 nm. The photocatalytic performance of the samples was evaluated by degradation of methylene blue (MB) as a model pollutant. The experimental results indicate that the photocatalytic performance of TiO₂ is greatly promoted by a synergetic effect between the overlapped light harvesting nanostructures and the improved charge carrier separation processes. The MB degradation over the optimal sample is much faster than that of pure TiO₂ film by a factor of 3.0 and 5.7 under UV light and UV + visible light irradiation, respectively. This study provides a simple strategy to develop film-shaped plasmonic photocatalysts with high efficiency.

1. Introduction

Since the discovery of hydrogen evolution by photoinduced water splitting over TiO₂ electrode [1], semiconductor-based photocatalysis has attracted great attention in the field of solar energy conversion and environment remediation [2–9], and considerable efforts have been dedicated to the design of various semiconductor photocatalysts with improved performance. TiO₂-based semiconductors with good chemical stability and environmental-friendly features have received far more attention in the field of photocatalytic water splitting, reduction of CO₂ with H₂O to form hydrocarbon fuels, and wastewater treatment by photodegradation of organic pollutants [10–15]. However, its utilization is negatively affected by the high recombination probability of photoexcited electron-hole pairs and its relatively large band gap (Eg = 3.2 eV). The latter makes TiO₂ without visible light (λ > 400 nm) activity, resulting in a poor solar energy utilization. As a consequence, intense research activities have been devoted to the development of visible light active TiO₂ with high photocatalytic efficiency, such as surface photosensitization, element doping, semiconductor combination, and structural control [16–28].

In 2008, Awazu et al. observed that the photocatalytic behavior of TiO₂ was greatly boosted by the localized surface plasmon resonance (LSPR) of Ag NPs during photocatalytic decomposition of methylene blue (MB) [29]. The enhancement is attributed to the enhanced near-field amplitudes of LSPR from Ag NPs. This enhanced near field could boost the excitation of electron-hole pairs in TiO₂ and result in an improved photocatalytic activity. It immediately sparked a surge of research into plasmonic photocatalysis, especially noble Ag and Au contained systems [30–38]. Further investigations reveal that the localized surface plasmonic resonance and the Schottky junction are two prominent features of plasmonic metal/semiconductor composites [39]. The former contributes to the strong absorption of visible light and the excitation of active charge carriers, whereas the latter facilitates charge separation and transfer, and they work together to achieve higher photocatalytic efficiency.
Although much work has been done to investigate LSPR-enhanced photocatalysis, the enhancement mechanism is still under debate. Jose et al. observed that the localized electric field created by Au NPs could not induce charge carriers in the near-surface region of TiO$_2$, because the LSPR-absorption of Au NPs does not overlap with the TiO$_2$ absorption [40]. The LSPR-absorption band of Au NPs is usually larger than 500 nm, and the overlap between the absorption of TiO$_2$ and LSPR-absorption of Au NPs is very weak, leading to a relative poor photocatalytic activity. Ingram et al. observed that N-doping could improve the optical overlap between TiO$_2$ and Ag NPs, and Ag-loaded N-TiO$_2$ composite exhibited much higher visible activity [41, 42]. Later, an enhanced photocurrent in a thin-film iron oxide photoanode coated on arrays of Au nanopillars was observed by Gao et al. [43]. The enhancement was attributed primarily to the increased optical absorption originating from both surface plasmon resonances and photonic-mode light trapping in the nanostructured topology. Their study provides an applicable solution to concentrating light in the active regions of semiconductors. In order for efficiency energy and charge transfer to take place between the metal NPs and the semiconductor photocatalyst, it is important that the spectral enhancement of the metal NPs overlaps with the spectrum absorption of the semiconductor photocatalyst. This is crucial factor for reaching maximum plasmon enhancement [41]. To the best of our knowledge, the investigation on enhanced light trapping in metal/semiconductor systems has not received much attention.

In this work, Au/TiO$_2$ nanosheet film was successfully fabricated through a joint hydrothermal method and microwave-assisted reduction process. This film-shaped photocatalyst can eliminate the necessity of inconvenient filtration processes required by powdered catalysts, suggesting attractive perspectives for on-site utilization. More importantly, an overlapped light harvesting phenomenon was observed in Au/TiO$_2$ composite film due to the unique nanostructures of TiO$_2$ film and LSPR of Au NPs. We found that the overlapped light harvesting nanostructures can greatly enhance the LSPR-absorption of Au NPs and improve the photocatalytic activity of Au/TiO$_2$ system.

2. Experiment

2.1. Preparation of Au/TiO$_2$ Nanosheet Films. Au/TiO$_2$ nanosheet films were fabricated through a joint hydrothermal method and microwave-assisted reduction process. The detailed experimental process is shown in Figure 1. First, TiO$_2$ film was obtained via a one-step hydrothermal method described in our previous study [44]. In detail, surface polished Ti sheet (99.5% purity, 2.1 mm × 4.2 mm × 0.5 mm) was immersed and sealed in a 100 mL Teflon-lined vessel containing NaOH aqueous solution (50 mL, 1 mol·L$^{-1}$) and then maintained at 180°C for 24 h. Subsequently, the sheet was cleaned with water and immersed in 0.25 wt% HCl aqueous solutions for 24 h and then washed with water again. Finally, it was annealed at 450°C for 2 h to obtain TiO$_2$ nanosheet film.

Au NPs were deposited on the surface of TiO$_2$ film by a microwave-assisted reduction process in PVP-DEG solution medium inspired by Park's work [29]. First, polyvinylpyrrolidone (PVP) was dispersed in diethylene glycol (DEG) and stirred vigorously to give a transparent solution (solution A). Meanwhile, HAuCl$_4$·4H$_2$O was dissolved in water and kept stirring in dark for use (solution B). Subsequently, solution B was poured into solution A and kept stirring for 20 min to obtain solution C. Thereafter, pure TiO$_2$ film was immerged into the above solution C, and then they were exposed to microwave irradiation. Finally, Au/TiO$_2$ film was obtained after washing the sheet with water and ethanol for several times. The obtained samples were denoted as xAu/TiO$_2$, with x representing the millimolar concentration of Au$^{3+}$ in reaction solution. In this work, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 Au/TiO$_2$ films were prepared by changing the concentration of HAuCl$_4$·4H$_2$O precursor.

2.2. Characterizations and Photocatalytic Activity Test. The crystalline phases and morphologies of the samples were characterized by a Shimadzu XRD-6000 powder diffractometer and a scanning electron microscopy (SEM, JEOL JSM-6390A). The UV-Vis diffuse reflectance spectra were obtained on a Shimadzu UV-3600 UV/vis/NIR spectrophotometer with an integrating sphere detector, and BaSO$_4$ was used as the reflectance standard material. Besides, photoluminescence (PL) spectra were investigated on Hitachi F-7000 fluorescence spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed by Kratos AXIS NOVA spectrometer. Photocatalytic degradation of MB was carried out in an outer irradiation-type quartz reactor, which irradiated using a 300 W Xe-lamp (Beijing Perfectlight Technology Co. Ltd., China, Microsolar300UV, ultraviolet light: 6.6 W, visible light: 17.6 W, and the light flux about 3400 lm). Two filters were employed to achieve UV light (UVREF, λ < 400 nm) and visible light (UV/CEPT400, λ > 400 nm) irradiation, respectively. The system was shielded by a black box during...
the reaction to prevent interference from outside light. The film was immersed in 100 mL MB aqueous solution (10 mg/L, the pH value of MB solution is about 6.3) and air was bubbled through the system continuously. It was kept in the dark for 1 h prior to irradiation for establishing adsorption-desorption equilibrium. At different times, the absorbance of MB solution was determined using a Shimadzu UV-3600 spectrophotometer. The concentration variation of MB was obtained according to the concentration-absorbance relationship (λ = 664 nm).

3. Results and Discussion

3.1. Characteristics of the Photocatalysts. The crystalline phases of the samples were investigated by XRD (Figure 2). All the peaks can be indexed using the Ti substrate (JCPDS file No: 65-6233), anatase TiO\(_2\) (JCPDS file No: 21-1272), rutile TiO\(_2\) (JCPDS file No: 21-1276), and metallic Au (JCPDS file number: 65-2870), respectively. The content of rutile TiO\(_2\) is very low and it has very little effect on the UV-Vis absorption of TiO\(_2\) (see Figure 5). Besides, the introduction of Au NPs does not affect the phase structure of TiO\(_2\) film. The signals around 44.6° and 64.6° are attributed to metallic Au NPs, they can only be observed in the samples with a higher Au concentration. Aside from XRD analysis, the existence of Au NPs is also observed by SEM, XPS and UV-Vis investigations below (Figures 3 to 5).

Figure 3(a) presents a typical SEM image of pure TiO\(_2\) film, which is composed by a large number of continuous distributed TiO\(_2\) nanosheets, which are hard to detach from the Ti substrate. This is beneficial for the practical utilization of film-shaped photocatalysts. Figure 3(b) shows a typical SEM image of Au modified TiO\(_2\) film. It can be observed that lots of spherical nanoparticles are uniformly deposited on the surface of the sheets. This two dimensional nanosheet with a rough surface can provide more active sites for the adsorption of reactant molecules, and the photogenerated charge carriers can effectively contribute to the chemical reactions on the surface. It is also worth noting that the density of Au NPs can be effectively regulated by changing the initial concentration of HAuCl\(_4\)-4H\(_2\)O according to Figures 3(c)–3(h), indicating that the microwave-assisted reduction process is a good method to deposit Au NPs. However, Au NPs with a relatively bigger size is observed when a higher concentration of HAuCl\(_4\)-4H\(_2\)O employed (Figure 3(h)).

The components and chemical status of the films were investigated by XPS. As shown in Figure 4, the signals of Ti 2p, O 1s, Au 4f and C 1s (data not shown) are detected. XPS spectrum of Ti 2p displays two peaks at 458.7 eV and 464.4 eV in Figure 4(a), they are assigned to Ti 2p\(_{3/2}\) and Ti 2p\(_{5/2}\) spin-orbit components of Ti\(^{4+}\) [45]. The signal at 530.0 eV is attributed to the lattice oxygen of TiO\(_2\) in Figure 4(b) [46]. Figure 4(c) shows the Au 4f XPS spectrum with two peaks at 83.4 eV and 87.0 eV for Au 4f\(_{7/2}\) and Au 4f\(_{5/2}\), respectively, suggesting Au species are in metallic Au\(^0\) state in the composites. The relative negative shift (0.6 eV) of Au 4f\(_{5/2}\) peak with respect to bulk Au (4f\(_{5/2}\) peak at 84.0 eV) may be caused by the electron redistribution (from TiO\(_2\) to Au) at the contact interface when their Fermi levels are aligned [47]. Further investigations reveal that the chemical state of Au NPs is maintained after the reaction (Figure 4(c)).

Figure 5 shows a comparison of UV-Vis diffuse reflection absorption spectra of P25 (a kind of widely used commercial TiO\(_2\) photocatalyst), pure TiO\(_2\) film and Au/TiO\(_2\) films. Aside from an enhanced UV light absorption compared with P25, the as-prepared TiO\(_2\) film also exhibits excellent visible light trapping property due to its unique nanostructures. It is usually attributed to the scattering of light caused by pores or cracks in the film [46, 48–50]. Those pores or cracks may function as “black hole” to trap the incident light (Figure 3(f)). The absorption of pure TiO\(_2\) film in UV light region shows a clear absorption edge shorter than 390 nm due to the intrinsic band gap absorption of anatase TiO\(_2\) (E\(_g\) = 3.2 eV). It is worth mentioning that the TiO\(_2\) films loaded with Au NPs show a broad absorption in the visible region, this originates from the outstanding light trapping property of Au NPs for their LSPR effect. The absorption intensity of Au/TiO\(_2\) films increases with increasing the initial concentration of HAuCl\(_4\)-4H\(_2\)O, which can lead to more Au NPs deposited on the TiO\(_2\) surface (Figures 3(c)–3(h)). In addition, the photographs of the samples under natural sunlight exhibits a distinct color change from gray to dark red after the loading of Au NPs (not shown here). This is in line with the UV-Vis absorption spectra of the samples in Figure 5.

3.2. Photocatalytic Activities of MB Degradation. The degradation of MB was firstly conducted under UV light and visible light irradiations without filters, the elections and holes play very important roles during the degradation. The adsorbed dye molecules can be oxidized directly due to the strong oxidizing property of active holes on the surface of catalyst. The excited electrons trapped by oxygen molecule can form \(\cdot O_2^-\) and \(\cdot OH\) active radicals and they can also oxidize dyes. As shown in Figure 6(a), all the Au/TiO\(_2\) films exhibit higher activity for MB degradation than for pure TiO\(_2\) film.
Figure 3: SEM images of (a) pure TiO$_2$ film, (b) Au modified TiO$_2$ film, and the magnification of (c) 0.1 Au/TiO$_2$, (d) 0.2 Au/TiO$_2$, (e) 0.3 Au/TiO$_2$, (f) 0.4 Au/TiO$_2$, (g) 0.5 Au/TiO$_2$, and (h) 0.6 Au/TiO$_2$ films.
(about 50% of MB is degraded), and the degradation efficiency increases with increasing the content of Au NPs, indicating that Au NPs has a great effect on the performance of TiO$_2$ film. However, the increase is no longer apparent when Au NPs are over deposited. The degradation percentage of MB is almost the same over 0.5 Au/TiO$_2$ and 0.6 Au/TiO$_2$ after long-term irradiation, and about 97% of MB can be degraded after 2h irradiation. Although 0.6 Au/TiO$_2$ exhibits good visible light harvesting property (Figure 5), the adsorption-desorption of MB may be the rate controlling process at the end of the degradation. A pseudo-first-order kinetic model was employed to fit the degradation data by using the following equation: $-\ln(C/C_0) = kt$ ($k$ is the kinetic constant) [13, 16, 51]. Figure 6(b) shows the degradation rate constant $k$ of MB over different samples, and 0.6 Au/TiO$_2$ film shows the highest catalytic activity with a $k$ of 0.0287 min$^{-1}$, about 5.7 times higher than that of pure TiO$_2$ film ($k = 0.0050$ min$^{-1}$).

To further reveal the roles of Au NPs, the experiment was conducted over pure TiO$_2$ and 0.6 Au/TiO$_2$ films under UV light and visible light irradiations, respectively. The experimental results are presented in Figure 7. Under UV light irradiation, 0.6 Au/TiO$_2$ film exhibits higher activity than that of pure TiO$_2$ film, the corresponding degradation percentage is 66% and 38% after 2h of irradiation, and $k$ of 0.6 Au/TiO$_2$ film is 0.0086 min$^{-1}$, about 3.0 times higher than that of pure TiO$_2$ film ($k = 0.0029$ min$^{-1}$). This is because the Schottky junction between Au and TiO$_2$ can facilitate charge separation. The work function of Au ($\Phi = 5.1$ eV) is higher than anatase TiO$_2$ ($\Phi = 4.2$ eV). Hence the generation probability of electrons from anatase TiO$_2$ under UV irradiation and their transfer to the Au NPs is high [52], and it is similar to Ag/TiO$_2$ systems [53–55]. The electrons transfer from the conduction band of TiO$_2$ to Au NPs can reduce the recombination chance of electrons and holes, facilitating the photoreaction process. It is verified by the PL spectra in Figure 8. The emission peaks around 467 nm and 397 nm are due to the radioactive recombination of photogenerated electron-hole pairs [56, 57]. Fluorescence quenching is observed after Au deposition under the excitation of 220 nm. This can be attributed to
Figure 6: (a) The normalized concentration of MB over different samples under UV light and visible light irradiations; (b) the corresponding kinetics of MB degradation (where $C$ is the concentration of MB at the irradiation time $t$ and $C_0$ is the concentration of adsorption equilibrium with the catalyst before irradiation).

Figure 7: The normalized concentration of MB over pure TiO$_2$ and 0.6 Au/TiO$_2$ films under UV light irradiation and visible light irradiation, respectively.

Figure 8: PL spectra of pure TiO$_2$ and 0.6 Au/TiO$_2$ films under the excitation of 220 nm (PMT voltage: 650 V).

the effective capture of photoexcited electrons by Au NP, leading to lower emission intensity.

Under visible light irradiation, the unique nanostructures of TiO$_2$ film can enhance the MB photosensitization by trapping the visible light and accelerate the degradation process, and 23% of MB is degraded over pure TiO$_2$ film after 2 h irradiation. Compared with the pure TiO$_2$ film, 0.6 Au/TiO$_2$ film exhibits a relatively higher photocatalytic performance and 49% of MB is degraded after 2 h irradiation. This is benefit from the overlapped visible light absorption between Au NPs and TiO$_2$ film. On the one hand, the MB photosensitization over pure TiO$_2$ film may be improved by Au NPs under visible light irradiation due to LSPR-absorption, by which the light energy can be effectively coupled into MB molecule and promote photosensitization. On the other hand, the activity of Au/TiO$_2$ composites under visible light may result from the LSPR effect of Au NPs. It has been proven that LSPR-absorption of Au NPs can generate plasmon induced
photoexcited electrons with a more negative potential at the Au NPs, they can inject into the conduction band of TiO\textsubscript{2} and trigger photoreaction [39, 58, 59]. Besides, the LSPR-absorption of Au NPs may activate TiO\textsubscript{2} to generate photoexcited electrons and holes directly under visible light irradiation [39, 60].

On the basis of above results, we believe that the overlapped light harvesting nanostructures of Au/TiO\textsubscript{2} films play an important role in the improved visible light photoactivity. The LSPR-absorption of Au NPs on the surface of TiO\textsubscript{2} film can give valid evidence, which exhibits a broad response ranging from 350 nm to 750 nm with two peaks at 389 nm and 540 nm in Figure 9(a). It is different to the narrow LSPR-absorption of Au NPs in the solution (Figure 9(b)). This is because Au NPs and TiO\textsubscript{2} film are responsive to visible light simultaneously, and the incident light captured by TiO\textsubscript{2} film is overlapped with the LSPR-absorption of Au NPs in the visible light range. This overlapped harvesting phenomenon suggests a strong interaction between Au NPs and TiO\textsubscript{2} film and implies that they can work as a visible-light-driven photocatalyst. The absorption peak at 389 nm may be related to the bang gap of anatase TiO\textsubscript{2}, which shows a clear absorption edge shorter than 390 nm. The light (\(\lambda < 390\) nm) captured by TiO\textsubscript{2} film can be used to generate charge carriers, and the rest of the captured light (\(\lambda > 390\) nm) can be reused by Au NPs due to the overlapped light harvesting nanostructures, leading to an enhanced LSPR-absorption (Figure 9(a)). Therefore, the improved optical overlap between the absorptions of TiO\textsubscript{2} film and Au NPs is the main cause for the enhanced LSPR-absorption of Au NPs. The enhanced light absorption in the visible light region can improve the activity of TiO\textsubscript{2} by increasing the quantities of photoexcited charge carriers or by enhancing the energy of trapped electron.

The stability of the photocatalysts is essential to the practical applications. The photocatalytic stability of the 0.6 Au/TiO\textsubscript{2} film was evaluated by cycling degradation experiments and the corresponding results are shown in Figure 10. It can be seen clearly that 0.6 Au/TiO\textsubscript{2} film maintains an efficient and stable photocatalytic activity even after five cycles. The XPS spectra shown in Figure 4 indicate that there is an inappreciable change of the chemical state and the content of Au nanoparticles in the composite before and after cycling.
photodegradation experiments. All these analyses indicate that Au/TiO$_2$ film possesses high activity and stability.

3.3. The Enhancement Mechanism of Photocatalytic Degradation of MB. A tentative photocatalytic mechanism is proposed and schematically illustrated in Figure II. (i) Under UV light irradiation, the Schottky junction between Au NPs and TiO$_2$ can facilitate charge separation, leading to an enhanced photocatalytic activity. (ii) Under visible light irradiation, on the one hand, LSPR-induced electrons in Au NPs can transfer from Au NPs to TiO$_2$ and trigger photo-reaction. On the other hand, the LSPR effect of Au NPs is induced by the visible light, forming a strong local electronic field to enhance the energy of trapped electrons, making them transfer and react with electron acceptors more easily. In any case, the enhanced LSPR-absorption is positive for the photocatalytic process. (iii) Overlapped light harvesting nanostructures can provide a strong interaction between Au NPs and TiO$_2$ film, and visible light trapped by TiO$_2$ can be reused by Au NPs, leading to an enhanced LSPR-absorption. Besides, the overlapped absorption may be also beneficial for the MB photosensitization. Based on what has been observed and discussed above, it is reasonable to conclude that the enhanced photocatalytic activity could be attributed to the charge transfer property of Au NPs and the efficient light utilization based on the overlapped light harvesting nanostructures of composite film. As shown in Figure 6(b), the highest MB degradation rate is obtained under UV and visible light irradiations, which results from the synergetic effect between charge transfer and overlapped light harvesting properties in Au/TiO$_2$ composite.

4. Conclusion

A novel visible light responsive plasmonic Au/TiO$_2$ films with two dimensional nanosheet structures were successfully fabricated by the combination of a hydrothermal process and a microwave-assisted reduction route. The prepared samples exhibit an obviously overlapped light absorption due to the localized surface plasmon resonance of Au NPs and unique nanostructures of TiO$_2$ film. The light trapped by TiO$_2$ nanosheet film can be reused by the LSPR of Au NPs. The MB degradation over 0.6 Au/TiO$_2$ film is much faster than that of pure TiO$_2$ film by a factor of 5.7 under UV light and visible light irradiations. The improved activity of Au/TiO$_2$ composite is ascribed to the charge transfer property of Au NPs and the overlapped light harvesting nanostructures. A synergy between charge transfer and overlapped absorption can greatly enhance the degradation efficiency of MB. This study suggests a simple strategy to develop LSPR-enhanced photocatalysis systems with film-shaped nanostructures and high efficiency.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


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