Article

Silver@mesoporous Anatase TiO₂ Core-Shell Nanoparticles and Their Application in Photocatalysis and SERS Sensing

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Abstract: Nanostructured noble metal-semiconductor materials have been attracting increasing attention because of their broad application in the field of environmental remediation, sensing and photocatalysis. In this study, a facile approach for fabricating silver@mesoporous anatase TiO₂ (Ag@mTiO₂) core-shell nanoparticles employing sol-gel and hydrothermal reaction is demonstrated. The Ag@mTiO₂ nanoparticles display excellent surface-enhanced Raman scattering (SERS) sensitivity and they can detect the methylene blue (MB) molecules with the concentration of as low as 10^{−8} M. They also exhibit outstanding photocatalytic activity compared with mTiO₂, due to the efficient separation and recombination restrain of electron–hole pairs under ultraviolet light. The Ag@mTiO₂ nanoparticles also present good stability and they can achieve recyclable photocatalytic degradation experiments for five times without loss of activity. Subsequently, the nanoparticles with dual functions were successfully used to in situ monitor the photodegradation process of MB aqueous solution. These results, demonstrating the multifunctional Ag@mTiO₂ nanoparticles, hold promising applications for simultaneous SERS analysis and the removal of dye pollutants in environmental field.

Keywords: photocatalytic degradation; surface-enhanced Raman scattering; TiO₂; Ag nanoparticle; core-shell

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1. Introduction

With the expansion of the manufacturing industry, there is an increase in the total amount of organic pollutants. In particular, organic dye pollutants are highly soluble in water exhausted by printing sewage, paper mills and leather manufacture [1,2]. In addition, various pathogens, such as bacteria, virus, and microbes in dye wastewater may react with the organics, which will lead to more harmful contaminations and even produce toxicity. Their accumulation in the environment has caused substantial damage to the aquatic ecosystem and poses a threat to human safety, as they may lead to chronic or immediate illness [3]. For the purpose of treating dye contaminations in wastewater, their accurate detection [4–6] and degradation are one of the expressed problems to be solved. Different kinds of physical, chemical and biochemical measures have been devoted to deal with these problems, including membrane separation [7], advanced oxidation [8], photocatalytic degradation [9,10] and anaerobic treatment [11]. Among them, photocatalysis technique employed in wastewater treatment has great promise, because it can create strong oxidation agents to break down organic matters into carbon dioxide and water. In addition, this simple process has no need for sophisticated equipment or expensive cost. It is observed that TiO₂, as a semiconductor, has received a great deal of attention, owing to its excellent photocatalytic activity, good chemical inertia, thermal stability and non-toxicity, as well as biocompatibility and low cost [12,13]. Nevertheless, as a single component, TiO₂ has a low capacity to exploit solar energy due to its intrinsically wide bandgap, which is

3.2 eV [14,15]. In order to advance photocatalyst applications and meet more functional requirements, modifications of TiO_2 forming a heterostructure are being investigated. Many research groups demonstrated the beneficial effects of the integration of noble metals in TiO_2 -based photocatalysts, such as Au, Ag, Pt and Pd [16–21]. Cheng et al. [22] fabricated 3D Ag/ZnO bifunctional composite, acting as a SERS-active substrate and photocatalyst, to detect and degrade organic dye pollutant. Wang et al. [23] prepared Ag/GO/ TiO_2 nanorod arrays that displayed excellent photocatalytic properties and SERS sensitivities. Their SERS enhancement factor was determined to be as high as 5.86×10^5 and was employed to degrade rhodamine 6G under solar light illumination.

In addition, the morphology of nanomaterials is also an important factor to promote photocatalytic property [24–26]. Yolk-shell structured $\text{Fe}_3\text{O}_4@\text{TiO}_2$ as a Photo-Fenton-like catalyst, which contains the Fe_3O_4 core inside a void space surrounded by a TiO_2 shell, has been developed for the highly efficient elimination of tetracycline, because of its high and specific surface area and abundant active reaction sites [27]. Du et al. [28] prepared $\text{Au}@\text{TiO}_2$ hollow microspheres with controllable size and shell thickness; their photocatalytic activity increased by 30% compared with that of P25. Zhao et al. [29] synthesized sea urchin-like $\text{Fe}_3\text{O}_4@\text{TiO}_2@\text{Ag}$ nanocomposites with tunable cavity sizes. The hybrid via localized surface plasmon resonance (LSPR) absorption of noble metals enhanced the bandgap absorption of TiO_2 ; the special structure also provided many active sites for redox reactions during the photocatalysis. More importantly, mesoporous TiO_2 has larger specific surface area and relatively large pore volume compared with the amorphous structure, which can ensure large enrichment capability and high mass transport efficiency [30]. However, there are few reports on the photocatalytic performance of the mesoporous TiO_2 shell-coated Ag($\text{Ag}@\text{mTiO}_2$), which may also provide a great quantity of active sites as well as “hot spots” for different usages.

In this report, the $\text{Ag}@\text{mTiO}_2$ core-shell nanostructures are fabricated; they are composed of an Ag core and a mesoporous TiO_2 shell. The TiO_2 shell is capable of protecting Ag from corrosion and the mesoporous morphology may adsorb many target molecules, while also being beneficial for the Ag core to exhibit its local surface plasmon resonance effect. The nanocomposites served not only as SERS substrates, but also as reusable photocatalysts, and were successfully applied to the in situ SERS monitor photocatalytic degradation process of organic dyes.

2. Experiment

2.1. Chemicals

Acetonitrile ($\text{C}_2\text{H}_6\text{N}$, AR), trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, AR), silver nitrate (AgNO_3 , 99.0%), methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$), ethanol (EtOH , 99.7%) and ammonia ($\text{NH}_3 \cdot \text{H}_2\text{O}$, 28%) were obtained from Sinopharm Chemical Reagent Co. Ltd. Shanghai, China. Titaniumbutoxide (TBOT, 98%), methylene blue ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \cdot 3\text{H}_2\text{O}$) and rhodamine 6G ($\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3\text{Cl}$, 95%) were bought from Aladdin Reagent Co. Ltd. Shanghai, China. All chemicals were applied without any purification. Deionized water purified by a Millipore-Q System ($18.2 \text{ M}\Omega/\text{cm}$) was used in all experiments.

2.2. Preparation of Ag Nanoparticles

Ag nanoparticles were prepared using a similar approach to the previous report [21]. A total of 90 mg of solid AgNO_3 were charged into 250 mL of deionized water and heated to a boil. Afterwards, 10 mL of trisodium citrate (1 wt%) aqueous solution were introduced into the above solution and boiled at 100°C for an hour. Then, the reaction solution was cooled to room temperature by an ice bath. The resultant Ag nanoparticles were obtained by centrifuging at 8000 rpm for 10 min. Finally, the prepared Ag nanoparticles were dispersed in 10 mL of deionized water to obtain the concentration of 0.5 mg/mL for the following experiments.

2.3. Synthesis of Ag@TiO₂ Core-Shell Nanoparticles

The Ag@TiO₂ nanoparticles were synthesized according to the following method. In a typical experiment, 2 mL of the prepared Ag dispersion solution, 35 mL of acetonitrile, 105 mL of ethanol and 0.5 mL of ammonia were introduced into a 250 mL glass beaker. The mixture was magnetically stirred for 20 min. After that, 0.5 mL of TBOT was dissolved in 15 mL of ethanol and 5 mL of acetonitrile, and then the mixed solution was slowly added into the above reaction solution. The reaction was allowed to proceed for 1.5 h at room temperature under continuous magnetic stirring. The resultant products were collected and washed 3 times using ethanol by centrifuging at 6000 rpm, and finally dispersed in 5 mL of ethanol for further use.

2.4. Preparation of Ag@mTiO₂ Nanoparticles

Ag@TiO₂ nanoparticles were subjected to a simple hydrothermal process to obtain Ag@mTiO₂ nanoparticles. In a typical procedure, 5 mL of the prepared Ag@TiO₂ nanoparticles were mixed with 10 mL of deionized water and 20 mL of ethanol. After ultrasonication for 5 min, the mixture was sealed into a Teflon-lined stainless-steel autoclave (100 mL capacity). The autoclave was heated at 160 °C for 8 h. Then, it was allowed to naturally cool to room temperature. The resulting products were collected and washed using ethanol by centrifuging for several times. Finally, the prepared Ag@mTiO₂ nanoparticles were dispersed in 5 mL of deionized water for further examinations.

2.5. Photocatalytic Property of Ag@mTiO₂ Nanoparticles

The photocatalytic activity of the nanoparticles was investigated by the degradation of methylene blue aqueous solution at ambient conditions under ultraviolet lamp light. A commercial Hg lamp (350 W, CEAULIGHT, Beijing, China) with $\lambda \approx 254$ nm (light intensity of 12 mW/cm²) was used to supply this light. Specifically, Ag@mTiO₂ nanoparticles and 40 mL of 10^{−5} M MB aqueous solution were added into a 50 mL quartz vessel, and then magnetically stirred in a dark condition for 60 min to reach the adsorption and desorption equilibrium of the MB with the nanoparticles. Afterwards, the solution was exposed to UV radiation with a Hg lamp located 10 cm away from the solution surface to initiate the degradation reaction. During the photodecomposition experiment, 3 mL of the reaction solution for different time intervals was taken out from the reaction suspension and centrifuged to separate the catalyst. The supernatant was analyzed with a UV-vis spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) to monitor the residual concentration of MB. Degradation ratio of MB was calculated through the intensities of absorbance at 664 nm according to the following equation:

$$\text{Degradation ratio (\%)} = [(C_0 - C_t)/C_0] \times 100\% \quad (1)$$

where C_0 represents the initial concentration of MB, C_t is the concentration of MB at time t . Control experiments of different catalysts and various concentrations of MB were carried out using the same steps and conditions in order to eliminate the influence of different parameters on the photocatalytic experiments.

2.6. SERS Property of Ag@mTiO₂ Nanoparticles

MB is used as a model Raman molecule to assess the SERS activity of Ag@mTiO₂ nanoparticles. Specifically, 0.5 mL of Ag@mTiO₂ dispersion was mixed with 3 mL of MB aqueous solution at different concentrations and then the mixed solution was kept in the dark for 24 h to achieve adsorption equilibrium. The MB functionalized nanoparticles were collected by centrifuging, and then they were washed twice with deionized water. Afterwards, the MB functionalized composites were suspended in 0.5 mL of deionized water and put into a quartz cuvette with a 1 cm path length for SERS detection.

2.7. In Situ SERS Monitoring of Photocatalytic Reactions by Ag@mTiO₂ Nanoparticles

Photocatalytic experiments monitored by in situ SERS were conducted in a liquid system at room temperature and the detailed procedure was described as follows. Firstly, Ag@mTiO₂ nanoparticles and 20 mL of 10^{−5} M MB aqueous solution were added into a 50 mL centrifuge tube, and kept in a dark condition for 24 h to attain the adsorption equilibrium of the MB with the nanoparticles. Next, the MB functionalized nanoparticles were collected by centrifuging and washed twice with deionized water. Afterwards, the MB functionalized nanoparticles were suspended in 10 mL of deionized water; then, the solution was transferred to a quartz vessel of 20 mL and exposed to the ultraviolet irradiation. A total of 2 mL of reaction solution was taken out every 3 min and placed in a quartz cuvette with a 1 cm path length for SERS analysis to monitor the progress of the reaction.

2.8. Characterizations

The ultraviolet-visible (UV-vis) spectra were collected using a Cary 60 spectrometer (Agilent Technologies, Santa Clara, CA, USA). X-ray diffraction (XRD) patterns were carried out on a Bruker AXS D8 Advance diffractometer at a scanning rate of 0.02 (Cu-K α radiation, $\lambda = 1.54056 \text{ \AA}$, Bruker, Nasdaq, MA, USA). The 2θ angles are in a range of 20° to 80°. Surface morphology and size analysis of samples were obtained with a transmission electron microscopy (TEM, JEM-2100, JEOL, Tokyo, Japan) at an accelerating voltage of 200 kV and field-emission scanning electron microscopy (FESEM, ZEISS, Oberkochen, German). The specific surface area was determined using N₂ adsorption-desorption isotherms at 77 K on the basis of Brunauer–Emmett–Teller (BET, ASAP 2020, Quantachrome, FL, USA). Energy dispersive X-ray (EDX, ZEISS, Oberkochen, German) analysis was recorded on a Gemini-SEM 300 microscope. Photoluminescence spectroscopy (PL, Edinburgh Instruments, Edinburgh, England) was employed to explore the charge-carrier generation, transfer and separation efficiency of Ag@mTiO₂ samples by using Edinburgh FLS1000. Raman spectra were recorded through a portable Raman spectrometer (Ocean Optics, London, England) with a red laser (785 nm) and the laser power was 392 mW. The acquisition time was 30 s for one time of scanning. The photocatalytic experiments were carried out in the CEL-LB70 photochemical reaction box (CEAULIGHT, Beijing, China).

3. Results and Discussion

3.1. Synthesis of Ag@mTiO₂ Nanoparticles

The Ag@mTiO₂ nanoparticle consists of an Ag nanoparticle as a core and a mesoporous TiO₂ shell, and the fabrication process is depicted in Scheme 1. The Ag nanoparticles were prepared by a wet chemistry approach and their TEM image in Figure 1a demonstrates that they are homogeneous spheres with an average size of 70 nm. Afterwards, the Ag@TiO₂ core-shell nanoparticles were synthesized via the sol-gel method using TBOT as the Ti source to form TiO₂ shells encapsulating around Ag nanoparticles [31]. As can be observed in the TEM image (Figure 1b), the differentiation of the TiO₂ shell from the Ag nanoparticle in a Ag@TiO₂ core-shell nanoparticle is obvious, owing to the higher electron density of Ag relative to TiO₂ and allowing for fewer electrons to penetrate. The TEM image of Ag@TiO₂ presents a distinct contrast between the lighter outer shell and the dark inner core, confirming that the TiO₂ was successfully encapsulated over the Ag nanoparticles; the shell thickness is about 20 nm. Figure 1c shows the representative TEM image of Ag@mTiO₂ obtained by the hydrothermal treatment of Ag@TiO₂ nanoparticles. It can be observed that the compact TiO₂ shell changed into porous morphology, suggesting that the Ag@mTiO₂ nanoparticles were obtained, which offers a large surface area beneficial for photocatalysis. We used UV-vis spectroscopy to characterize the optical property of Ag, Ag@TiO₂ and Ag@mTiO₂ nanoparticles. As shown in Figure 1d, the Ag nanoparticles display a narrow LSPR peak positioned at 408 nm. The LSPR peak of the Ag@TiO₂ nanoparticles is shifted to a higher wavelength (452 nm), together with a broadening in peak width, resulting from the increase of the refractive index around the Ag nanoparticles [32]. Upon hydrothermal

reaction, the LSPR peak of the Ag@mTiO₂ nanoparticles is further shifted from 452 to 504 nm, indicating the formation of mesoporous TiO₂ shell. It is worth mentioning that the strong LSPR intensities of the Ag@TiO₂ and Ag@mTiO₂ nanoparticles greatly verifies that the Ag nanoparticles are kept in good condition during the coating of TiO₂ layer and hydrothermal reaction. The high-resolution TEM (HRTEM) image in the Figure 1 exhibits clear lattice fringes with spacings of 0.204 and 0.235 nm corresponding to the (200) and (111) planes of Ag, as well as the spacing of 0.352 nm corresponding to the (101) plane of anatase TiO₂.

Scheme 1. The formation of Ag@mTiO₂ core-shell nanoparticles.

Figure 1. Typical TEM images of (a) Ag, (b) Ag@TiO₂ and (c) Ag@mTiO₂ nanoparticles. (d) UV-vis spectra of Ag (blue line), Ag@TiO₂ (green line) and Ag@mTiO₂ (red line). (e) The HRTEM image of an Ag@mTiO₂ nanoparticle.

Energy dispersive X-ray (EDX) was employed to identify the composition of the Ag@mTiO₂ nanoparticles. As shown in Figure 2a, the spectrum clearly displays strong peaks of the elements Ag, Ti and O, confirming the successful coating of the TiO₂ layer onto the Ag nanoparticles. Of note, the Si element detected in the sample originates from silicon wafer.

Figure 2. (a) EDX spectrum and (b) XRD pattern of Ag@mTiO₂ nanoparticles. (c) Nitrogen adsorption–desorption isotherms and (d) the Barrett–Joyner–Halenda (BJH) pore diameter distribution curves of Ag@TiO₂ and Ag@mTiO₂.

The crystalline nature of Ag@mTiO₂ nanoparticles was further characterized by XRD. The XRD profile in Figure 2b illustrates strong diffraction peaks with 2θ values of 38.1°, 44.3°, 64.4°, and 77.3°, which can be indexed to the (111), (200), (220), and (311) crystalline planes of face centered cubic Ag (JCPDS card No. 04-0783), respectively, verifying the presence of Ag nanoparticles. We also observe the peaks located at 25.3°, 48.09°, and 53.9°, which correspond to the (101), (200), and (105) planes of anatase TiO₂ (JCPDS card No. 21-1272), indicating the formation of anatase TiO₂ [33]. Figure 2c,d exhibits the N₂ adsorption–desorption isotherms and pore diameter distribution curves of Ag@TiO₂ and Ag@mTiO₂. It is clear that the surface area of the Ag@TiO₂ nanoparticles is 80.7 m²/g and the average diameter is 3.8 nm, while after the hydrothermal reaction, the obtained Ag@mTiO₂ nanoparticles present a large surface area of 84 m²/g; the average pore diameter is 27.7 nm, suggesting a mesoporous structure. Importantly, the large surface area and characteristic pore properties of Ag@mTiO₂ nanoparticles make them advantageous for promoting adsorption performance.

3.2. Photocatalytic Property of Ag@mTiO₂ Nanoparticles

3.2.1. Comparison of Photocatalytic Property of Various Nanoparticles

The photocatalytic degradation of MB under UV light was investigated using Ag, mTiO₂ (the preparation method is described in Supporting Information, and FESEM images are shown in Figures S1 and S2) and Ag@mTiO₂ nanoparticles. The results in Figure 3a display the Ag@mTiO₂ nanoparticles that exhibit the highest degradation ratio compared with pure mTiO₂ and Ag nanoparticles, which are 91%, 88% and 60% in 21 min, respectively. This result demonstrating the Ag nanoparticles is significantly helpful for enhancing the photocatalytic activity of mTiO₂. In order to acquire further insight about the enhancement mechanism of Ag nanoparticles, the photoluminescence (PL) spectra of mTiO₂

and Ag@mTiO₂ with an excitation wavelength of 225 nm were obtained (Figure 3b). PL spectroscopy can clearly demonstrate the persistence of the charge recombination process and migration behavior of the electrons. As observed in Figure 3b, for Ag@mTiO₂ nanoparticles, the PL emission intensity located at 397 nm is reduced, which demonstrates that the electron–hole recombination process is delayed [34,35]. Hence, the PL spectra indicate that the prepared Ag@mTiO₂ nanoparticles experience a delay of the electron–hole recombination process due to the presence of Ag nanoparticles. This is in good agreement with previous reports [16,23]. The Fermi level of Ag is lower than that of anatase TiO₂; therefore, a Schottky barrier can form between the Ag and TiO₂ interface, which could act as an efficient electron trap, thus preventing a photo-excited electron–hole recombination.

Figure 3. (a) Photocatalytic degradation of MB by different catalysts. (b) PL spectra of mTiO₂ and Ag@mTiO₂ nanoparticles (excitation wavelength is 225 nm). (c) UV-vis absorption spectra of MB solution for different times. (d) Photograph of MB solution at different times catalyzed by Ag@mTiO₂ nanoparticles.

It is well known that the photocatalytic activity is primarily influenced by the effective separation and transportation of photogenerated electron–hole pairs. For Ag@mTiO₂ nanoparticles, with the decrease of the recombination of electron–hole pairs, more electrons and holes will be involved in the photocatalytic reaction of MB. We proposed the photocatalytic mechanism of Ag@mTiO₂ nanoparticles, as shown in Scheme 2. Figure 3c displays UV-vis spectra of MB with Ag@mTiO₂ nanoparticles as photocatalysts; Figure 3d shows photographs of the MB aqueous during the photocatalytic reaction. It is obvious that the absorption intensities of MB at 664 nm gradually decline, and finally disappear in 21 min. This is in agreement with the photographs shown in Figure 3d, with the color of MB fading away during the reaction, reaching colorless after a 21 min illumination.

Scheme 2. Proposed photocatalytic mechanism of Ag@mTiO₂ nanoparticles.

3.2.2. Effect of Ag@mTiO₂ Nanoparticle Dosage

The effect of the Ag@mTiO₂ dosage on MB degradation is depicted in Figure 4. The experiments were carried out using a different mass of Ag@mTiO₂ when fixing the initial volume and concentration of MB and the reaction time. It can be observed that with increasing the nanoparticle mass from 2 to 4 mg, the degradation ratio (calculated by Equation (1)) increases from 67.3% to 91% (Figure 4a). This is because more Ag@mTiO₂ nanoparticles provide more active sites, resulting in higher photocatalytic activity. However, when the nanoparticle mass increases to 6 mg, the degradation ratio decreases to 84.2%. This result indicates more nanoparticles may block light scattering and transmittance, and thus decrease the photocatalytic behavior. In addition, the aggregation of the nanoparticles occurs at a high dosage, leading to a decrease in the number of active sites [33].

Figure 4. (a) Effect of Ag@mTiO₂ dosage on photocatalytic degradation of MB. (b) Kinetic plots of $-\ln(C/C_0)$ versus time.

To better elucidate the photocatalytic degradation of MB, the reaction kinetics are described in Figure 4b in following the kinetics equation:

$$-\ln(C/C_0) = kt \quad (2)$$

where C_0 refers to the initial concentration of MB, C represents the concentration of MB at reaction time t , and k is the degradation kinetic rate constant obtained from the slope of the linear plot. As observed in Figure 4b, the catalytic dose of 4 mg obviously exhibits the largest k value, which is about 2.18 folds and 1.23 folds higher than the values at 2 and 6 mg. All of the above results suggest that the catalytic dose of 4 mg presents the best photocatalytic activity.

3.2.3. Effect of Initial Concentration

The effect of the initial MB concentration is investigated in a range of 2×10^{-5} to 5×10^{-6} M with 4 mg of Ag@mTiO₂ nanoparticles. Figure 5a depicts the photodegradation of MB in different concentrations. It is clear that the degradation ratio (calculated by

Equation (1)) of MB increases from 59.3% to 91%, when the MB concentrations drop from 2×10^{-5} to 1×10^{-5} M, because photocatalyst active sites are occupied by excess MB molecules, which lead to the deactivation of the active sites and reduces the generation of active species [36,37]. Additionally, the obstruction of light reaching the nanoparticles may occur resulting from the increased density of MB molecules [22]. When the MB concentrations further decreases to 8×10^{-6} and 5×10^{-6} M, the degradation ratios of MB, as expected, reduce to 83.8% and 85.5%, due to the lower MB concentration, resulting in a lower probability of reaction with the rapid generation of active species [38]. The degradation rates are exhibited straight in Figure 5b and the k values are 0.0425, 0.11593, 0.08772, and 0.09358 min^{-1} , respectively, for 2×10^{-5} to 5×10^{-6} M.

Figure 5. (a) Effect of MB initial concentrations on photocatalytic degradation. (b) Kinetic plots of $-\ln(C/C_0)$ versus time.

3.2.4. Recyclability of Ag@mTiO₂ Nanoparticles

The photocatalytic stability is an important parameter of property evaluation for its practical application or commercial use; therefore, a recycle experiment was performed to evaluate the recyclable stability of Ag@mTiO₂ nanoparticles under the same conditions for decomposing MB in 25 min. The UV-vis spectra of the XRD profiles of the Ag@mTiO₂ nanoparticles after five cyclic photodegradation experiments were collected in Figure 6a,b, demonstrating no obvious change in the LSPR peak intensity and diffraction peaks of the Ag@mTiO₂ nanoparticles after five cycles, compared with the original samples. The results suggest that Ag@mTiO₂ nanoparticles have wonderful structural stability during the ultraviolet light illumination. Figure 6c displays the degradation efficiency of MB with five cycles. We can observe that the degradation efficiency of MB is still high, up to 94%, after five runs. Consequently, the prepared Ag@mTiO₂ nanoparticles could act as reversible photocatalysts with high robustness.

3.2.5. Photodegradation of Various Organic Dyes

To confirm the universal applicability of Ag@mTiO₂ as photocatalysts, they were employed to photocatalytically decompose various organic dyes, for example, the methyl orange (MO) and rhodamine 6G (R6G) aqueous solutions (both of the initial concentrations of the organic dyes were 1×10^{-5} M) under UV irradiation. Figure 7a,b displays the UV-vis absorption spectra of dye solution after UV irradiation for different times and the relationships of the concentration of dye versus reaction time, using Ag@mTiO₂ as a photocatalyst. The results show that MO and R6G are completely degraded in 15 and 36 min, respectively. Figure 7c,d depicts the linear relationship of $-\ln(C/C_0)$ versus reaction time, indicating that all the photocatalytic reactions obey pseudo-first-order kinetics. The apparent first-order rate constants are 0.179 and 0.056 min^{-1} , respectively, for R6G and MO.

Figure 6. (a) UV-vis spectra of Ag@mTiO₂ dispersion in water after MB degradation reaction for 5 consecutive cycles. (b) XRD patterns of Ag@mTiO₂ nanoparticles before and after 5 consecutive cycles. (c) The degradation ratio of MB with 5 consecutive cycles.

Figure 7. UV-vis absorption spectra of (a) R6G and (b) MO solution under UV irradiation for different times. Kinetic plots of $-\ln(C/C_0)$ versus time of (c) R6G and (d) MO.

3.3. SERS Property of Ag@mTiO₂ Nanoparticles

To demonstrate the SERS sensitivity of Ag@mTiO₂ nanoparticles, MB is chosen as a probe molecule in our experiment. Figure 8 reveals the SERS signals of MB, with different concentrations ranging from 10^{-5} to 10^{-8} M. All of them clearly exhibit two dominant Raman peaks of MB, positioned at 1396 and 1621 cm^{-1} , which are assigned for C–N symmetrical stretching and C–C ring stretching [39], respectively. The detection limit of MB is as low as 10^{-8} M. The intensive SERS enhancement can be ascribed to the strong

surface plasmon resonance effect resulting from Ag nanoparticles [40–42]. Moreover, the mesoporous TiO₂ shell may also adsorb more MB molecules [30].

Figure 8. SERS spectra of MB with different concentrations enhanced by Ag@mTiO₂ nanoparticles.

3.4. In situ SERS Monitoring Photodegradation of MB by Ag@mTiO₂ Nanoparticles

In light of the excellent SERS and photocatalytic activity of Ag@mTiO₂ nanoparticles, they can serve as SERS active substrates to monitor the photodegradation process of MB under ultraviolet light illumination in real time [43–46]. Figure 9a shows the SERS signals of MB in the period of the degradation reaction. It is clear that the SERS characteristic peaks of MB at 1396 and 1621 cm^{−1} gradually reduce with the increasing irradiation time. After 18 min, the primary bands of MB almost disappeared without the appearance of new peaks because the degradation products are Raman inactive. To determine the kinetic parameters accurately, the peaks at 1396 and 1621 cm^{−1} were selected to fit the linear relationship of $-\ln(I_t/I_0)$ versus the reaction time, as displayed in Figure 9b. The action rate constants are determined from the slope to be 0.127 and 0.12 min^{−1} with an R² as high as 0.968 and 0.95, respectively.

Figure 9. (a) SERS signals of MB molecules during the photodegradation reaction by Ag@mTiO₂ nanoparticles. (b) The $-\ln(I_t/I_0)$ against reaction time for SERS bands of MB at 1396 and 1621 cm^{−1}.

4. Conclusions

In conclusion, we have successfully synthesized bifunctional Ag@mTiO₂ core-shell nanoparticles combined with SERS and photocatalytic activity. They presented excellent LSPR properties resulting from the Ag cores and a large surface area due to the mesoporous TiO₂ shells. They were used as SERS substrates to detect MB molecules with a limit of detection of 10^{−8} M. In addition, the optical properties of Ag@mTiO₂ nanoparticles indicated that electron–hole recombination can be effectively inhibited due to the presence of Ag. Their photocatalytic activity was demonstrated and the rate of the photodegradation of MB was superior to that of pure TiO₂ nanoparticles. Furthermore, due to their excellent catalytic and SERS properties, Ag@mTiO₂ nanoparticles, in situ, effectively monitored the SERS photodegradation process of MB. Therefore, the Ag@mTiO₂ nanoparticles can be

used as convenient SERS and photocatalytic materials in the detection and degradation of organic dye contaminants.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/coatings12010064/s1>, Figure S1. FESEM image of TiO₂ nanospheres (the size is about 90 nm), Figure S2. FESEM image of mTiO₂ nanospheres (the size is about 90 nm).

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