Synthesis and Characterization of ZnO/TiO₂ Photocatalyst Decorated with PbS QDs for the Degradation of Aniline Blue Solution

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Abstract: A ZnO/TiO₂ photocatalyst decorated with PbS quantum dots (QDs) was synthesized to achieve high photocatalytic efficiency for the decomposition of dye in aqueous media. A TiO₂ porous layer, as a precursor photocatalyst, was fabricated using micro-arc oxidation, and exhibited irregular porous cells with anatase and rutile crystalline structures. Then, a ZnO-deposited TiO₂ catalyst was fabricated using a zinc acetate solution, and PbS QDs were uniformly deposited on the surface of the ZnO/TiO₂ photocatalyst using the successive ionic layer adsorption and reaction (SILAR) technique. For the PbS QDs/ZnO/TiO₂ photocatalyst, ZnO and PbS nanoparticles are uniformly precipitated on the TiO₂ surface. However, the diameters of the PbS particles were very fine, and their shape and distribution were relatively more homogeneous compared to the ZnO particles on the TiO₂ surface. The PbS QDs on the TiO₂ surface can induce changes in band gap energy due to the quantum confinement effect. The effective band gap of the PbS QDs was calculated to be 1.43 eV. To evaluate their photocatalytic properties, Aniline blue decomposition tests were performed. The presence of ZnO and PbS nanoparticles on the TiO₂ catalysts enhanced photoactivity by improving the absorption of visible light. The PbS QDs/ZnO/TiO₂ heterojunction photocatalyst showed a higher Aniline blue decomposition rate and photocatalytic activity, due to the quantum size effect of the PbS nanoparticles, and the more efficient transport of charge carriers.

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1. INTRODUCTION

Crystalline TiO₂ material is recognized as one of the most efficient photocatalysts, due to its high photocatalytic activity, and consequently has many potential technological applications. However, TiO₂ photocatalyst not only exhibits a relatively large band gap (~3.2 eV for anatase) which restricts its activity in the visible region, but also a low charge transfer efficiency due to the easy recombination of photogenerated electron-hole pairs. These factors are detrimental to photocatalytic efficiency. Therefore, in order to widen the application of TiO₂ in various industrial fields, various attempts have been made to enhance its photocatalytic

activity by the use of a heterojunction between the TiO₂ and a semiconductor that has a narrow energy band gap. For example, to enhance photocatalytic activity during the photocatalytic reaction, the ZnO/TiO₂ coupling method [1,2] has been utilized. In this case, an energy potential bias between the ZnO and TiO₂ is formed, which facilitates the transport of photoinduced electrons, by the injection of conduction band electrons from the ZnO to TiO₂. In this way, by separating the photoinduced electrons and holes, the recombination of charge carriers can be avoided, which allows the photocatalytic activity to be improved [3].

However, despite efficient charge carrier transport through the ZnO/TiO₂ heterojunction, the heterostructure still has difficulty effectively absorbing light in the visible range, because both ZnO and TiO₂ possess a large energy band gap. To more efficiently utilize the incident photon energies in the visible light region, heterojunctions

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of TiO_2 with a semiconductor with a narrower energy band gap have been actively investigated. In particular, PbS can be easily excited by visible light, and can efficiently produce electron hole pairs, because of its narrow band gap energy of 0.41 eV [4]. Moreover, PbS nanoparticles easily allow the quantum confinement effect, due to their large exciton Bohr radius [4, 5]. PbS quantum dots (QDs) have received much attention because it is possible to tune their energy band gap [6] by controlling their size and shape [7].

Various techniques of fabricating the TiO_2 layer as precursor photocatalyst have been reported, including sol-gel [8], spin coated TiO_2 film [9], hydrothermal crystallization [10], chemical vapor deposition [11,12], chemical bath deposition [13], spray pyrolysis [14], sputtering [15], and laser sintering methods [16]. However, to fabricate TiO_2 photocatalysts for use in aqueous media, the micro-arc oxidation (MAO) process [17,18] has attracted considerable interest, due to its low cost, non-toxicity, easy control of fabrication, and high reactivity. Moreover, the anodic TiO_2 layer synthesized by the MAO process has useful advantages for application in photocatalysis because of its strong adhesion to the titanium substrate, high specific surface area related to the porous cell structure, and chemical stability. With these features in mind, this study aimed to synthesize an efficient photocatalyst by both improving the charge carrier transport process, and by extending the absorption band of the photocatalyst into the visible light region.

For this purpose, TiO_2 photocatalyst was prepared by the MAO process, and then a ZnO-deposited TiO_2 layer was fabricated. Finally, PbS quantum dots (QDs) were deposited directly on the ZnO/ TiO_2 catalyst using the successive ionic layer adsorption and reaction (SILAR) technique [19-22]. To investigate their surface characteristics, the PbS/ZnO/ TiO_2 heterojunction photocatalysts were analyzed by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). To evaluate their photocatalytic properties, photoluminescence (PL) spectra and dye decomposition tests were performed.

2. EXPERIMENTAL

2.1 Synthesis of photocatalysts

In order to fabricate the TiO_2 photocatalyst, titanium sheets (99.5 %, commercial grade) were cleaned with acetone and ethanol, and rinsed with deionized water. Then, the micro-arc oxidation (MAO) process was carried out in 0.5 M H_2SO_4 solution, using a constant voltage of 200 V for 20 min. The MAO process was performed using a two-electrode system controlled by a DC power supply in a glass cell, and a wide titanium sheet was used as the cathode. After the TiO_2 photocatalysts were fabricated, the specimens were rinsed with deionized water, and dried.

To synthesize the ZnO/ TiO_2 photocatalyst, a simple procedure [23] was utilized. Briefly, anodic TiO_2 photocatalyst and 0.01 M zinc acetate dihydrate $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 99.9% Sigma-Aldrich)/methanol solution were prepared. The TiO_2 specimen was then immersed into the 0.01 M $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ solution, and maintained at 60 °C for 72 h. In this process, new particles were precipitated on the surface of the TiO_2 photocatalyst. After that, the TiO_2 specimen was washed with methanol solution, and dried.

For crystallization of the ZnO particles on the TiO_2 , the ZnO/ TiO_2 sample was annealed at 500 °C for 1 h in air, and the ZnO/ TiO_2 crystalline photocatalyst was prepared. Finally, PbS QDs were deposited onto the ZnO/ TiO_2 photocatalyst using the successive ionic layer adsorption and reaction (SILAR) method. In this procedure, the ZnO/ TiO_2 specimen was immersed in a 0.5 M $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (99%, Sigma-Aldrich) solution for 5 min, and thoroughly rinsed with DI water for 60 s, then dipped into 0.5 M $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ solution for 5 min, and rinsed with DI water for 60 s. The above procedure was termed cycle 1, and the PbS/ZnO/ TiO_2 photocatalyst was prepared by repeating each cycle 5 times. The fabrication process is shown in Fig. 1.

2.2 Surface characteristics of the photocatalyst

To characterize the morphology of the prepared photocatalysts, scanning electron microscopy (SEM, JEOL-JSM5410) was employed, and the crystalline phase of the photocatalysts was identified by X-ray diffraction (XRD; Philips, PW1710). A UV-vis spectrometer (Cary 500 Scan UV-vis-NIR spectrophotometer) was used to determine the light absorption characteristics of the composite photocatalysts. Photoluminescence spectra were measured at room temperature on a Fluorescence Spectrophotometer (F-7000, Hitachi,

Fig. 1. Schematic process flow for fabrication of TiO₂ photocatalytic layer decorated with ZnO and PbS nanoparticles.

Japan) with an excitation wavelength of 350 nm. The scanning speed was 1200 nm/min, and the width of the spectral slit was 5.0 nm.

2.3 Dye decomposition efficiency

For the dye decomposition test, 83 μ M Aniline blue solution (pH 4.00) was prepared, and the dye degradation efficiency was evaluated with a 8 mL solution in a quartz tube, with an irradiating 100 W Hg lamp as the light source. In order to determine the decomposition rate of the Aniline blue solution, UV-vis spectroscopy (Unicam 8700) was performed at a wave length of 600 nm.

3. RESULTS AND DISCUSSION

3.1 Surface characteristics of the photocatalysts

SEM images of surface and cross-sectional areas of the photocatalysts are shown in Fig. 2.

Figure 2(a) shows the bare TiO₂ layer as a precursor catalyst, which was synthesized by the MAO process at 200 V for 20 min in 0.5 M H₂SO₄ solution. The bare TiO₂ catalyst exhibits an irregular porous cell structure, which

consists of various pores with small diameters (100-300 nm). Figure 2(b) shows that the thickness of the TiO₂ layer to be about 4 μ m. Energy dispersion X-ray (EDX) results of the TiO₂ photocatalyst are shown in Fig. 2(c). Only Ti and O peaks were detected in the EDX pattern in Fig. 2(c), and the elemental peaks originated from the TiO₂ crystal structure.

Figure 2(d) shows the ZnO nanoparticles on the TiO₂ photocatalyst surface. Their size and distribution could be controlled by adjusting the concentration of the zinc acetate dihydrate solution and the immersion time. The shape and distribution of the PbS nanoparticles on the TiO₂ surface are shown in Fig. 2(e). As shown in Fig. 2(d) and 2(e), the PbS and ZnO were finely precipitated on the TiO₂ surface. However, the diameters of the PbS particles are very fine, and their shape and distribution are relatively more homogeneous, compared to the ZnO particles on the TiO₂ surface.

Figure 2(f) shows the surface morphology of the PbS/ZnO/TiO₂ photocatalyst, and the inset in Fig. 2(f) shows the magnified morphology, while Fig. 2(g) shows the morphology of a cross-sectional area of the PbS/ZnO/TiO₂ layer. Figure 2(f) and 2(g) show that the PbS and ZnO fine

Fig. 2. SEM micrographs of (a) TiO_2 surface, (b) cross-sectional area of TiO_2 fabricated by the MAO process, and (c) corresponding EDX pattern of (a). SEM images of the (d) ZnO particles decorated TiO_2 catalyst surface (ZnO/TiO_2), (e) PbS particles decorated TiO_2 catalyst (PbS/TiO_2), and (f) ZnO and PbS particles co-decorated TiO_2 catalyst ($\text{PbS}/\text{ZnO}/\text{TiO}_2$). (g) The morphology of the cross-sectional area of the $\text{PbS}/\text{ZnO}/\text{TiO}_2$ layer, and (h) EDX spectra of the $\text{PbS}/\text{ZnO}/\text{TiO}_2$ surface.

particles were precipitated homogeneously on the TiO_2 surface, as well as on surfaces inside the pores.

The EDX results of the $\text{PbS}/\text{ZnO}/\text{TiO}_2$ photocatalyst are shown in Fig. 2(h). The elemental signals of Ti, Zn and O in Fig. 2(h) were attributed to the TiO_2 and ZnO. The Pb and S peaks were attributed to the precipitation of PbS nanoparticles onto the ZnO/TiO_2 surface. Importantly, the size and homogeneous distribution of the precipitated particles on the TiO_2 surface can be important factors that affect photocatalytic activity. Therefore, the size and distribution of the ZnO and PbS nanoparticles on the TiO_2 surface were estimated using the Gaussian function, and the results are shown in Fig. 3. As shown in Fig. 3, the ZnO particles precipitated on the TiO_2 surface have a center of size distribution of 21.17 nm, while the PbS particles on the TiO_2 surface have a center of size distribution of 3.94 nm. The diameters of the PbS particles are very fine, which can be expected to lead to extensive quantum size effects.

Fig. 3. The particle size distribution on porous TiO_2 catalyst surface for (a) ZnO, and (b) PbS particles. The histogram was fitted using Gaussian function.

3.2 X-ray diffraction pattern of the photocatalysts

The X-ray diffraction patterns of the synthesized photocatalysts are shown in Fig. 4. Figure 4(a) shows the

Fig. 4. XRD patterns of the synthesized photocatalysts: (a) bare TiO_2 , (b) ZnO/TiO_2 , (c) PbS/TiO_2 , and (d) $\text{PbS}/\text{ZnO}/\text{TiO}_2$ photocatalysts.

XRD patterns of the anodic TiO_2 photocatalyst prepared by the MAO process. For the bare TiO_2 photocatalyst, as shown in Fig. 4(a), the peaks at 25.28° , 38.58° , 48.05° , 53.89° , and 55.06° can be assigned to the diffraction planes (101), (111), (200), (105), and (211) of the anatase phase (JCPDS No. 21-1272), while the peaks at 27.45° , 36.09° , and 41.23° can be assigned to the diffraction planes (110), (101), and (111) of the rutile phase (JCPDS No. 21-1276), respectively. At the same time, titanium peaks originating from the titanium substrate were observed. Therefore, anatase and rutile phases were revealed as the major crystalline structures in the TiO_2 photocatalyst fabricated by the MAO process.

For the ZnO particles on TiO_2 catalyst, Fig. 4(b) and 4(d) show diffraction peaks at 36.33° and 56.52° , which correspond to reflections from the (111) plane for the ZnO cubic phase (JCPDS No. 77-0191), and the (110) plane for the ZnO hexagonal phase (JCPDS No. 77-0191), respectively. Similarly, Figs. 4(c) and 4(d) show X-ray patterns corresponding to the PbS particles. The peaks are observed at 30.11° , 43.10° , and 68.96° , which correspond to the (200), (220), and (331) planes of the PbS cubic phase (JCPDS No. 78-1901), respectively.

In the diffraction peaks of the ZnO and PbS particles in Fig. 4, the amount and size of the precipitated nanoparticles are so small that the peak intensities appear to be very weak. Nonetheless, the XRD results indicate that ZnO and PbS nanoparticles were successfully precipitated on the surface of TiO_2 photocatalyst.

Fig. 5. UV-vis diffuse reflectance absorption spectra of the synthesized photocatalysts: (a) bare TiO_2 , (b) ZnO/TiO_2 , (c) PbS/TiO_2 , and (d) $\text{PbS}/\text{ZnO}/\text{TiO}_2$ photocatalysts.

3.3 Absorbance response of the photocatalysts

In order to investigate the light absorption properties of the bare TiO_2 , ZnO/TiO_2 , PbS/TiO_2 , and $\text{PbS}/\text{ZnO}/\text{TiO}_2$ heterojunction photocatalysts, UV-vis diffuse reflectance absorption spectra were measured by UV-vis spectrophotometer, and the results are shown in Fig. 5.

Figure 5(a) shows that the absorbance response of the bare TiO_2 catalyst exhibits lower adsorption in the visible light region, whereas Figs. 5(b) and 5(c) reveal a red-shift for the ZnO or PbS particle decorated TiO_2 photocatalysts and more absorption in the range of wavelengths from 400 to 700 nm. In particular, Fig. 5(d) shows that the ZnO and PbS co-decorated TiO_2 photocatalyst exhibits strong light absorption in the visible and UV-vis range. Therefore, the results of the light absorption response suggest that the presence of ZnO or PbS nanoparticles on the TiO_2 catalysts can promote photoactivity by enhancing visible light absorption. Moreover, strong absorbance in the visible light range was observed for the ZnO and PbS co-decorated TiO_2 photocatalyst. Thus, from the results of the light absorption spectra, it can be expected that the $\text{PbS}/\text{ZnO}/\text{TiO}_2$ heterojunction catalyst will show higher photoactivity efficiency, based on more effective light absorbance, compared to other photocatalysts.

Fig. 6. Photocatalytic degradation rate of Aniline blue on (a) bare TiO₂, (b) ZnO/TiO₂, (c) PbS/TiO₂, and (d) PbS/ZnO/TiO₂ photocatalysts under light irradiation.

3.4 Photocatalytic efficiency

Figure 6 shows the photocatalytic efficiency of the photocatalysts for Aniline blue decomposition with irradiation by a 100 W Hg lamp. To determine the actual dye degradation efficiency of the photocatalysts, blank tests were carried out under Hg lamp irradiation, and a small degradation of dyes occurred due to the Hg lamp irradiation. This value was compensated during the evaluation of the dye degradation rate.

In a dye decomposition test of 300 min with bare TiO₂ photocatalyst, 59.7% of the Aniline blue was removed. The corresponding dye removal rates were 62.4% for the ZnO/TiO₂ sample, 70.6% for the PbS/TiO₂ sample, and 82.0% for the PbS/ZnO/TiO₂ photocatalyst sample, respectively. As shown in Fig. 6, the PbS/ZnO/TiO₂ heterojunction photocatalyst showed much higher photocatalytic efficiency than the other photocatalytic samples.

To conduct a kinetic analysis of the Aniline blue decomposition, the rate constants of the photocatalytic reactions of the photocatalysts were evaluated. Performance could also be explained in terms of the first order reaction rate [25,26]. The change in concentration with reaction time can be written as:

$$-\frac{dC}{dt} = kC \quad (1)$$

where, C is the dye concentration in solution. From Eq. (1),

Fig. 7. Dependence of $\ln(C_0/C_t)$ vs. time (min) for dye (Aniline blue) decomposition on (a) bare TiO₂, (b) ZnO/TiO₂, (c) PbS/TiO₂, and (d) PbS/ZnO/TiO₂ photocatalysts under light irradiation.

the kinetic constant can be expressed as:

$$\ln\left(\frac{C_0}{C_t}\right) = kt, \quad (2)$$

where, C_0 represents the initial concentration, and C_t is the resultant concentration of dye after the photocatalytic reaction time (min). The relationships between $\ln(C_0/C_t)$ and the photocatalytic reaction times for the tested dyes are presented in Fig. 7.

The rate constants for the degradation of Aniline blue were $3.03 \times 10^{-3} \text{ min}^{-1}$ for the bare TiO₂ photocatalyst, $3.27 \times 10^{-3} \text{ min}^{-1}$ for the ZnO/TiO₂, and $4.05 \times 10^{-3} \text{ min}^{-1}$ for the PbS/TiO₂ photocatalyst. These results indicate that the presence of ZnO or PbS nanoparticles on the TiO₂ catalysts play a significant role in the photocatalytic reaction, which is beneficial for enhancing the absorption of light in the visible range, and the charge transport of photoinduced electrons. Moreover, the ZnO and PbS co-decorated TiO₂ photocatalyst showed a much higher rate constant ($5.78 \times 10^{-3} \text{ min}^{-1}$) for the dye degradation, than those of the other photocatalysts.

These results suggest that the high rate constants for the degradation of Aniline blue can be attributed to synergistic effects resulting from the presence of nanoparticles and the effective nanojunctions of nanoparticles on the TiO₂ photocatalyst, which are greatly affected by both the size of nanoparticles, and the formation of circuit routes between

nanoparticles. The nanoparticle size induces a change in the energy band gap due to quantum confinement effects, while the suitable nanojunction between the nanoparticles improves the efficient transport of photoinduced electrons.

3.5 Band gap energy depending on nanoparticle size

According to research on semiconductor potential energy [2-4, 27], the band gap energy of bulk ZnO (about 3.2 eV at room temperature) is similar to that of bulk TiO₂, but the potentials of the conduction band and valence band of bulk ZnO are located slightly higher than those of the bulk TiO₂, with respect to the absolute vacuum level. Thus, a heterojunction between TiO₂ and ZnO, as shown in Fig. 9, allows the injection of conduction band electrons from ZnO to TiO₂, and valence band hole transport from the TiO₂ to ZnO.

With regard to the effect of particle size on band gap energy, the ZnO particles with a slightly higher average diameter of 21.17 nm, as shown in Fig. 3(a), are too large to induce quantum confinement effects. Therefore, the ZnO particles on the TiO₂ photocatalyst do not influence the change in band gap energy caused by the particle size effect.

Bulk PbS is known as a promising semiconductor material due to its narrow band gap energy of 0.41 eV [4], which can easily be excited by visible light, and efficiently produce electron hole pairs. However, when bulk PbS material is deposited on the ZnO/TiO₂ catalyst, the potential of the conduction band of the bulk PbS is -4.74 eV, which is lower than that of TiO₂ (-4.21 eV) or ZnO (-4.19 eV). This suggests that the transport of photoelectrons in the conduction band of PbS towards TiO₂ (or ZnO) would be inhibited, and the photocatalytic activity of the PbS/ZnO/TiO₂ photocatalyst could be decreased.

However, the average diameter of the PbS QDs precipitated on the TiO₂ photocatalyst surface in this work, as shown in Fig. 3(b), were observed to be 3.94 nm, which can lead to changes in the band gap energy [28-30] due to small particle size effect, compared to ZnO and TiO₂. In particular, PbS nanoparticles have a large exciton Bohr radius of 18 nm [4,5], due to their high dielectric constant ($\epsilon = 17.3$) and small electron effective mass, which allows a quantum confinement effect, even in relatively large sized quantum

dots.

Therefore, as the particle size of the PbS QDs is reduced, the band gap energy of the PbS QDs increases through splitting of the conduction band. A quantitative model for the relationship between band gap and particle size has been proposed by Brus [31], and by Wang et al. [32]. For the PbS QDs with their large exciton Bohr radius, the quantitative model by Wang has been reported to be more suitable [33]. Therefore, the band gap energy depending on nanoparticle size can be estimated using the following equation:

$$E_g = \left[E_{g,bulk}^2 + 2h^2 \cdot E_{g,bulk} \cdot \left(\frac{1}{d_p} \right)^2 \cdot \frac{1}{m^*} \right]^{1/2} \quad (3)$$

where, E_g is the effective band gap energy due to the quantum confinement effect, $E_{g,bulk}$ is the band gap of bulk PbS, h is the Planck constant, d_p is the nanoparticle diameter, and m^* is the reduced mass of the electron and hole. The value of m^* is considered to be $0.085 m_o$, and m_o is the free electron mass. By using the estimated diameter of 3.94 nm, as shown in Fig. 3(b), the evaluated effective band gap of PbS QDs is calculated to be 1.43 eV.

As the band gap energy of the PbS QDs is increased from 0.41 to 1.43 eV, the minimum energy level of the conduction band of the PbS QDs is slightly higher than those of the ZnO and TiO₂ catalysts. In the PbS QDs/ZnO/TiO₂ heterojunction, the photoinduced electrons are sequentially transferred from PbS QDs to the ZnO and TiO₂ surface, whereas the photoinduced holes move in the reverse direction. This suggests that the photogenerated electron-hole pairs are effectively separated at the interfaces, and this can suppress the recombination of the electron-hole pairs. Therefore, more photogenerated electrons and holes are able to participate in the photocatalytic reactions.

Figure 8 shows the proposed energy band gap alignment and charge separation in the PbS QDs/ZnO/TiO₂ heterojunction photocatalyst. The increase in photocatalytic efficiency in the PbS QDs/ZnO/TiO₂ photocatalyst may be attributed to the PbS QDs, whose narrow band gap enhances light absorption in the visible range, allowing more absorption of the incident photons for the generation of electron-hole pairs, which are beneficial to high photocatalytic efficiency. Moreover, the alignment of band gap energy due to the PbS QDs facilitates a more efficient

Fig. 8. Illustration of the energy band gap alignment and charge separation in the PbS QDs/ZnO/TiO₂ heterojunction photocatalyst.

charge transport process before recombination occurs, which also enhances the photoactivity efficiency. Accordingly, the maximum photocatalytic efficiency was obtained for the PbS QDs/ZnO/TiO₂ heterojunction photocatalyst, compared to the TiO₂, ZnO/TiO₂, and PbS/TiO₂ photocatalysts. The results of the UV-vis absorption spectra and Aniline blue decomposition tests, as shown in Figs. 5, 6, and 7, are in good agreement with the above description.

3.6 Photoluminescence behavior of the photocatalysts

To further investigate the electronic and optical characteristics of the photocatalysts, the photoluminescence (PL) spectra of the TiO₂, ZnO/TiO₂, PbS/TiO₂, and PbS/ZnO/TiO₂ photocatalysts were measured in the wavelength range of 400–700 nm, and the results are shown in Fig. 9. In the PL spectra of the TiO₂ photocatalysts, as shown in Fig. 9, the main peaks [34,35] were observed at 440 (2.82 eV), 455 (2.72 eV), 470 (2.64 eV) and 550 nm (2.25 eV), which is attributed to oxygen vacancies and localized surface states in the TiO₂ [36,37].

Figure 9 also shows that the PL intensity decreased with the presence of nanoparticles (ZnO or PbS) on the TiO₂ surface. At the same time, for the PbS/ZnO/TiO₂ heterojunction catalyst, PL intensity was greatly reduced compared to the other samples. It is known that PL intensity is correlated directly with the recombination of electron-hole pairs photogenerated from the TiO₂ surface [38]. Just as the lower PL intensity suggests a lower recombination rate of

Fig. 9. Photoluminescence spectra of (a) bare TiO₂ photocatalytic film, (b) ZnO/TiO₂, (c) PbS/TiO₂, and (d) PbS/ZnO/TiO₂ heterojunction photocatalysts.

electron-hole pairs, the decrease in the intensity of the PL spectra indicates that the recombination of electron-hole pairs is reduced, and that photoinduced electrons are being transferred more effectively.

Therefore, the results of the PL measurement confirm that the maximum photocatalytic activity can be obtained using the PbS QDs/ZnO/TiO₂ heterojunction photocatalyst, compared to the other photocatalyst samples.

4. CONCLUSIONS

A PbS QDs/ZnO/TiO₂ heterojunction photocatalyst was synthesized to achieve high photocatalytic efficiency for the decomposition of organic pollutants in aqueous media. The TiO₂ porous layer, as precursor photocatalyst, was fabricated using micro-arc oxidation, which introduces irregular porous cell features with anatase and rutile crystalline structures. Then, a ZnO-deposited TiO₂ catalyst was fabricated using zinc acetate solution, and PbS QDs were uniformly deposited on the surface of the ZnO/TiO₂ photocatalyst using the SILAR method.

ZnO particles with an average diameter of 21.17 nm and PbS QDs with an average diameter of 3.94 nm were precipitated homogeneously on the TiO₂ surface, as well as on surfaces inside the pores, to produce the PbS QDs/ZnO/TiO₂ heterojunction photocatalyst. The results of the light

absorption response suggest that the presence of ZnO or PbS nanoparticles on the TiO₂ catalysts enhanced photoactivity by improving visible light absorption. Moreover, the absorbance ability in the visible light range was observed to be more effective for the ZnO and PbS QDs co-decorated TiO₂ photocatalysts, compared to the other photocatalysts. From the dye degradation evaluation results, the rate constants for the degradation of Aniline blue were found to be $3.03 \times 10^{-3} \text{ min}^{-1}$ for the bare TiO₂, $3.27 \times 10^{-3} \text{ min}^{-1}$ for the ZnO/TiO₂, $4.05 \times 10^{-3} \text{ min}^{-1}$ for the PbS QDs/TiO₂, and $5.78 \times 10^{-3} \text{ min}^{-1}$ for the PbS QDs/ZnO/TiO₂ photocatalysts.

The PbS QDs/ZnO/TiO₂ heterojunction photocatalyst showed a higher Aniline blue decomposition rate and photocatalytic activity, due to the quantum confinement effect of the PbS QDs. Furthermore, the new aligned band gap energy due to the PbS QDs facilitates a more efficient charge transport process before recombination occurs. Thus, the maximum photocatalytic efficiency was measured for the PbS QDs/ZnO/TiO₂ heterojunction photocatalyst, compared to the TiO₂, ZnO/TiO₂, and PbS QDs/TiO₂ photocatalysts.

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