

Article

# The Effect of AgInS<sub>2</sub>, SnS, CuS<sub>2</sub>, Bi<sub>2</sub>S<sub>3</sub> Quantum Dots on the Surface Properties and Photocatalytic Activity of QDs-Sensitized TiO<sub>2</sub> Composite

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**Abstract:** The effect of type (AgInS<sub>2</sub>, SnS, CuS<sub>2</sub>, Bi<sub>2</sub>S<sub>3</sub>) and amount (5, 10, 15 wt%) of quantum dots (QDs) on the surface properties and photocatalytic activity of QDs-sensitized TiO<sub>2</sub> composite, was investigated. AgInS<sub>2</sub>, SnS, CuS<sub>2</sub>, Bi<sub>2</sub>S<sub>3</sub> QDs were obtained by hot-injection, sonochemical, microwave, and hot-injection method, respectively. To characterize of as-prepared samples high-resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), UV-Vis spectroscopy and photoluminescence (PL) emission spectroscopy were applied. The size of AgInS<sub>2</sub>, SnS, CuS<sub>2</sub>, Bi<sub>2</sub>S<sub>3</sub> QDs were 12; 2–6; 2–3, and 1–2 nm, respectively. The QDs and QDs-sensitized TiO<sub>2</sub> composites obtained have been tested in toluene degradation under LEDs light irradiation ( $\lambda_{\max} = 415$  nm and  $\lambda_{\max} = 375$  nm). For pristine QDs the efficiency of toluene degradation increased in the order of AgInS<sub>2</sub> < Bi<sub>2</sub>S<sub>3</sub> < CuS < SnS under 375 nm and AgInS<sub>2</sub> < CuS < Bi<sub>2</sub>S<sub>3</sub> < SnS under 415 nm. In the presence of TiO<sub>2</sub>/SnS QDs\_15% composite, 91% of toluene was degraded after 1 h of irradiation, and this efficiency was about 12 higher than that for pristine QDs under 375 nm. Generally, building the TiO<sub>2</sub>/AgInS<sub>2</sub> and TiO<sub>2</sub>/SnS exhibited higher photoactivity under 375 nm than the pristine TiO<sub>2</sub> and QDs which suggests a synergistic effect between QDs and TiO<sub>2</sub> matrix.

**Keywords:** photocatalysis; TiO<sub>2</sub>; quantum dots; metal sulphides; air purification

## 1. Introduction

Air pollution poses a major threat to public health globally by virtue of its prevalence and emission by various sources. Among these sources, some volatile organic compounds (VOCs) become a prominent problem due to their toxicity even at low concentrations. Moreover, VOCs, along with inorganic oxides, can be transported over long distances producing secondary air pollutants, and can be responsible for acid rain and global warming [1–3]. In this regard, there is a high demand for an efficient, low-cost and eco-friendly technology, which can be implemented for air purification, even at low pollutant concentration levels. Application of solar light induced photocatalysis could be one of the technologies solving these problems [1,4]. Heterogeneous nano-semiconductor photocatalysis (e.g., TiO<sub>2</sub> NPs) is an efficient method facilitating the degradation of air pollutants, inactivation of bacteria, hydrogen production and photoconversion CO<sub>2</sub> into light hydrocarbon [5–8]. The recombination rate of photogenerated electron–hole pairs and the low visible light utilization of TiO<sub>2</sub> limit its applications in these areas. In recent years, there has been significant interest in the

application of metal sulfides ( $M_xS_y$ ) for wide band semiconductors modification, because of their high charge separation efficiency and narrow band gaps, which possibly enable light harvesting at longer wavelengths [9]. Liu et al. studied the efficiency of  $AgInS_2/TiO_2$  heterostructures in 1,2-dichlorobenzene (o-DCB) degradation under visible light [10]. They observed that  $AgInS_2/TiO_2$  composites could expand the visible-light response range and greatly decreased the recombination of photogenerated electron–hole pairs in the composites. The degradation of o-DCB for the most active sample reaches about 50% after 8h of irradiation. Jang et al. prepared  $Ag-Sn-TiO_2$  nanocomposite for methylene blue and rhodamine B degradation under simulated sunlight [11]. The photoactivity of the produced photocatalysts was about 2–3 times higher than that of P25. Compared with bare  $TiO_2$  the  $CuS/TiO_2$  [12],  $CdS/TiO_2$  [13–15],  $SnS/TiO_2$  [16],  $Ag_2S/TiO_2$  [17,18],  $CuInS_2/TiO_2$  [19–21],  $Bi_2S_3/TiO_2$  [22–24] nanocomposites present a significant improvement on photocatalytic reactions due to the decreasing recombination of electron–hole pairs and the broadened light absorption spectra. However, the metal sulfides commonly employed for  $TiO_2$  modification have been used in nanoparticle sizes and not in quantum dots sizes. Further, it has been shown that the size of metal sulfides (MS) particles can have an impact on its physicochemical and optical properties. Recently, the literature data demonstrated that the decrease in particle size lowers the recombination of the electron-hole pair within the semiconductor particle. Quantum dots (QDs) with particles size in range from 2 to 20 nm exhibit distinctive properties owing to their high surface-to-volume ratio [25]. Band gap tailoring of QDs is contingent by controlling particle size. Thus, light absorption range and the energy of charge carriers can be modulated. So far, QDs decorated semiconductors particles have aroused attention due to high charge separation efficiency and quantum confinement effects of QDs. To date, the  $CdS$  QDs-decorated semiconductors NPs [26–30] a mostly investigated in photocatalytic reaction, but  $CdS$  QDs are not stable in the water splitting reaction, which are known to be toxic. Moreover, the use of  $CdS$  is restricted due to photocorrosion. To date, metal sulfides quantum dot (MS QDs)-sensitized  $TiO_2$  were not often studied in air purification process. Mazierski et al. synthesized the  $Ag$  NPs/ $Bi_2S_3$  QDs/ $TiO_2$  nanotubes (NTs) with the improved photocatalytic efficiency in phenol and toluene degradation which was assigned to the notably increased the electron–hole separation/transfer and synergistic effect between the ordered structure of  $TiO_2$  NTs and the well-distributed  $Pt$  NPs and  $Bi_2S_3$  QDs [31]. However, other types of composites, e.g.,  $C$  QDs/ $Bi_2WO_6$  NPs [32],  $N$ -doped  $C$  QDs/ $TiO_2$  NPs [33],  $CdTe$  QDs/ $KTaO_3$  NPs [34],  $CdTe$  QDs/ $SrTiO_3$  NPs [35],  $CdTe$  QDs/ $SrTiO_3$  NPs [35] were investigated in pollutants degradation in the gas phase.

Based on the above considerations, this paper focuses on the synthesis methods, surface properties and photocatalytic activity of MS QDs and MS QDs-decorated  $TiO_2$  composites. Herein, a series of non-toxic quantum dots (e.g.,  $AgInS_2$ ,  $SnS$ ,  $CuS_2$ ,  $Bi_2S_3$ ) have been applied to investigate the effect of QD type and amount (5, 10, 15 wt%) on the activity of obtained QDs- $TiO_2$  hybrids. The proposed hybrid systems are discussed with respect photoactivity in air purification process in the presence of low-powered and low-cost irradiation sources (LEDs  $\lambda_{max} = 415$  nm and  $\lambda_{max} = 375$  nm), which reduce the costs of photocatalytic processes.

## 2. Results and Discussion

Sample labeling, preparation method and photocatalytic activity of prepared QDs and QDs-sensitized  $TiO_2$  are given in Table 1. Initially, we investigated the effect type ( $AgInS_2$ ,  $SnS$ ,  $CuS_2$ ,  $Bi_2S_3$ ) and amount of QDs (5, 10, 15 wt%) on the optical properties and efficiency of toluene degradation in the gas phase using the LEDs.

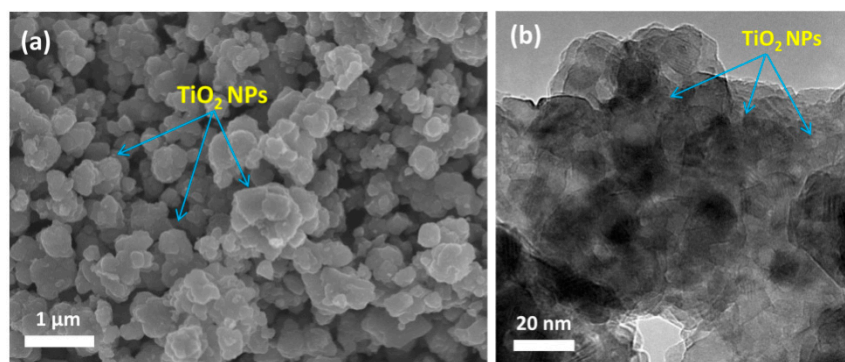


**Table 1.** Sample label, preparation method and photocatalytic activity of prepared photocatalysts.

Sample Label	Loading of QDs (wt%)	Preparation Method	Toluene Degradation after 1 h Irradiation (%)	
			$\lambda_{\max} = 415 \text{ nm}$	$\lambda_{\max} = 375 \text{ nm}$
TiO <sub>2</sub> NPs	0	hydrothermal	45.1	79.1
AgInS <sub>2</sub>	0	hot-injection	56.2	59.3
TiO <sub>2</sub> /AgInS <sub>2</sub> _5	5	adsorption/calcination	71.1	78.6
TiO <sub>2</sub> /AgInS <sub>2</sub> _10	10	adsorption/calcination	70.7	86.3
TiO <sub>2</sub> /AgInS <sub>2</sub> _15	15	adsorption/calcination	56.1	89.2
SnS	0	sonochemical	14.8	6.50
TiO <sub>2</sub> /SnS_5	5	adsorption/calcination	13.7	87.9
TiO <sub>2</sub> /SnS_10	10	adsorption/calcination	34.6	79.9
TiO <sub>2</sub> /SnS_15	15	adsorption/calcination	36.6	91.1
CuS	0	microwave	25.9	28.1
TiO <sub>2</sub> /CuS_5	5	adsorption/calcination	24.7	37.3
TiO <sub>2</sub> /CuS_10	10	adsorption/calcination	36.5	46.3
TiO <sub>2</sub> /CuS_15	15	adsorption/calcination	40.2	45.6
Bi <sub>2</sub> S <sub>3</sub>	0	hot-injection	21.8	35.2
TiO <sub>2</sub> /Bi <sub>2</sub> S <sub>3</sub> _5	5	adsorption/calcination	29.8	56.3
TiO <sub>2</sub> /Bi <sub>2</sub> S <sub>3</sub> _10	10	adsorption/calcination	29.7	52.5
TiO <sub>2</sub> /Bi <sub>2</sub> S <sub>3</sub> _15	15	adsorption/calcination	34.7	49.4

### 2.1. Morphology

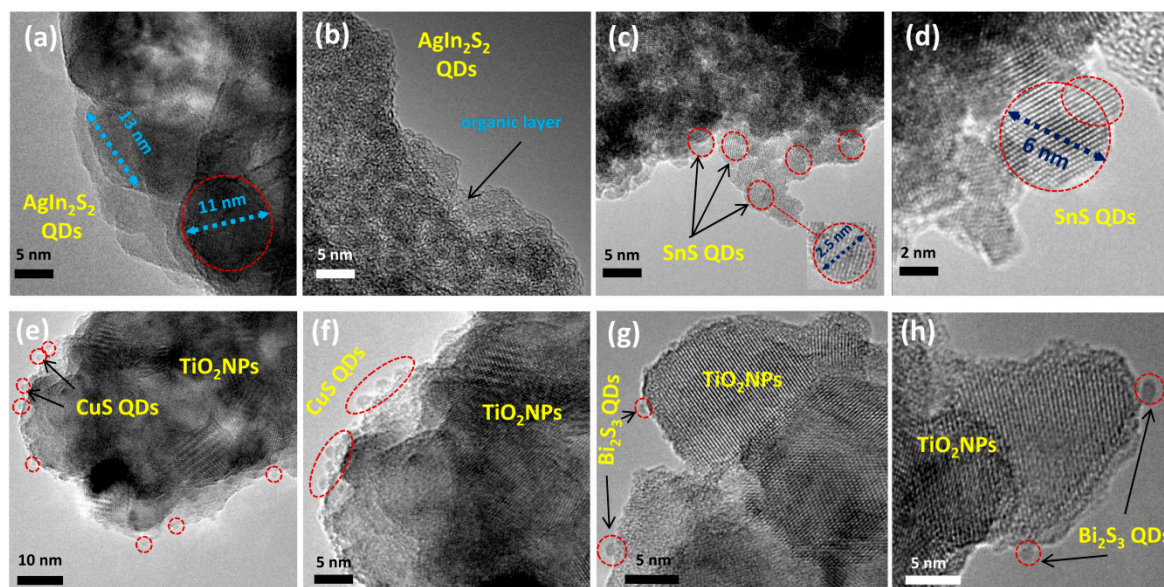
To determine the morphology of the obtained TiO<sub>2</sub>, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) images have been performed (Figure 1). As clearly shown, TiO<sub>2</sub> showed an irregular particles and porous surface morphology. The average size of TiO<sub>2</sub> was in the range of 100–800 nm.



**Figure 1.** (a) SEM and (b) HR-TEM images for TiO<sub>2</sub> NPs.

The HRTEM measurements were performed to characterize the morphology of obtained QDs (Figure 2). The average size of AgInS<sub>2</sub> QDs was about 12 nm (Figure 2a). However, the accurate size of AgInS<sub>2</sub> QDs was difficult to determine, due to the presence of an amorphous layer, indicating the presence of oleic acid, 1-octadecene, dodecanethiol and oleylamine (used during the synthesis) on surface of AgInS<sub>2</sub> QDs (Figure 2b). As clearly shown SnS QDs were small in size and have spherical shape with average size from 2 to 6 nm (after 15 min. in ultrasonic bath) (Figure 2c–d). Cheraghizade et al. obtained SnS QDs by applying different sonication times of 10, 15, and 20 min. They observed that the sizes of the SnS QDs decreased from 7.15 to 3.66 nm with the times of sonication were enhanced [36]. Based on Figure 1e–f, the average size of CuS QDs obtained by microwave method

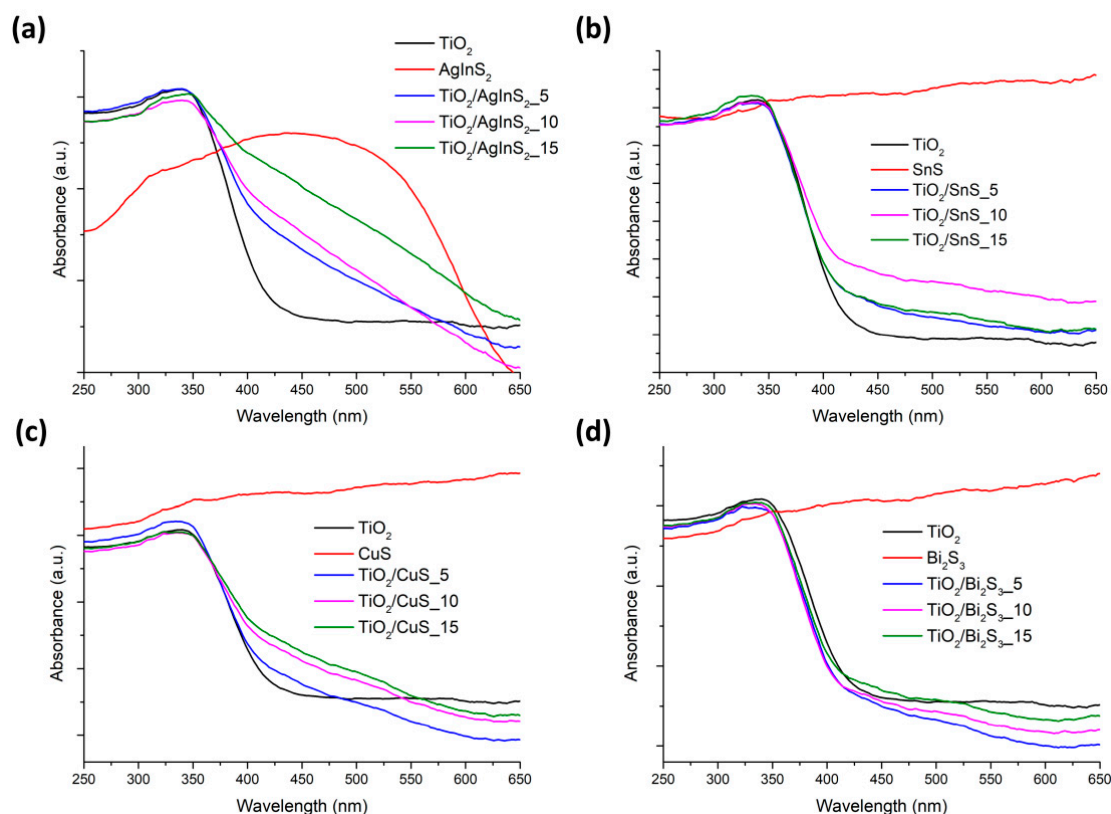
during 9 min. were in the range of 2–3 nm. Chaudhary et al. also obtained CuS QDs with size of 2–3 nm in 2 min using microwave and water as medium [37]. The Figure 2g–h clearly shows very small Bi<sub>2</sub>S<sub>3</sub> quantum dots embedded on the surface of TiO<sub>2</sub> NPs. Bi<sub>2</sub>S<sub>3</sub> QDs were spherical with size in the range of 1–2 nm. In addition, Table S1 presents the transmission electron microscopy energy-dispersive X-ray spectroscopy (TEM-EDX) analysis. These results show the combination of QDs and the TiO<sub>2</sub> NPs which have resulted in the formation of heterojunction structure between these two components. Furthermore, this composed interaction between TiO<sub>2</sub> and QDs may play an crucial role in accelerating the separation of the photogenerated charge carriers [34,38].



**Figure 2.** HR-TEM images for (a,b) AgInS<sub>2</sub> QDs, (c,d) SnS QDs, (e,f) TiO<sub>2</sub>/CuS<sub>15</sub> QDs, and (g,h) TiO<sub>2</sub>/Bi<sub>2</sub>S<sub>3-15</sub> QDs.

## 2.2. UV-Vis Spectra

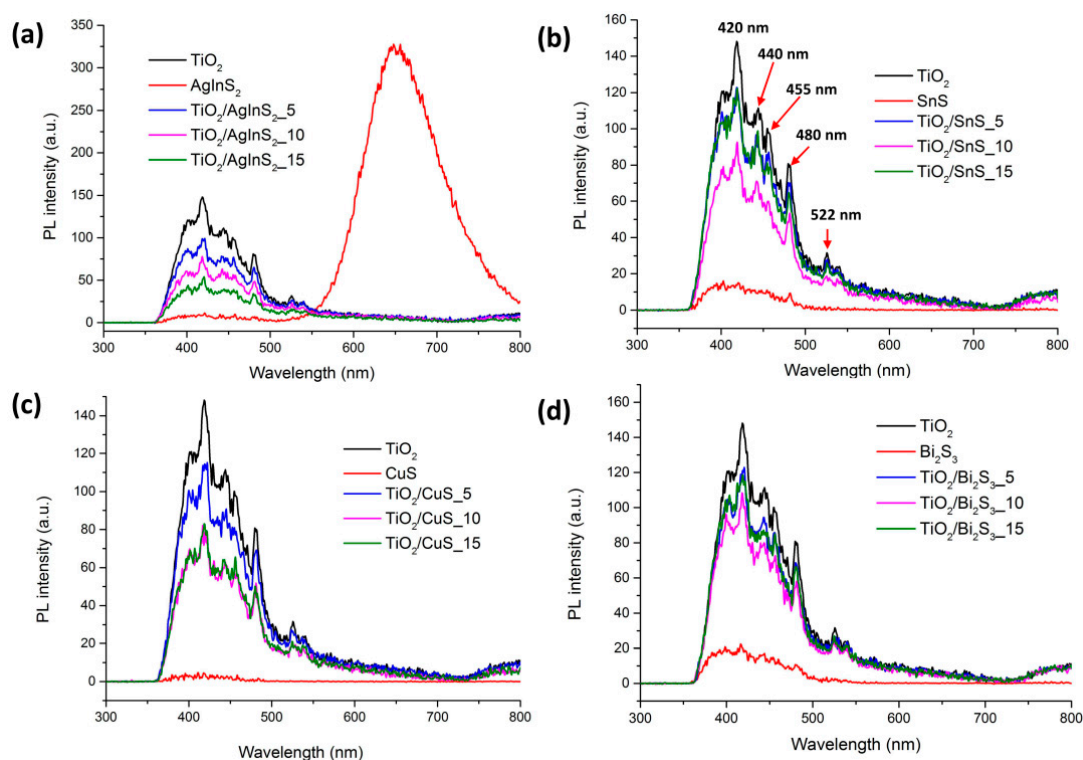
The optical properties for all prepared photocatalysts were investigated by UV–vis spectra analysis with the wavelength from 250 to 650 nm (Figure 3). The characteristic sharp edge was observed at 390–400 nm which is in agreement with the intrinsic band-gap absorption of anatase TiO<sub>2</sub> (3.2eV). For AgInS<sub>2</sub> the onset of absorption peak was observed at 600 nm with a maximum at 450 nm (Figure 3a). All TiO<sub>2</sub> modified with AgInS<sub>2</sub> QDs exhibit enhanced absorption in the visible light spectrum, in comparison with the pure TiO<sub>2</sub>. Furthermore, the increased absorption in the visible range with increasing amount (from 5 to 15%) of AgInS<sub>2</sub> QDs can be seen. It is worth mentioning that the highest amount of AgInS<sub>2</sub> QDs (15 wt%) onto TiO<sub>2</sub> surface led to induced absorption in range from 400 to 650 nm. Therefore, these results confirm that QDs have been successfully combined with the TiO<sub>2</sub> NPs and the heterojunctions in the fabricated composites were formed. Significantly widened absorption spectrum into the visible region has been achieved by introducing SnS QDs onto TiO<sub>2</sub> NPs matrix (Figure 3b). For TiO<sub>2</sub> modified with CuS QDs, it can also be seen that the absorbance peaks were shifted to longer wavelengths, compared with pristine TiO<sub>2</sub> (Figure 3c). The bare SnS QDs and CuS QDs have shown remarkable absorption in both the UV and visible regions. No significant effect was observed on absorption properties by coupling TiO<sub>2</sub> NPs with the black colored Bi<sub>2</sub>S<sub>3</sub> QDs in comparison to pristine TiO<sub>2</sub> [24]. (Figure 3d).



**Figure 3.** UV-Vis spectra for (a)  $\text{TiO}_2$ ,  $\text{AgInS}_2$  and  $\text{TiO}_2$  modified with  $\text{AgInS}_2$  (5, 10, 15 wt%), (b)  $\text{TiO}_2$ ,  $\text{SnS}$  and  $\text{TiO}_2$  modified with  $\text{SnS}$  (5, 10, 15 wt%), (c)  $\text{TiO}_2$ ,  $\text{CuS}$  and  $\text{TiO}_2$  modified with  $\text{CuS}$  (5, 10, 15 wt%), (d)  $\text{TiO}_2$ ,  $\text{Bi}_2\text{S}_3$  and  $\text{TiO}_2$  modified with  $\text{Bi}_2\text{S}_3$  (5, 10, 15 wt%).

### 2.3. Photoluminescence Properties

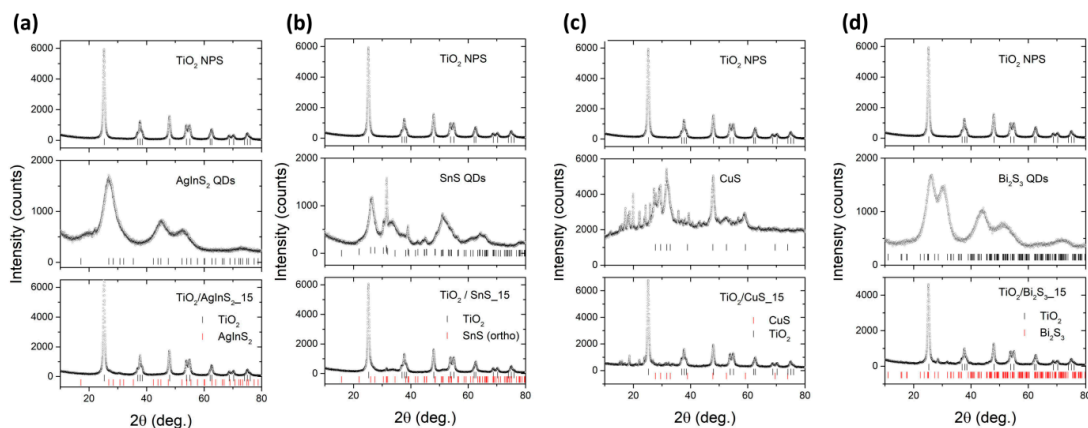
It is essential to study the photoluminescence (PL) emission spectra of semiconductor photocatalysis, which can provide information regarding electron-hole recombination processes. The PL signal is obtained from emitted photons by electron-hole pair recombination in a photocatalysis [39]. The higher PL emission signal the more efficient the recombination process, and the lower the activity for photocatalysis [40]. Figure 4 displays PL emission spectra of prepared photocatalysts at an excitation wavelength of 330 nm. Pristine  $\text{TiO}_2$  exhibited the highest PL intensity due to its low separation efficiency. PL spectra of anatase  $\text{TiO}_2$  materials are attributed to three kinds of physical origins: Self-trapped excitons (420 nm), oxygen vacancies (420, 440 and 455) and surface states/defects (480, 522 nm) [39]. The emission around 480 nm has been observed for all prepared samples, which can be attributed to the charge transfer from  $\text{Ti}^{3+}$  to oxygen anion in a  $\text{TiO}_6^{8-}$  complex associated with oxygen vacancies at the surface [41,42]. The maximum of emission band of  $\text{AgInS}_2$  QDs synthesized by hot-injection method at  $130^\circ\text{C}$  for 6 min is located around 650 nm (Figure 4a). Along with the increase in the  $\text{AgInS}_2$  QDs content, the PL intensity dropped down and achieved its lowest level at 15 wt% QDs content, suggesting the highest separation and transfer efficiency of photogenerated electron-hole pairs. Among the  $\text{TiO}_2/\text{SnS}$  and  $\text{TiO}_2/\text{Bi}_2\text{S}_3$  photocatalysts, the lowest PL was observed for the sample containing 10 wt% of QDs (Figure 4b,d). Based on a comparison of changes in PL intensity of all  $\text{TiO}_2$  modified with  $\text{CuS}$ , it can be observed that the luminescence intensity decreased with increasing amount of  $\text{CuS}$  QDs (Figure 4c). Considering these results, the proposed QDs can raise the effective separation of the photogenerated electrons and holes in  $\text{TiO}_2/\text{QDs}$  heterojunction, thus promoting the charge separation and improving the photocatalytic performance.



**Figure 4.** PL spectra of (a)  $\text{TiO}_2$ ,  $\text{AgInS}_2$  and  $\text{TiO}_2$  modified with  $\text{AgInS}_2$  (5, 10, 15 wt%), (b)  $\text{TiO}_2$ ,  $\text{SnS}$  and  $\text{TiO}_2$  modified with  $\text{SnS}$  (5, 10, 15 wt%), (c)  $\text{TiO}_2$ ,  $\text{CuS}$  and  $\text{TiO}_2$  modified with  $\text{CuS}$  (5, 10, 15 wt%), (d)  $\text{TiO}_2$ ,  $\text{Bi}_2\text{S}_3$  and  $\text{TiO}_2$  modified with  $\text{Bi}_2\text{S}_3$  (5, 10, 15 wt%).

#### 2.4. XRD Analysis

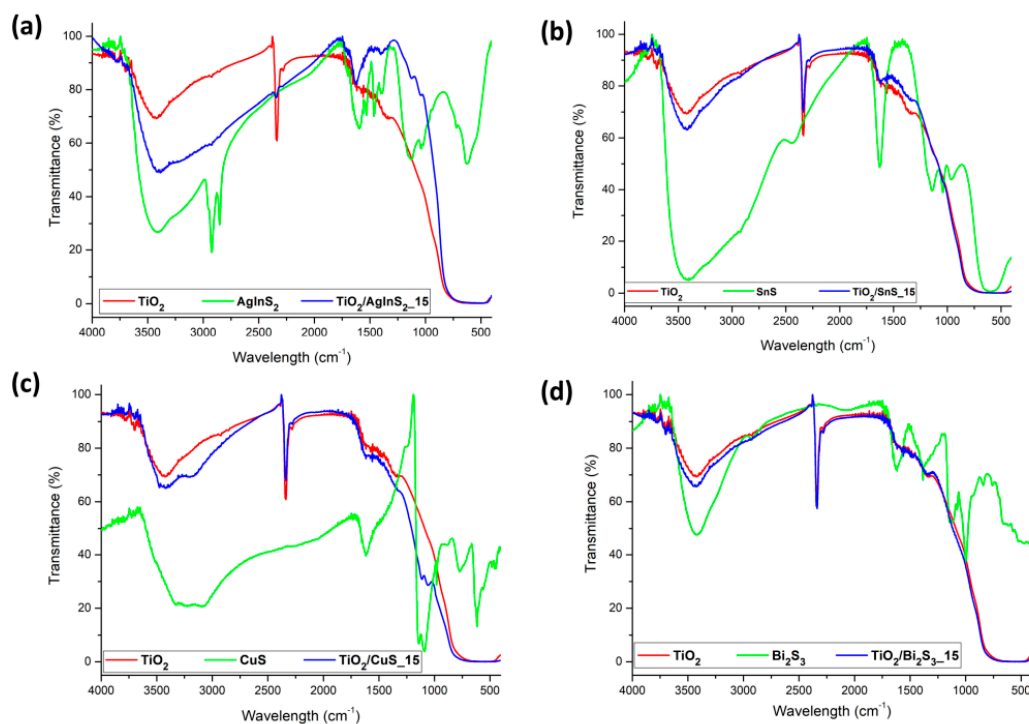
Figure 5 shows the X-ray diffraction (XRD) patterns of pristine  $\text{TiO}_2$ , QDs and  $\text{TiO}_2/\text{QDs}_{15}$  composites. The peak diffraction observed at the  $2\theta$  values of 25, 37.8, 48.1, and 53.9° can be assigned to (101), (004), (200), and (105) crystallographic plane of anatase  $\text{TiO}_2$  with tetragonal crystal structure [31,43]. Three peaks at  $2\theta$  values of 26.5, 44.7, and 52.3° corresponding to the (112), (220), and (312) indices of the tetragonal crystal structure of  $\text{AgInS}_2$  QDs, respectively (Figure 5a) [44]. The broad diffraction peaks show the fine grains of the  $\text{AgInS}_2$  QDs. Orthorhombic structured  $\text{SnS}$  QDs is identified from the XRD pattern in Figure 5b. Three peaks at  $2\theta$  values of 25.9, 31.48 and 44.4° corresponds to planes (120), (111) and (141) [45]. For  $\text{CuS}$  QDs peaks around 27.7, 29.3, 31.8, and 47.9° can be assigned to the corresponding (100), (102), (103) and (110) crystal planes of  $\text{CuS}$ , which can be indexed as a hexagonal structure [46] (Figure 5c). The diffraction peaks that were matched to the orthorhombic structure of  $\text{Bi}_2\text{S}_3$  QDs can be observed (Figure 5d) [47]. The very broad diffraction peaks show the fine grains of the  $\text{Bi}_2\text{S}_3$  QDs. After loading 15 wt% of QDs, the XRD patterns of the QDs-sensitized  $\text{TiO}_2$  composite were almost the same as that of pure  $\text{TiO}_2$  confirming that surface modification did not influence the crystalline properties of  $\text{TiO}_2$ .



**Figure 5.** XRD analysis for (a)  $\text{TiO}_2$ ,  $\text{AgInS}_2$  and  $\text{TiO}_2/\text{AgInS}_2_{15}$ , (b)  $\text{TiO}_2$ ,  $\text{SnS}$  and  $\text{TiO}_2/\text{SnS}_{15}$ , (c)  $\text{TiO}_2$ ,  $\text{CuS}$  and  $\text{TiO}_2/\text{CuS}_{15}$ , (d)  $\text{TiO}_2$ ,  $\text{Bi}_2\text{S}_3$  and  $\text{TiO}_2/\text{Bi}_2\text{S}_3_{15}$ .

### 2.5. FT-IR Analysis

Figure 6 shows fourier transform infrared (FT-IR) spectra for pure  $\text{TiO}_2$  NPs, pure QDs and for  $\text{TiO}_2$  modified with 15% weight of selected sulphide. The groups of very weak, sharp bands occurring at wave numbers above  $3600\text{ cm}^{-1}$  and  $1600\text{--}1800\text{ cm}^{-1}$  are attributed to water vapor. Likewise strong doublet at  $2336\text{ cm}^{-1}$  clearly comes from carbon dioxide, exactly from  $\text{O}=\text{C}=\text{O}$  stretching vibrations [48]. Mentioned above both compounds are contaminations that may have been present at measurement chamber during the analysis.



**Figure 6.** FT-IR spectra for QDs and  $\text{TiO}_2$  modified by (a)  $\text{TiO}_2$ ,  $\text{AgInS}_2$  and  $\text{TiO}_2/\text{AgInS}_2_{15}$ , (b)  $\text{TiO}_2$ ,  $\text{SnS}$  and  $\text{TiO}_2/\text{SnS}_{15}$ , (c)  $\text{TiO}_2$ ,  $\text{CuS}$  and  $\text{TiO}_2/\text{CuS}_{15}$ , (d)  $\text{TiO}_2$ ,  $\text{Bi}_2\text{S}_3$  and  $\text{TiO}_2/\text{Bi}_2\text{S}_3_{15}$ .

Furthermore  $\text{CO}_2$  can be adsorbed on the surface of  $\text{TiO}_2$  NPs as the case band is very distinct. The FTIR spectrum of pure  $\text{TiO}_2$  was given in Figure 6 a–d (red line) is characterized by several bands, which are evidence of the presence of specific functional groups. A very broad absorption band, centered in  $3420\text{ cm}^{-1}$ , originates from O–H stretching vibrations from hydroxyl groups of molecules

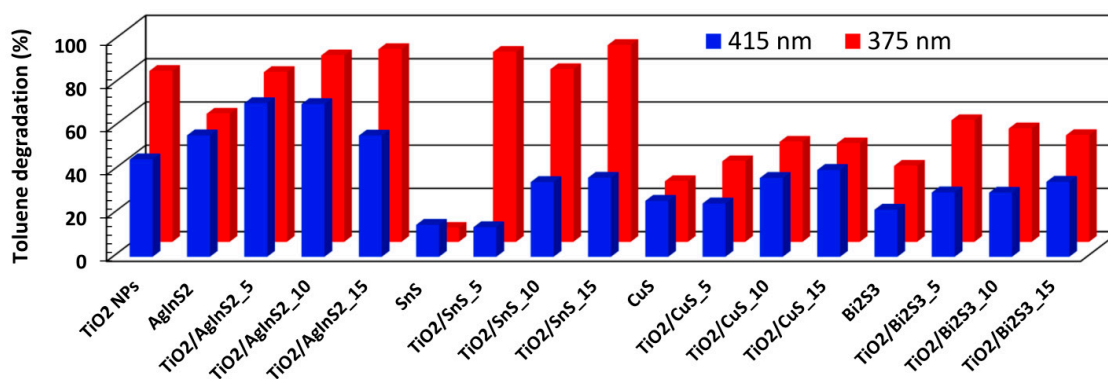
surface. Medium band at  $1620\text{ cm}^{-1}$  corresponds to water bending vibrations [49]. These two bands are repeated in most of the spectra presented in this chapter. Whereas peak at  $1370\text{ cm}^{-1}$  and the strongest flat region between  $400\text{--}850\text{ cm}^{-1}$  are typical for Ti–O and Ti–O–Ti stretching oscillation [50]. FT-IR AgInS<sub>2</sub> spectra are given at Figure 6a. A strong pronounced doublet observed at 2923 and  $2853\text{ cm}^{-1}$  are attributed to symmetric and asymmetric stretching modes of C–H [51]. Absorption, in this case, is strong because oleic acid (OA) was used to preparation probe therefore long chain hydrocarbon fragments were introduced. Bands at 1590, 1530 and twice peaks 1464,  $1393\text{ cm}^{-1}$  corresponding to C=O stretching, N–H and H–C–H bending vibrations, respectively. The above bands are evidence of the presence of amide or amine groups that can form next bonds, two peaks at 1135 and  $1032\text{ cm}^{-1}$  are attributed to C–N stretching modes. It confirms the existence of amide functional groups [44]. Strong peaks at 722 and  $630\text{ cm}^{-1}$  are the result of H–C–H rocking and C–S stretching oscillation, respectively. TiO<sub>2</sub>/AgInS<sub>2</sub>\_15 is the only case in which the shape of the spectrum is clearly closer to the shape of the pure AgInS<sub>2</sub> than the TiO<sub>2</sub> spectra. Each peak described for the AgInS<sub>2</sub> is also visible in the spectrum of modified TiO<sub>2</sub>, the only exceptions are the peaks in the range  $500\text{--}700\text{ cm}^{-1}$ . Also, the sharp, strong absorption band visible on every spectrum at  $2336\text{ cm}^{-1}$  (attributed to CO<sub>2</sub>) has been reduced in the TiO<sub>2</sub>/AgInS<sub>2</sub> chart. The above analysis demonstrates that, in this case, the absorption AgInS<sub>2</sub> on the surface of TiO<sub>2</sub> occurred with the highest efficiency in this publication. At Figure 6b was presented spectra TiO<sub>2</sub> modified with tin(II) sulphide. Namely bands at SnS spectra in 613,  $950\text{--}1150$  and  $2440\text{ cm}^{-1}$  are typical for this compound [52,53]. Strengthened signal for  $1620\text{ cm}^{-1}$  results from overlapping water and N–H bending vibrations amine group becomes from ammonium used in synthesis of semiconductor [54]. TiO<sub>2</sub>/SnS\_15 spectrum exhibit features of both components although at first it seems identical to pure TiO<sub>2</sub> NPs. Transmittance at wave numbers corresponding to characteristic bands of SnS is reduces which is visible as subtle peaks. Wavy spectra between  $950\text{--}1150\text{ cm}^{-1}$  and slight signal at  $2440\text{ cm}^{-1}$  are evidence of an effective adsorption process, SnS on TiO<sub>2</sub> surface. CuS spectra are given at Figure 6c peak obtained for CuS in  $3090\text{ cm}^{-1}$  comes from functional groups on surface of semiconductor, exactly N–H stretching vibrations. Two very strong vibrations at 1140 and  $1090\text{ cm}^{-1}$  corresponds to C–O and S–O stretching [8]. These three bands described above are also visible in the TiO<sub>2</sub>/CuS\_15 spectrum. Furthermore, oscillation localized between  $500\text{--}700\text{ cm}^{-1}$  are typical for Cu–S stretching and are only clearly visible in the CuS spectra [55,56]. In Figure 6d was shown the effect of TiO<sub>2</sub> modification using Bi<sub>2</sub>S<sub>3</sub>. The most important peaks are situated under  $1500\text{ cm}^{-1}$ , namely, a sharp band at  $1390\text{ cm}^{-1}$  is due to the complex Bi<sup>3+</sup> and citrate anions, which results from the type of precursors used for synthesis. Strong, sharp peaks at 1150 and  $1000\text{ cm}^{-1}$  are attributed to stretching asymmetric and symmetric O–S–O vibrations. The band characteristics for Bi appear in the range  $400\text{--}600\text{ cm}^{-1}$  [57]. All bands described above, except those in the range  $400\text{--}600\text{ cm}^{-1}$ , are reflected in spectra of TiO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>\_15. Waved lines were observed in corresponding to interpreted peaks. Invisible bands in the  $400\text{--}600\text{ cm}^{-1}$  range are masked by very strong, broad absorption band of TiO<sub>2</sub>. A similar phenomenon occurs in all spectra in this paragraph.

## 2.6. Photocatalytic Activity in the Gas Phase

In order to investigate the photocatalytic activity of obtained photocatalysts, photocatalytic degradation of toluene in the gas phase were studied under 375 and 415 nm light irradiation. Under 375 nm for pristine QDs the efficiency of toluene degradation increased in the order of AgInS<sub>2</sub> < Bi<sub>2</sub>S<sub>3</sub> < CuS < SnS. All samples containing SnS quantum dots boosted the photocatalytic activity of TiO<sub>2</sub> NPs under 375 nm light irradiation (Table 1, Figure 7). Cheraghizade et al. showed that SnS QDs photocatalytic activity depends on particle size. Prolonged sonication-assisted synthesis results in smaller crystallite size SnS QDs with higher photocatalytic activity. This is due to the reduced size of SnS QDs, in which the ratio of surface-to-volume is enhanced and so electron-hole creation of samples are also increased [36]. Although, pristine SnS QDs had very low activity in toluene photodegradation, the application of SnS QDs onto TiO<sub>2</sub> surface most boosted reaction yield. The TiO<sub>2</sub>/SnS\_15 sample exhibited the highest performance among other photocatalysts with 91.1% toluene



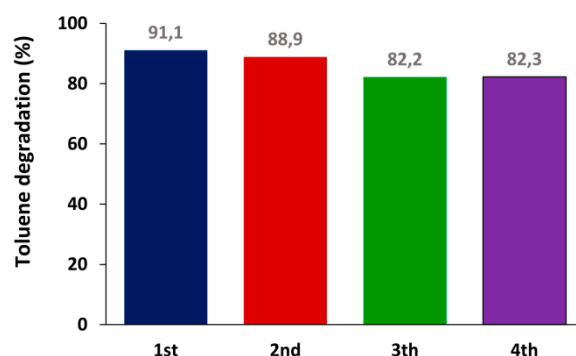
degradation after 1 hour irradiation under 375 nm which proves that the load of 15% SnS QDs on TiO<sub>2</sub> NPs matrix improved the photocatalytic activity of bare TiO<sub>2</sub> NPs and pristine QDs by 1.15, and 12 times, respectively. High efficiency toluene degradation was also observed for TiO<sub>2</sub>/SnS<sub>5</sub> and TiO<sub>2</sub>/SnS<sub>10</sub>, i.e., 87.9 and 79.7% of toluene was degraded after 1 h under 375 nm, respectively. These SnS QDs, when decorated onto the surfaces of TiO<sub>2</sub> enable precise engineering of the band structure of the obtained composite. Through decoration of SnS QDs of suitable sizes, the charge separation of the TiO<sub>2</sub> NPs is improved, while maintaining a suitable electronic potential to generate extra oxidizing species for toluene degradation [58]. High toluene degradation was observed for TiO<sub>2</sub>/AgInS<sub>2</sub>\_10 and TiO<sub>2</sub>/AgInS<sub>2</sub>\_15, while 5% modification (TiO<sub>2</sub>/AgInS<sub>2</sub>\_5) decreased the activity of TiO<sub>2</sub> NPs under 375 nm. Generally, it was observed, that in case of TiO<sub>2</sub>/AgInS<sub>2</sub> composites, enhancement of concentration (from 5 to 15 wt.%) resulted in a linear increase of photoactivity under 375 nm and clear decrease in the recombination of electron hole pairs. The efficiency of toluene degradation increased from 78.6; 86.3 to 89.2% for TiO<sub>2</sub>/AgInS<sub>2</sub>\_5, TiO<sub>2</sub>/AgInS<sub>2</sub>\_10, and TiO<sub>2</sub>/AgInS<sub>2</sub>\_15, respectively. The optimal content of quantum dots for TiO<sub>2</sub>/CuS composites was 10 wt.%. After 1 h, 46.3% toluene was degraded in the presence of TiO<sub>2</sub>/CuS<sub>10</sub> under 375 nm. Further increase in CuS QDs concentration (to 15 wt.%) resulted in a slight drop of photoactivity to 45.6 % for the sample TiO<sub>2</sub>/CuS<sub>15</sub>. The TiO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>\_5 sample exhibited the highest performance among TiO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub> composites under 375 nm (56.3%). Further increase in Bi<sub>2</sub>S<sub>3</sub> concentration (to 15 wt.%) resulted in a drop of photoactivity to 49.4% for the sample TiO<sub>2</sub>/Bi<sub>2</sub>S<sub>3</sub>\_15. Lin et al. [59] reported that in case of CdSnO<sub>3</sub>-decorated CdS nanowire, for 2.5 at% of CdSnO<sub>3</sub> the highest charge carrier separation was observed. Generally, building the TiO<sub>2</sub>/AgInS<sub>2</sub> and TiO<sub>2</sub>/SnS composite resulted in a synergistic effect between QDs and TiO<sub>2</sub> matrix. It was also observed that increasing AgInS<sub>2</sub> QDs content on the surface TiO<sub>2</sub> NPs resulted in (i) improved light harvesting ability, (ii) reduced recombination of e-h pairs and (iii) improved photoactivity under UV irradiation. Whereas modification with CuS and Bi<sub>2</sub>S<sub>3</sub> showed lowered the activity than pristine TiO<sub>2</sub> but higher activity than pristine CuS and Bi<sub>2</sub>S<sub>3</sub> QDs under 375 and 415 nm. Under 415 nm for pristine QDs the efficiency of toluene degradation increased in the order of AgInS<sub>2</sub> < CuS < Bi<sub>2</sub>S<sub>3</sub> < SnS. An increase in SnS and CuS QDs concentration (from 5 to 15 wt.%) caused a linear increase in photoactivity under 415 nm. However, the highest toluene degradation was observed by AgInS<sub>2</sub> modified TiO<sub>2</sub> NPs while other modifications decreased the activity of TiO<sub>2</sub> NPs after 1 h under 415 nm. TiO<sub>2</sub>/AgInS<sub>2</sub>\_5 had the higher photocatalytic activity compare to TiO<sub>2</sub>/AgInS<sub>2</sub>\_10 and TiO<sub>2</sub>/AgInS<sub>2</sub>\_15 with 71.1% toluene degradation (Table 1, Figure 7). Therefore, it can be suggested that the most active sample for toluene degradation adheres to the type of the light irradiation. This is probably due to the electronic band structure of the TiO<sub>2</sub> NPs and quantum dots that affect the photoexcited electrons and holes transfer route in the photocatalysts [21,60]. In summary, the photocatalytic activity was dependent on (i) type of QDs, (ii) amount of QDs and (iii) wavelength of the light irradiation.



**Figure 7.** Photocatalytic activities of obtained photocatalysts for toluene photodegradation after 1 h irradiation of LEDs  $\lambda_{\max} = 375$  nm and  $\lambda_{\max} = 415$  nm.

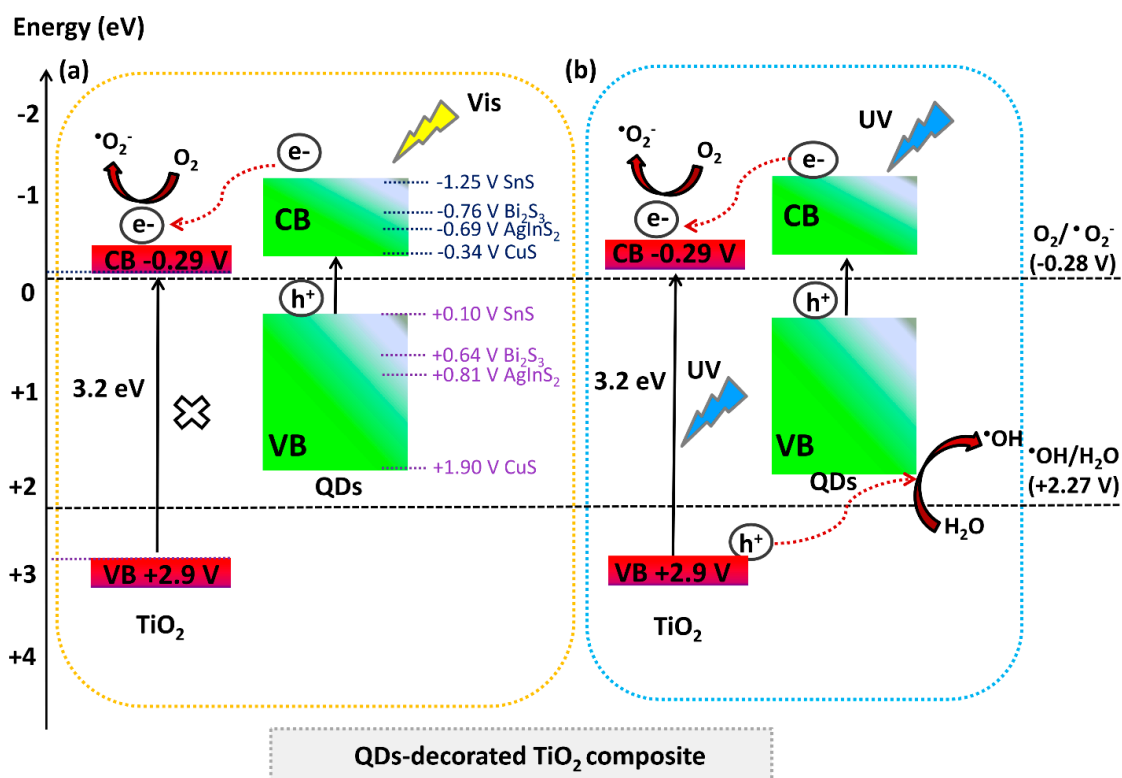


In addition to those, the photostability of the most active sample under 375 nm irradiation, TiO<sub>2</sub>/SnS<sub>15</sub>, was tested by carrying out 4 subsequent cycles. At the end of the cycle, the activity of TiO<sub>2</sub>/SnS<sub>15</sub> diminished by 9.65% (Figure 8). This deactivation can be explained mainly by the partial oxidation of toluene that leads to formation of intermediates such as benzaldehyde, benzyl alcohol, benzoic acid, benzene, and phenol which remain on the photocatalysis surface by strong adsorption [61]. In particular, with benzoic acid intermediate, more carbonyl group arises on the photocatalysis surface, which inhibits the electron density of the benzyl ring that makes the benzyl ring more inert, thus hard to break it [62,63].



**Figure 8.** Photostability of TiO<sub>2</sub>/SnS<sub>15</sub> measured in the fourth subsequent cycles in the toluene degradation reaction in the presence of LED  $\lambda_{\max} = 375$  nm.

The photocatalytic mechanism for QDs-sensitized TiO<sub>2</sub> composite under visible and UV irradiation has been proposed (Figure 9). All tested non-toxic QDs has narrow band gap and more negative conduction band (CB) energy level than CB of TiO<sub>2</sub> (Table 2).



**Figure 9.** Proposed mechanism of photocatalytic reactions in the presence of QDs-sensitized TiO<sub>2</sub> composite under (a) visible, and (b) UV irradiation.

**Table 2.** Band gap values and positions of the VB and CB for tested samples.

Type of Sample	Band Gap Eg (eV)	Position of VB (V)	Position of CB (V)	Ref.
TiO <sub>2</sub> NPs	3.2	+2.9	−0.29	[64]
AgInS <sub>2</sub> QDs	1.5	+0.81	−0.69	[65]
SnS QDs	1.35	+0.1	−1.25	[66]
CuS QDs	2.25	+1.9	−0.34	[67]
Bi <sub>2</sub> S <sub>3</sub> QDs	1.4	+0.64	−0.76	[31]

Photoexcited electrons are generated on the CB of QDs in upon the visible light absorption that leaves holes in the VB (Figure 9a). Since the CB of TiO<sub>2</sub> is more positive than the CB of QDs, the photoexcited electrons transfer from the photoexcited QDs into the CB of TiO<sub>2</sub> expectedly. Those electrons in CB of TiO<sub>2</sub> reduce the O<sub>2</sub> adsorbed on the surface of the photocatalyst to form •O<sub>2</sub><sup>−</sup>. The VB potentials of QDs are more negative than the redox potential of •OH/H<sub>2</sub>O (+2.27 V), indicating that the holes in the VB of QDs cannot oxidize H<sub>2</sub>O to produce •OH.

Under UV irradiation, both TiO<sub>2</sub> NPs and QDs was excited (Figure 9b). The electron from QDs can be inject into the CB of TiO<sub>2</sub> NPs. The electron transfer from QDs to the TiO<sub>2</sub> NPs is determined by the energy difference between the two CB positions energy levels, which acts as a driving force for interparticle electron transfer [25,68]. The highest difference between the CB positions energy levels were observed for TiO<sub>2</sub> and SnS QDs, which means fastest electron transfer from QDs to TiO<sub>2</sub> NPs and a high photocatalytic activity of those composites as showed in the experimental section. While, the holes formed in the VB of TiO<sub>2</sub> had oxidative potential and can be easily transferred to the VB of QDs and then oxidize H<sub>2</sub>O and •OH to produce •OH. In this way, the photogenerated electron-holes pairs can be effectively separated, which results in higher photoactivity in particular in presence of TiO<sub>2</sub>/AgInS<sub>2</sub> and TiO<sub>2</sub>/SnS composite.

### 3. Experimental

#### 3.1. Materials and Instruments

Tetrabutyl titanate (TBT, 97%, Sigma Aldrich, Saint Louis, MO, USA) and glycerol (99.5%, POCH, Gliwice, Poland) were used for TiO<sub>2</sub> NPs preparation. Silver nitrate (AgNO<sub>3</sub>, 99%, Sigma Aldrich, Saint Louis, MO, USA), indium (III) acetylacetonate (In(acac)<sub>3</sub>, 99.99%, Sigma Aldrich, Saint Louis, MO, USA), sulfur powder (S, 99.98%, POCH, Gliwice, Poland), 1-octadecene (ODE, 90%, Sigma Aldrich, Saint Louis, MO, USA), dodecanethiol (DDT, 98%, Alfa Aesar, Haverhill, MA, USA), oleylamine (OLA, 90%, ACROS ORGANICS, Gell Belgium), oleic acid (OA, 90%, Sigma Aldrich, Saint Louis, MO, USA) were used for AgInS<sub>2</sub> QDs synthesis. Tin chloride (SnCl<sub>2</sub>, 99%, POCH, Gliwice, Poland), ammonium acetate (CH<sub>3</sub>COONH<sub>4</sub>, 99%, Sigma Aldrich, Saint Louis, MO, USA), ammonia (NH<sub>3</sub>, 25%, Chempur, Piekary Śląskie, Poland) sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, 99.5%, POCH, Gliwice, Poland) were used for SnS QDs synthesis. Thioacetamide (C<sub>2</sub>H<sub>5</sub>NS, 99%, Sigma Aldrich, Saint Louis, MO, USA), copper chloride (CuCl<sub>2</sub>·xH<sub>2</sub>O, 99%, POCH, Gliwice, Poland) were used for CuS QDs synthesis. Sodium sulfide (Na<sub>2</sub>S, 99.9%, Sigma Aldrich, Saint Louis, MO, USA), ammonium bismuth citrate (99%, Sigma Aldrich, Saint Louis, MO, USA), starch (C<sub>6</sub>H<sub>12</sub>O<sub>5</sub>, pure p.a.) were used for Bi<sub>2</sub>S<sub>3</sub> QDs synthesis. Deionized water was used in all the experiments.

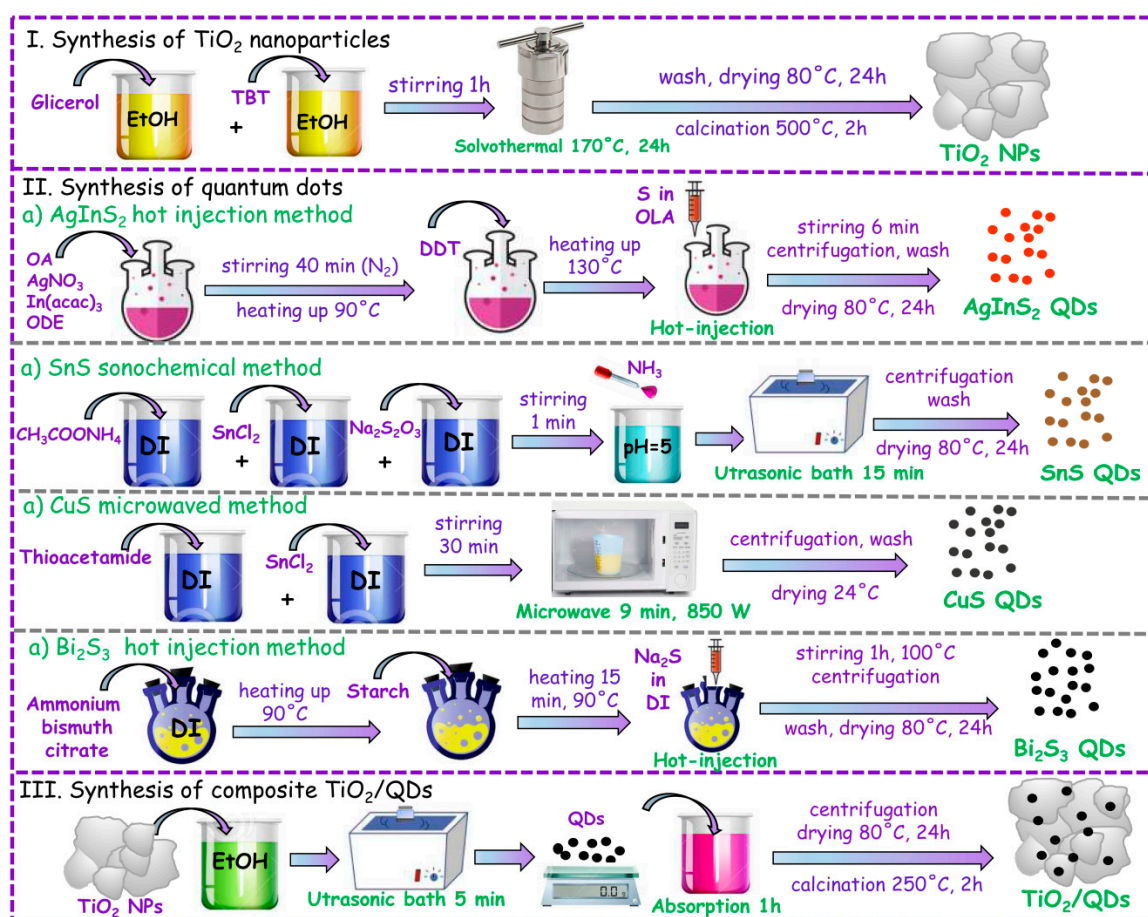
The UV–vis spectra of samples were recorded in the scan range 250–650 nm using UV–vis spectrophotometer (UV 2600, Shimadzu, Kyoto, Japan) equipped with BaSO<sub>4</sub> as the reference. The photoluminescence (PL) emission spectra were measured by a PerkinElmer Luminescence Spectrometer LS 50B (Hamamatsu, Japan) equipped with xenon discharge lamp as an excitation source. The samples were excited with 330 nm at room temperature and the emission was scanned between 300 and 800 nm. X-ray diffraction (X'Pert Pro MPD Philips diffractometer, Almelo, The Netherlands) with Cu Kα radiation λ = 1.5418 Å was used to determine the sample's composition. The measurements

were performed on the  $2\theta$  range of  $10\text{--}80^\circ$ . The morphology of samples have been analyzed by high-resolution transmission electron microscopy (HRTEM, Brno, Czech Republic, FEI Europe, model TecnaiF20 X-Twin) and scanning electron microscopy (JEOL, Tokyo, Japan, JSM-7610F operating at 15 kV). The preparation of the TEM samples was the following: sonication for 5 seconds of a few milligrams of sample in ethanol (99.8% anhydrous) using ultrasounds, then applying a drop of the solution of  $5\ \mu\text{l}$  on a carbon coated copper mesh with holes (Lacey type Cu 400 mesh, Plano), then the solvent was evaporating at room temperature. FT-IR spectra were obtained on a Bruker model IF S66 FTIR spectrometer using potassium bromide discs.

### 3.2. Sample Preparation

#### 3.2.1. $\text{TiO}_2$ NPs Preparation

The pristine  $\text{TiO}_2$  NPs were synthesized by one-step solvothermal method. In a typical procedure, TBT (2.99 g) and glycerol (1.99 g) were mixed with 45 mL absolute ethyl alcohol, respectively. Then, both solutions were mixed together, followed by stirring for 1h. Then obtained suspension was transferred into a Teflon-lined stainless steel autoclave (200 ml capacity) ( $170^\circ\text{C}$  for 24 h). After being cooled in the air to room temperature, the products were washed three times with ethanol and then dried in an oven at  $80^\circ\text{C}$  for 24 h. The white  $\text{TiO}_2$  powder was calcined at  $500^\circ\text{C}$  for 2 h (in air, heating rate of  $2^\circ\text{C}/\text{min}$ ) (Figure 10).



**Figure 10.** Schematic diagram for the formation of  $\text{TiO}_2$ , QDs ( $\text{AgInS}_2$ , SnS, CuS,  $\text{Bi}_2\text{S}_3$ ) and  $\text{TiO}_2/\text{QDs}$  composite.

### 3.2.2. Quantum Dots Preparation

#### (a) AgInS<sub>2</sub> QDs Preparation

The AgInS<sub>2</sub> QDs were synthesized by hot-injection method similar to that described by Ruan et al. [69]. AgNO<sub>3</sub> (0.0176 g), In(acac)<sub>3</sub> (0.208 g) and OA (0.47 mL) were mixed and added into a three-neck flask. Then, 8 ml of ODE was added to the obtained solution. The mixing solution was stirred and degassed with N<sub>2</sub> for 40 min. After that, the solution was heated to 90 °C and then DDT (1.0 mL) was injected into the flask. The obtained solution was then heated to 130 °C and the sulfur solution (0.0053 g S powder dissolved in 2.6 mL OLA) was quickly injected, and the solution continued stirring for 6 min. The resulting liquid product was orange color. After being cooled to room temperature, the products were collected by centrifugation (6000 rpm, 10 min) and washed 3× with ethanol. Finally, the AgInS<sub>2</sub> QDs was dried (80 °C for 24 h) (Figure 10).

#### (b) SnS QDs Preparation

The SnS QDs were synthesized by sonochemical method [36]. In a first step, three solutions were prepared (i) SnCl<sub>2</sub> × 2H<sub>2</sub>O (0.9165 g) in 40 ml deionized water (DI), (ii) ammonium acetate (0.3119 g) in 40 ml DI, and (iii) Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.9578 g) dissolved in 20 ml DI. Then, all above solutions were mixed at 25 °C, followed by stirring for 1 minute and its pH was adjusted at 5 using addition of ammonia. After that the reaction mixture was introduced into an ultrasonic bath for 15 min. The products were washed times with deionized water, centrifuged (10 min. 6000 rpm) and dried (80 °C for 24 h). The resulting product was brown color (Figure 10).

#### (c) CuS QDs Preparation

The CuS QDs were prepared by through a simple and cost-effective microwave method [37]. In a typical procedure, CuCl<sub>2</sub> × 2H<sub>2</sub>O (0.1344 g dissolved in 100 mL H<sub>2</sub>O) and thioacetamide (0.0901 g dissolved in 100 ml H<sub>2</sub>O) were mixed for 30 min at 25 °C. Then, the resulting solution was placed into the microwave 9 min at 850 W and the formation of black precipitates appeared. The CuS QDs were collected by centrifugation (6000 rpm, 20 min), washed 3 times with DI and dried at 25 °C (Figure 10).

#### (d) Bi<sub>2</sub>S<sub>3</sub> QDs Preparation

Bi<sub>2</sub>S<sub>3</sub> QDs were obtained by the hot-injection method using a starch capping agent [68]. Firstly, ammonium bismuth citrate (0.4043 g) was dissolved in 20 ml DI. Then mixture was heated to 95 °C and soluble starch (0.2015 g) was added and was kept at 95 °C for about 15 min. Then, the Na<sub>2</sub>S (0.4051 g dissolved in 20 mL of deionized water) was added into to the ammonium bismuth citrate solution and stirred at 100 °C for 1 h. The powder was collected by centrifugation (6000 rpm, 10 min), and washed 3× with DI. Finally, the Bi<sub>2</sub>S<sub>3</sub> QDs was dried at 80 °C for 24 h (Figure 10).

### 3.2.3. Preparation of Quantum Dot-sensitized TiO<sub>2</sub> Composites

TiO<sub>2</sub>/QDs (AgInS<sub>2</sub>, CuS, SnS, Bi<sub>2</sub>S<sub>3</sub>) photocatalysts were synthesized by absorption method (Figure 10). Typically, 30 mL of ethanol containing the TiO<sub>2</sub> NPs was ultrasonicated for 5 min to make NPs completely dispersed. Then, a different amount of QDs (5,10,15% wt%) was added to suspension of photocatalysts, followed by stirring for 6 h (250 rpm/min.). After that, TiO<sub>2</sub>/QDs photocatalysts were collected by centrifugation (7000 rpm, 20 min) and dried at 70 °C for 24 h. Finally, the powder was calcined at 250 °C for 2 h (in air, heating rate of 3 °C/min). The description of the as-prepared photocatalysts is shown in Table 1.

### 3.3. Measurement of Photocatalytic Activity

The photocatalytic activity was determined in the toluene degradation process [70]. As an irradiation source, an array of 25 LEDs ( $\lambda_{\max} = 375$  nm, 13.16 mW/cm<sup>2</sup>) and ( $\lambda_{\max} = 415$  nm, 1.6 mW/cm<sup>2</sup>) (Optel, Opole, Poland), these diodes contain a part of UV radiation) were used. In a typical procedure, a thin film of the photocatalyst was prepared by suspending of photocatalyst (0.01 g) in water and loading it on a glass plate (3 cm × 3 cm) by painting technique. The gas mixture (with toluene concentration 200 ppm) was passed through the photoreactor (1 min), and the reactor was

kept in the dark for 30 min in order to achieve equilibrium. The toluene concentration was determined by using a GC (TRACE 1300, Thermo Scientific, Waltham, MA, USA, FID, Elite-5 capillary column).

#### 4. Conclusions

In summary, for pristine QDs the efficiency of toluene degradation increased in the order of  $\text{AgInS}_2 < \text{Bi}_2\text{S}_3 < \text{CuS} < \text{SnS}$  under 375 nm and  $\text{AgInS}_2 < \text{CuS} < \text{Bi}_2\text{S}_3 < \text{SnS}$  under 415 nm. All samples containing SnS quantum dots boosted the photocatalytic activity of  $\text{TiO}_2$  NPs under 375 nm light irradiation, which are related to a heterojunction with highest difference between the CB positions energy levels and thus faster electron transfer from SnS QDs to  $\text{TiO}_2$  NPs. The loading of 15% SnS QDs on  $\text{TiO}_2$  NPs matrix improved the photocatalytic activity of bare QDs 12 times. Generally, building the  $\text{TiO}_2/\text{AgInS}_2$  and  $\text{TiO}_2/\text{SnS}$  exhibited higher photoactivity under 375 nm than the pristine  $\text{TiO}_2$  and QDs, which resulted in a synergistic effect between QDs and  $\text{TiO}_2$  matrix. This enhancement can be also related with the improved light harvesting ability and decreasing recombination of electron–hole pairs by QDs-decorated  $\text{TiO}_2$ . Whereas, modification with CuS and  $\text{Bi}_2\text{S}_3$  showed lowered the activity than pristine  $\text{TiO}_2$  but higher activity than pristine CuS and  $\text{Bi}_2\text{S}_3$  QDs under 375 and 415 nm. The photocatalytic activity of pristine QDs and QDs-decorated  $\text{TiO}_2$  composites is different, which means that it is important to create the appropriate heterojunction between QDs and semiconductor nanoparticles. Our results may provide useful guide for designing of QDs-sensitized  $\text{TiO}_2$  composite for the air purification in the presence of low powered and low cost irradiation sources (LEDs), which reduce the costs of the photocatalytic processes. QD-decorated semiconductor NPs composites are considered to play an increasing role in photocatalytic applications in the near future.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/10/4/403/s1>, **Table S1.** TEM-EDX analysis for (a)  $\text{AgInS}_2$  QDs, (b) SnS QDs, (c)  $\text{TiO}_2/\text{AgInS}_2_{15}$ , (d)  $\text{TiO}_2/\text{SnS}_{15}$ , (e)  $\text{TiO}_2/\text{CuS}_{15}$ , (f)  $\text{TiO}_2/\text{Bi}_2\text{S}_3_{15}$ .

**Author Contributions:** Conceptualization, A.M.; funding acquisition, A.M.; experiment design, A.M., D.K., J.S., O.C., T.K. and G.T.; data analysis, A.M., J.S., O.C., A.Z.-M., T.K. and G.T.; writing—original draft, A.M., J.S., O.C., T.K. and A.Z.-M.; writing—review and editing, A.M. and A.Z.-M.; supervision, A.M. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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