

Article

Surface Properties and Photocatalytic Activity of KTaO_3 , CdS, MoS_2 Semiconductors and Their Binary and Ternary Semiconductor Composites

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Abstract: Single semiconductors such as KTaO_3 , CdS MoS_2 or their precursor solutions were combined to form novel binary and ternary semiconductor nanocomposites by the calcination or by the hydro/solvothermal mixed solutions methods, respectively. The aim of this work was to study the influence of preparation method as well as type and amount of the composite components on the surface properties and photocatalytic activity of the new semiconducting photoactive materials. We presented different binary and ternary combinations of the above semiconductors for phenol and toluene photocatalytic degradation and characterized by X-ray powder diffraction (XRD), UV-Vis diffuse reflectance spectroscopy (DRS), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) specific surface area and porosity. The results showed that loading MoS_2 onto CdS as well as loading CdS onto KTaO_3 significantly enhanced absorption properties as compared with single semiconductors. The highest photocatalytic activity in phenol degradation reaction under both UV-Vis and visible light irradiation and very good stability in toluene removal was observed for ternary hybrid obtained by calcination of KTaO_3 , CdS, MoS_2 powders at the 10:5:1 molar ratio. Enhanced photoactivity could be

related to the two-photon excitation in $\text{KTaO}_3\text{-CdS-MoS}_2$ composite under UV-Vis and/or to additional presence of CdMoO_4 working as co-catalyst.

Keywords: composites; photocatalysis; semiconductor; tantalate; sulfide; pollutant degradation

1. Introduction

Since the discovery of the photocatalytic splitting of water on TiO_2 photochemical electrodes by Fujishima and Honda in 1972 [1], semiconductor-based photocatalysts have attracted increasing interest due to their potential applications in solar energy conversion, hydrogen evolution and photodegradation of organic pollutants [2–11]. Among different photocatalysts, titanium dioxide has become the most studied and widely used semiconductor material, however, it can only be excited by UV light, leading to low efficiency for utilizing solar energy [12]. Therefore, it is still of great importance to develop new types of photocatalysts which should be highly active, photostable and activated by low powered and low cost irradiation sources. Furthermore, one of the promising approaches is combining some semiconductors to form composites which can improve the efficiency of a photocatalytic system because of novel or enhanced properties that do not exist in individual components [13–16]. It was demonstrated that the Bi_2WO_6 -based photocatalysts systems could be efficiently used in chemical synthesis and fuel production [7], whilst the graphene based composites seem to be a promising material for solar energy conversion and selective transformations of organic compounds [11]. Zhang *et al.* showed that the nanocomposites of TiO_2 -graphene exhibits much higher photocatalytic activity and stability than bare titanium dioxide toward the gas-phase degradation of benzene [17].

Among semiconductors, potassium tantalate with a wide band gap could be an interesting alternative to the well-known titanium dioxide. Tantalates possess conduction bands consisting of $\text{Ta}5d$ orbitals located at a more negative position than titanates ($\text{Ti}3d$) or niobates ($\text{Nb}4d$). Therefore, the high potential of the conduction band of tantalates could lead to being more advantageous in the photocatalytic reaction [18]. It has been reported by Liu *et al.* that sodium and potassium tantalates showed higher activities for water splitting than those of niobates synthesized by hydrothermal route. Moreover, the highest photocatalytic activity was exhibited by NaTaO_3 powder with cubic crystalline structure [19]. It was also observed that when NiO co-catalysts were loaded on the tantalate semiconductors, the photocatalytic activities were drastically increased [20]. Furthermore, there could be correlation between the photocatalytic activity of ABO_3 tantalates and preparation method as well as their crystal structure. Lin *et al.* showed that sol gel sodium tantalate with monoclinic crystalline structures exhibited higher photoactivity for water splitting than that with orthorhombic structure and obtained by solid-state method [21]. In other study Torres-Martínez *et al.* prepared sodium tantalate samples doped with Sm and La using sol-gel or solid state reaction methods. The best half-life time ($t_{1/2} = 65$ min) of photocatalytic degradation of methylene blue under UV light was shown by NaTaO_3 doped with Sm obtained by sol-gel technique and heat treated at 600 °C [22]. However, in the literature there is still not enough information about photocatalytic activity of tantalate for degradation of organic pollutants, especially potassium tantalate has received very little research attention in this area.



In contrast to potassium tantalate, cadmium sulfide is among the most exhaustively investigated semiconductors. It has a wide range of applications, including solar cells, optoelectronic devices, fluorescence probes, sensors, laser light-emitting diodes and photocatalysis [23–25]. Unfortunately, bare CdS photocatalyst has very low separation efficiency of photogenerated electron-hole pairs and undergoes photocorrosion which limit its practical application [26]. In order to improve photoactivity and to inhibit the photocorrosion, cadmium sulfide is usually coupled with other semiconductors, including CdS/TiO₂ [27–29], CdS/ZnO [30,31], CdS/ZnS [32], CdS/WO₃ [33] as well as CdS/MoS₂. In particular, MoS₂ semiconductor is an efficient co-catalyst. Moreover, the unique layered structure of MoS₂ endows many important properties, such as anisotropy, chemical stability and anti-photo corrosion. [34]. There were few studies on the MoS₂-CdS system obtained by impregnation [35], ball-milling combined calcination [36], electrodeposition and chemical bath deposition [37] or hydrothermal [38] methods for hydrogen production under visible light. Zong *et al.* showed that individual CdS and MoS₂ particles were almost inactive in hydrogen evolution compared to the MoS₂ particles deposited onto CdS. Moreover, researchers observed that the rate of hydrogen evolution on MoS₂/CdS was higher than on CdS particles loaded with other catalysts such as Pt, Ru, Rh, Pd and Au. This result was explained by the better electron transfer between MoS₂ and CdS [39].

Binary and ternary composites based on potassium tantalate, cadmium sulfide and molybdenum disulfide could be new examples of photoactive materials. In this study we obtained various combinations of KTaO₃, CdS, MoS₂ single semiconductors as well as their precursor solutions using calcination and hydro/solvothermal routes. The effect of the preparation method, type and amount of the composite components on the surface properties and photocatalytic activity in phenol degradation in the aqueous phase as well as activity and photostability in toluene degradation in the gas phase was investigated. Light emitting diodes (LEDs) were used in the gas phase measurements as a promising irradiation source, which allow to reduce power consumption and costs of photocatalytic processes.

2. Results and Discussion

2.1. BET Surface Area

The surface area and the pore volume of KTaO₃, CdS, MoS₂ semiconductors and their binary and ternary composites prepared by hydro/solvothermal as well as hydro/solvothermal mixed solutions and calcination methods are summarized in Table 1. The surface area of as-prepared samples fluctuated from less than 0.1 to 17.5 m²/g and was dependent on type and amounts of semiconductors as well as preparation methods. The pure CdS and MoS₂ semiconductors had BET surface area about 1.2 and 1.8 m²/g, respectively. The CdS-MoS₂ composites containing more or the same amounts of CdS as MoS₂ caused an increase in surface area whereas in the presence of the excess MoS₂ in the composite a drop in the surface area was observed as compared with pure semiconductors. The sample CdS-MoS₂ 4-1 presented the highest surface area (about 11.1 m²/g) from among CdS-MoS₂ composites. The KTaO₃-based composites prepared by hydro/solvothermal methods had higher BET surface areas than composites which were calcined. Extremely small surface area and nearly zero pore volume were observed for the KTaO₃-MoS₂ 10-1_C and KTaO₃-CdS-MoS₂ 10-1-1_C samples. In the case of binary KTaO₃-based composites it could be seen that potassium tantalate containing a small amount of MoS₂

had lower surface area than potassium tantalate containing a small amount of CdS. Moreover, in the case of ternary composites it could be also observed that the high loading of CdS resulted in a significant increase in surface area. The pore volumes of obtained photocatalysts were very low and fluctuated from zero to 0.0088 cm³/g. It was observed that the pore volumes increased with increasing the surface area.

Table 1. Sample label, preparation method, BET surface area and pore volume of obtained single semiconductors and their composites.

Sample Label	KTaO ₃ :CdS:MoS ₂ / Molar Ratio	Preparation Method	BET Surface Area/ [m ² /g]	Pore Volume/ [cm ³ /g]
KTaO ₃	1:0:0	hydrothermal	0.1	0.0001
CdS	0:1:0	solvothermal	1.2	0.0006
MoS ₂	0:0:1	hydrothermal	1.8	0.0009
CdS-MoS ₂ 5-1	0:5:1	solvothermal mixed solutions	5.0	0.0026
CdS-MoS ₂ 4-1	0:4:1	solvothermal mixed solutions	11.1	0.0056
CdS-MoS ₂ 1-1	0:1:1	solvothermal mixed solutions	10.4	0.0052
CdS-MoS ₂ 1-5	0:1:5	solvothermal mixed solutions	1.0	0.0006
KTaO ₃ -CdS 10-1_MS	10:1:0	solvothermal mixed solutions	17.5	0.0088
KTaO ₃ -CdS 10-1_C	10:1:0	hydro/solvothermal and calcination	0.4	0.0002
KTaO ₃ -MoS ₂ 10-1_MS	10:0:1	hydrothermal mixed solutions	2.8	0.0014
KTaO ₃ -MoS ₂ 10-1_C	10:0:1	hydrothermal and calcination	<0.1	~0
KTaO ₃ -CdS-MoS ₂ 10-1-1_MS	10:1:1	solvothermal mixed solutions	4.0	0.0019
KTaO ₃ -CdS-MoS ₂ 10-1-1_C	10:1:1	hydro/solvothermal and calcination	<0.1	~0
KTaO ₃ -CdS-MoS ₂ 10-5-1_MS	10:5:1	solvothermal mixed solutions	10.3	0.0051
KTaO ₃ -CdS-MoS ₂ 10-5-1_C	10:5:1	hydro/solvothermal and calcination	0.5	0.0003

2.2. XRD Analysis

Figure 1a shows XRD patterns for pure CdS and MoS₂ as well as CdS-MoS₂ samples with different CdS:MoS₂ molar ratio. Low observed intensity of the XRD peaks for MoS₂ and for CdS-MoS₂ with 1:5 ratio is likely caused by low crystallinity of the MoS₂ compound. As can be seen, adding less than 20% of CdS to MoS₂ causes a dramatic change in XRD pattern. CdS is a dominant phase and MoS₂ is hardly present. No traces of MoS₂ have been found for higher CdS concentration (CdS-MoS₂ 1:1 and CdS-MoS₂ 5:1 samples). Lattice parameters for CdS (*P6₃mc*, s.g. #186) were refined by using the LeBail method.

For CdS we obtained $a = 4.1341(8) \text{ \AA}$ and $c = 6.710(1) \text{ \AA}$ in very good agreement with reported by Wiedemeire *et al.* [40]. Adding MoS₂ does not change a lattice parameter, whereas c increases with increasing MoS₂ and for the sample which contains the highest amount of MoS₂ (sample b) the refined c is 6.733(3) Å. This clear change of the unit cell size and relative change of the intensity of three most dominant XRD peaks between 24 and 29 degrees, allow us to conclude that Mo atoms are incorporated into CdS hexagonal crystal structure. Figure 1b displays powder X-ray diffraction patterns for pure KTaO₃ prepared by the hydrothermal method. Two different methods were used to obtain KTaO₃-CdS and KTaO₃-MoS₂ composites. As can be seen from the XRD patterns for KTaO₃-CdS 10:1_C and KTaO₃-MoS₂ 10:1_C samples, the calcination method does not produce new phases and KTaO₃

together with CdS are observed. For the latest compound the most intense peaks are hardly visible between 25 and 30 deg. Contrary to the calcination method, the hydro/solvothermal mixed solutions route produces more complex compounds. For the system with CdS, the majority phase is Ta₂O₅ with small amount of TaS₂ and K₂Ta₁₅O₃₂. For the system with MoS₂ almost pure pyrochlore-like K₂Ta₂O₆ was found. This defect pyrochlore structure was described in details and also tested as a photocatalyst by Hu *et al.* [41].

Figure 1. Powder XRD patterns for (a) single CdS, MoS₂ and binary CdS-MoS₂ nanocomposites, (b) single KTaO₃ and binary KTaO₃-based nanocomposites, (c) ternary KTaO₃-based nanocomposites.

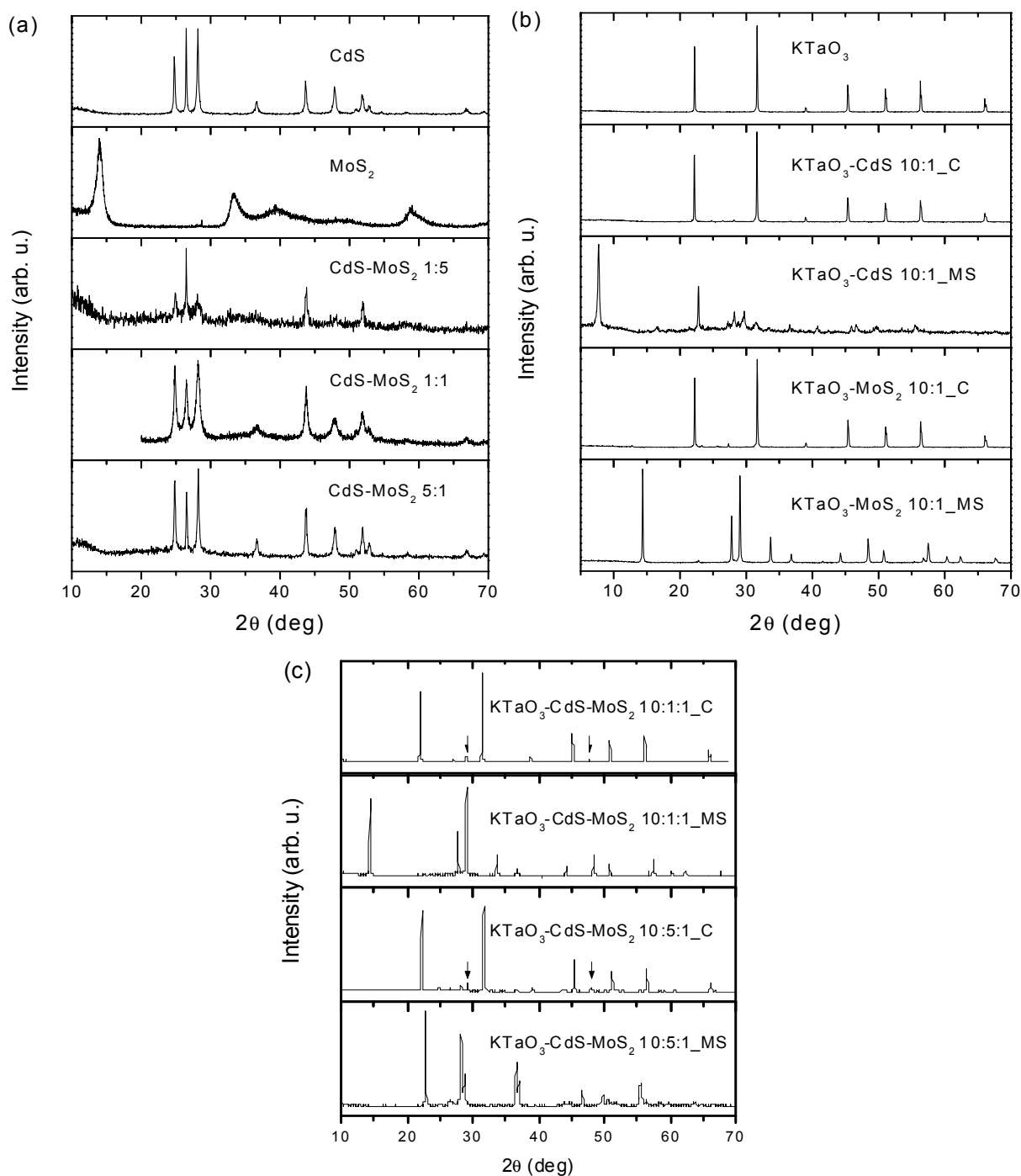


Figure 1c shows XRD patterns for ternary KTaO_3 -CdS- MoS_2 composites with two different molar ratios and two various preparation routes. Similarly to what was observed for binary composites produced by calcination method, the majority phase is KTaO_3 , however, a small amount of CdMoO_4 emerges with the two most intense peaks marked by arrow. While the solvothermal mixed solutions method causes decomposition of KTaO_3 , the main products detected are $\text{K}_2\text{Ta}_2\text{O}_6$ and Ta_2O_5 together with Mo-doped CdS for the sample 10:1:1 and 10:5:1, respectively.

2.3. Morphology

The morphology of the products was observed by SEM and is presented in the Figures 2–5. Figure 2 shows an SEM image of single semiconductors prepared by hydro/solvothermal methods. As clearly shown, the KTaO_3 have a cube-like shape with various sizes. Using higher magnification image of these particles, we notice that small KTaO_3 nanocubes with an average size of about $0.2\text{--}1\ \mu\text{m}$ grow at the surface of bigger cubes having widths of $5\text{--}8\ \mu\text{m}$. Pure CdS clearly indicates nanoleaf structures having the length of about $3\ \mu\text{m}$. In the case of MoS_2 we observed that the product has the shape of flower-like microspheres with an average diameter of $5\ \mu\text{m}$.

Figure 2. SEM images of single semiconductors obtained by hydrothermal method: (a,b) KTaO_3 ; (c) CdS; (d) MoS_2 .

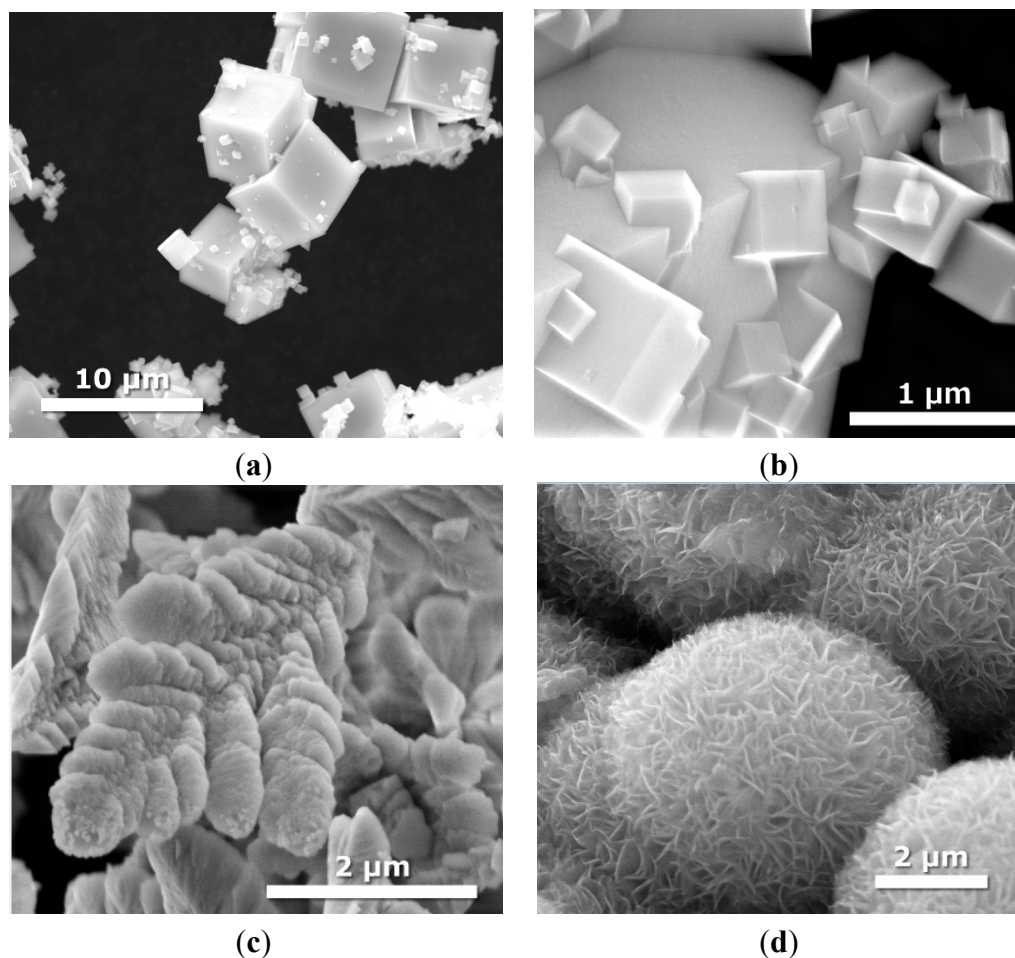


Figure 3 shows SEM images of binary CdS-MoS₂ composites with different CdS and MoS₂ molar ratios. In the case of CdS-MoS₂ 5-1 sample containing the highest molar ratio of CdS, we still observed nanoleaf structure indicating the presence of CdS. XRD analysis also showed that no traces of MoS₂ have been found for higher CdS concentration. The increase of MoS₂ ratio resulted in the formation of hexagonal shaped nanostructures with average edge size of about 100–125 nm (Figure 3b).

As can be seen from Figure 3c,d, further increase in molar ratio of MoS₂ to CdS causes a large change in microstructures. We can observe bonded structures of microspheres with diameters ranging from 0.08 to 1 μm.

Figure 3. SEM images of binary CdS-MoS₂ composites obtained by solvothermal mixed solution methods with different molar ratio of CdS: (a) CdS:MoS₂ = 5:1; (sample CdS-MoS₂ 5-1); (b) CdS:MoS₂ = 4:1 (sample CdS-MoS₂ 4-1); (c) CdS:MoS₂ = 1:1 (sample CdS-MoS₂ 1-1); and (d) CdS:MoS₂ = 1:5 (sample CdS-MoS₂ 1-5).

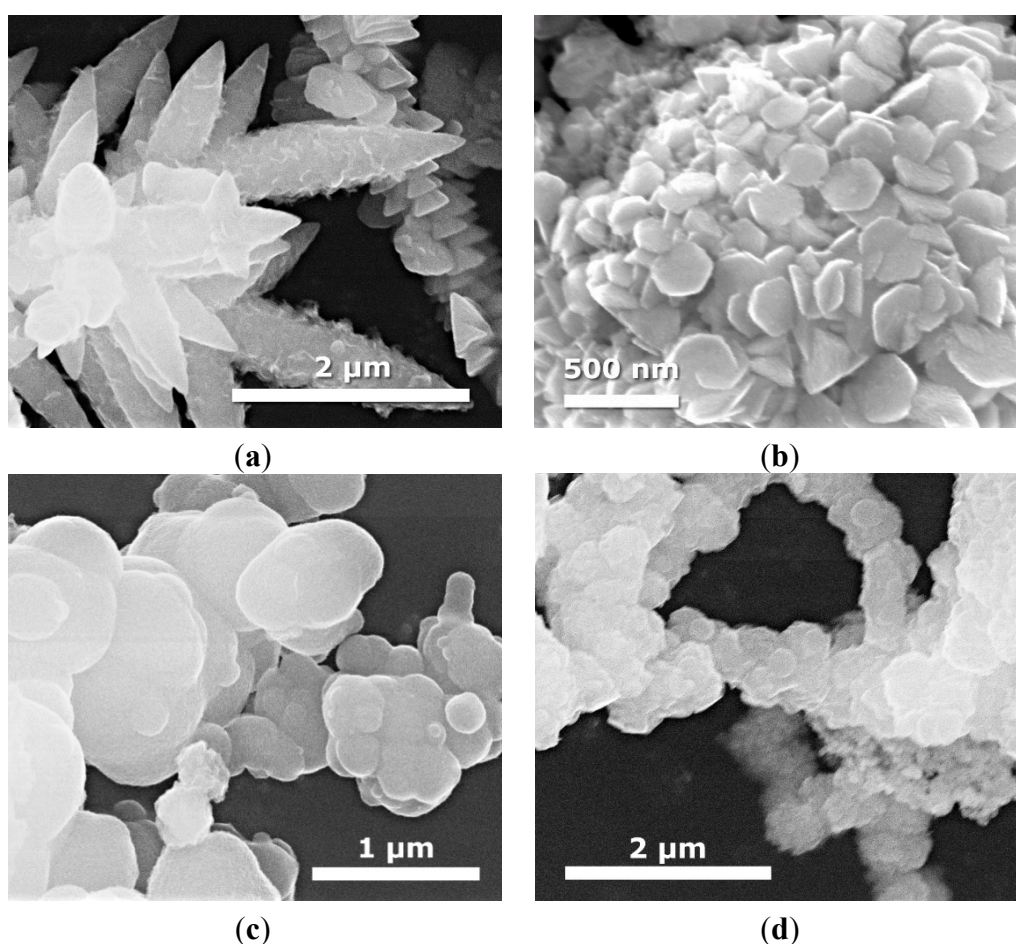
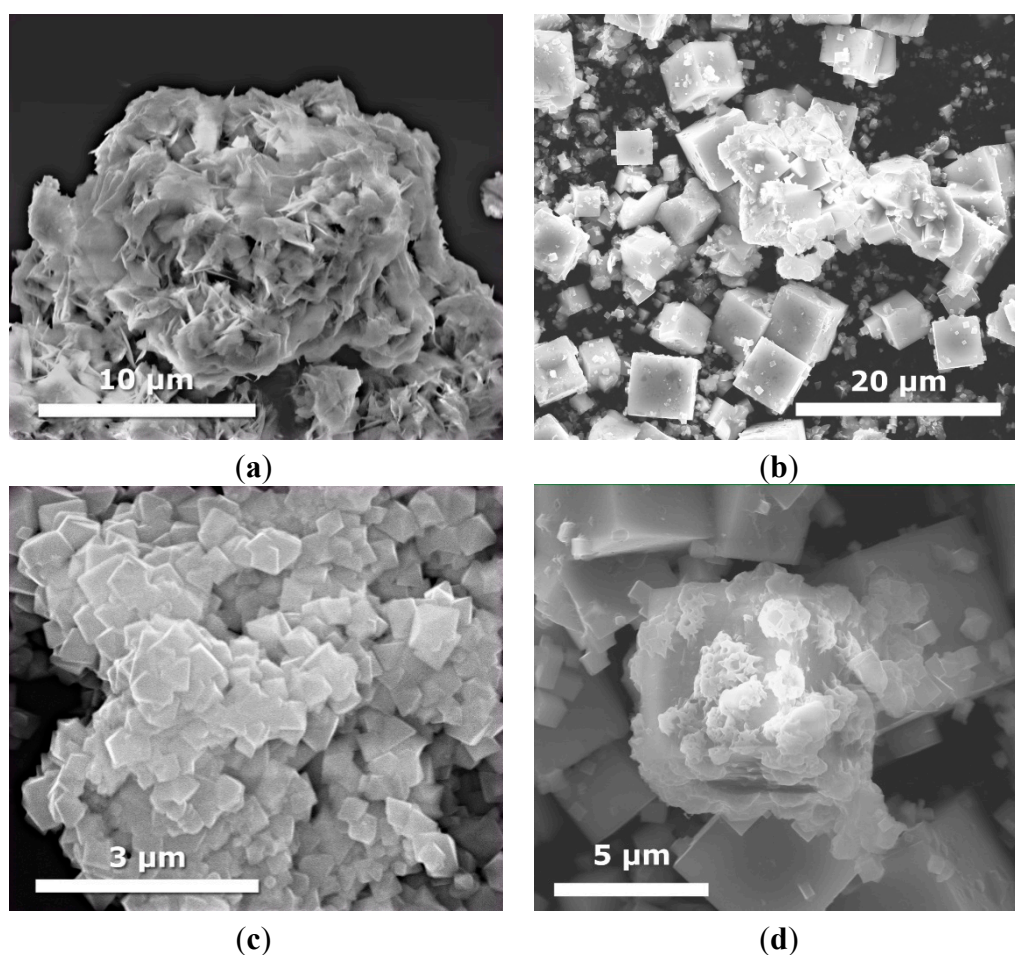


Figure 4 displays SEM images of binary KTaO₃-CdS and KTaO₃-MoS₂ composites prepared by two different routes. In the case of the KTaO₃-CdS and KTaO₃-MoS₂ samples, which were obtained by calcination, we can see mainly the structure of cubes, which indicates the presence of KTaO₃. In contrast, the solvothermal mixed solutions route leads to the formation of other nanostructures, suggesting the presence of more complex compounds: K₂Ta₁₅O₃₂, Ta₂O₅, TaS₂ and K₂Ta₂O₆ for the system with CdS and MoS₂ which were confirmed by XRD analysis. The transition of the KTaO₃ structure from cubic to octahedral was observed for the samples KTaO₃-MoS₂ 10-1 and KTaO₃-CdS-MoS₂ 10-1-1 obtained by

solvothermal mixed solutions. In the case of calcinated $\text{KTaO}_3\text{-CdS-MoS}_2$ 10-5-1 composite we can see nanoleaves of CdS deposited on the surface of large cubes of KTaO_3 (Figure 5d). Contrary to calcination, solvothermal mixed solutions method causes dramatic changes in the structure—neither cubes nor nanoleaf are observed (Figure 5c).

Figure 4. SEM images of binary $\text{KTaO}_3\text{-CdS}$ and $\text{KTaO}_3\text{-MoS}_2$ composites obtained with different molar ratio and using two preparation routes: (a) $\text{KTaO}_3\text{-CdS}$ (10:1) obtained by solvothermal mixed solutions (sample $\text{KTaO}_3\text{-CdS}$ 10-1_MS); (b) $\text{KTaO}_3\text{-CdS}$ (10:1) obtained by calcination of single previously synthesized semiconductors (sample $\text{KTaO}_3\text{-CdS}$ 10-1_C); (c) $\text{KTaO}_3\text{-MoS}_2$ (10:1) obtained by solvothermal mixed solutions (sample $\text{KTaO}_3\text{-MoS}_2$ 10-1_MS); and (d) $\text{KTaO}_3\text{-MoS}_2$ (10:1) obtained by calcination of single previously synthesized semiconductors (sample $\text{KTaO}_3\text{-MoS}_2$ 10-1_C).

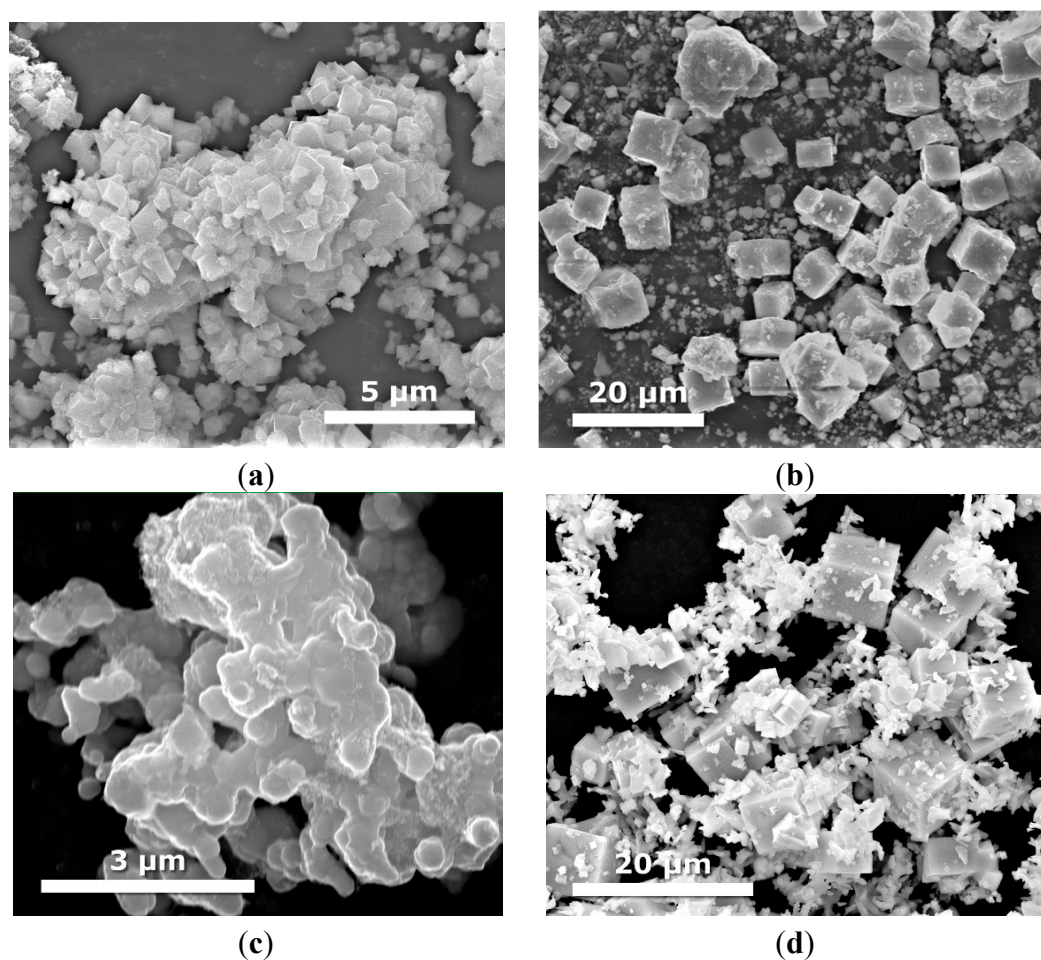


2.4. UV-Vis Properties

DRS UV-Vis absorption spectra in the wavelength range of 200–800 nm of as-prepared samples were investigated and the results are shown in Figure 6a–c. Figure 6a depicts the spectra for pure CdS and MoS_2 semiconductors and their binary composites with varying molar ratio between CdS and MoS_2 . As it can be seen, all the samples could absorb both UV and visible light. The absorption edge of single CdS is at about 510 nm, which coincides with the literature. Moreover, it was previously reported that the absorption properties of CdS are strongly shape-dependent [42]. It could also be seen

that the loading of MoS₂ on CdS improved the light absorption as compared with pure CdS. Liu *et al.* also presented enhanced absorption properties for CdS-MoS₂ composites to photocatalytic H₂ production [38]. In comparison with single CdS, composites with excess of CdS exhibited a red-shift and a less steep absorption edge.

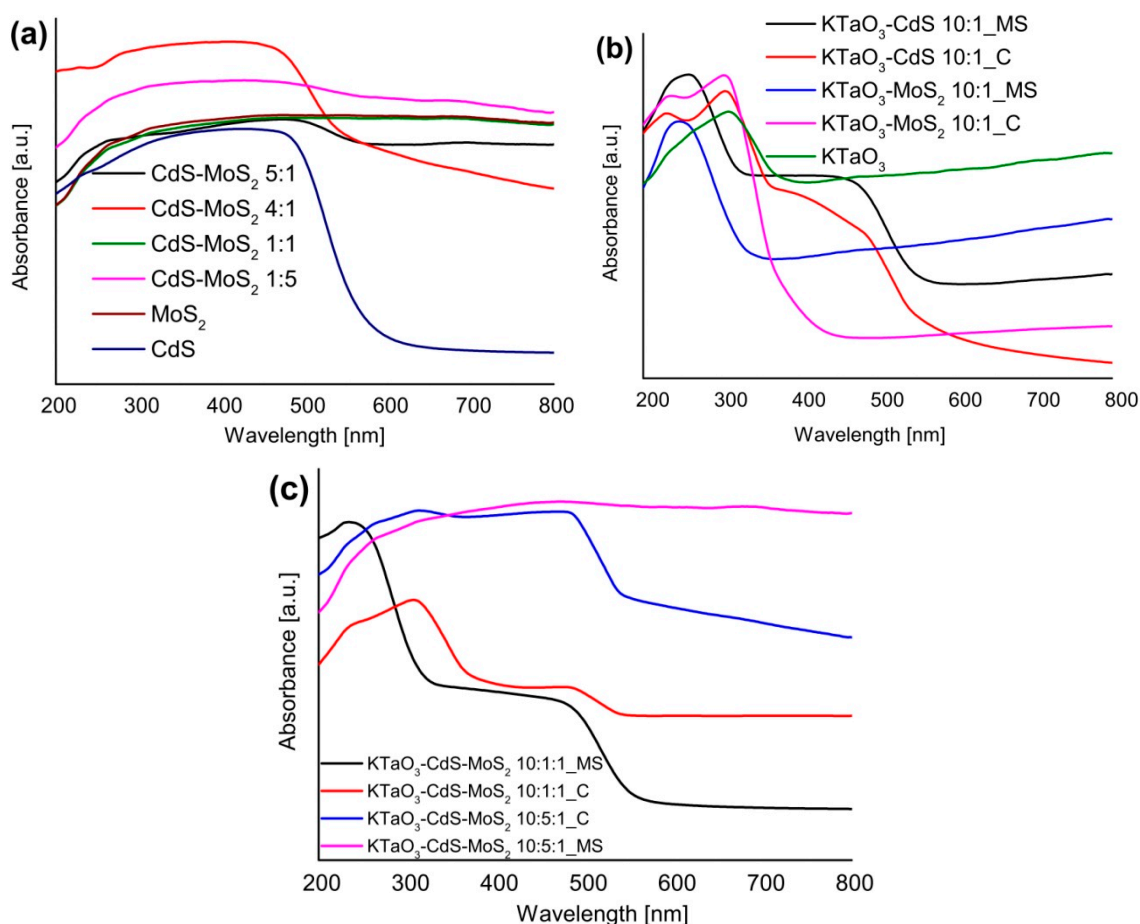
Figure 5. SEM images of ternary KTaO₃-CdS-MoS₂ composites obtained with different molar ratio and using two different preparation route: (a) KTaO₃-CdS-MoS₂ (10:1:1) obtained by solvothermal mixed solutions (sample KTaO₃-CdS-MoS₂ 10-1-1_MS); (b) KTaO₃-CdS-MoS₂ (10:1:1) obtained by calcination of single previously synthesized semiconductors (sample KTaO₃-CdS-MoS₂ 10-1-1_C); (c) KTaO₃-CdS-MoS₂ (10:5:1) obtained by solvothermal mixed solutions (sample KTaO₃-CdS-MoS₂ 10-5-1_MS); and (d) KTaO₃-CdS-MoS₂ (10:5:1) obtained by calcination of single previously synthesized semiconductors (sample KTaO₃-CdS-MoS₂ 10-5-1_C).



The absorbance was very similar for pure MoS₂ and composite with 1:1 molar ratio between components. However, for composites containing excess MoS₂, absorption was more intense. Figure 6b displays absorption spectra of single KTaO₃ and binary KTaO₃-based composites containing small amounts of CdS or MoS₂ and prepared by two different procedures. In the case of single KTaO₃, there is an obvious absorption band centered at about 310 nm and no absorption peak is detected above 310 nm. For octahedral KTaO₃ nanocrystalline obtained by Zou *et al.* using hydrothermal method, the absorption peak was detected at 265 nm [43]. It was also observed that binary KTaO₃-based composites

loaded with small amount of CdS or MoS₂ had steeper absorption edges and maximum absorption shifted to shorter wavelengths as compared with single potassium tantalate. Moreover, KTaO₃-CdS composites showed second steep absorption edges in the visible light region. Figure 6c shows the spectra for ternary KTaO₃-CdS-MoS₂ composites containing different amount of CdS and prepared by various methods. Loading of larger amounts of CdS onto KTaO₃-CdS-MoS₂ composites significantly improved the spectral absorption. For ternary composites containing greater amount of cadmium sulfide and obtained by both methods, there were widest absorption ranges among all obtained samples but only for a calcined composite a steep absorption edge (at about 510 nm) was observed. In general, loading MoS₂ onto CdS shifted absorbance peaks to longer wavelengths, just as loading CdS onto KTaO₃ enhanced absorption features. It may be suggested that the best adsorption properties could probably be achieved for the ternary KTaO₃-CdS-MoS₂ composites containing appropriate molar ratio between semiconductors.

Figure 6. The UV-Vis diffuse reflectance spectra of (a) single CdS, MoS₂, and binary CdS-MoS₂ nanocomposites, (b) single KTaO₃ and binary KTaO₃-based nanocomposites, (c) ternary KTaO₃-based nanocomposites.



2.5. The Photocatalytic Degradation of Phenol in the Aqueous Phase

Photocatalytic activity of as-prepared semiconductors and their nanocomposites was estimated by examining the reaction of phenol degradation in the presence of UV-Vis light irradiation and for

selected samples photoactivity under visible light was also analyzed. No degradation of phenol was observed in the absence of photocatalyst or illumination. Photocatalytic activity under UV-Vis and visible light is presented as phenol degradation rate (Table 2) and as efficiency of phenol removal after 60 min of irradiation (Figures 7 and 8). Commercially available P25 TiO₂ was used as a standard reference material in photocatalytic activity measurements.

Figure 7. The percentage degradation of phenol at various time intervals under UV-Vis light in the presence: (a) single CdS, MoS₂, and CdS-MoS₂ nanocomposites; (b) single KTaO₃ and binary KTaO₃-based nanocomposites; (c) ternary KTaO₃-based nanocomposites.

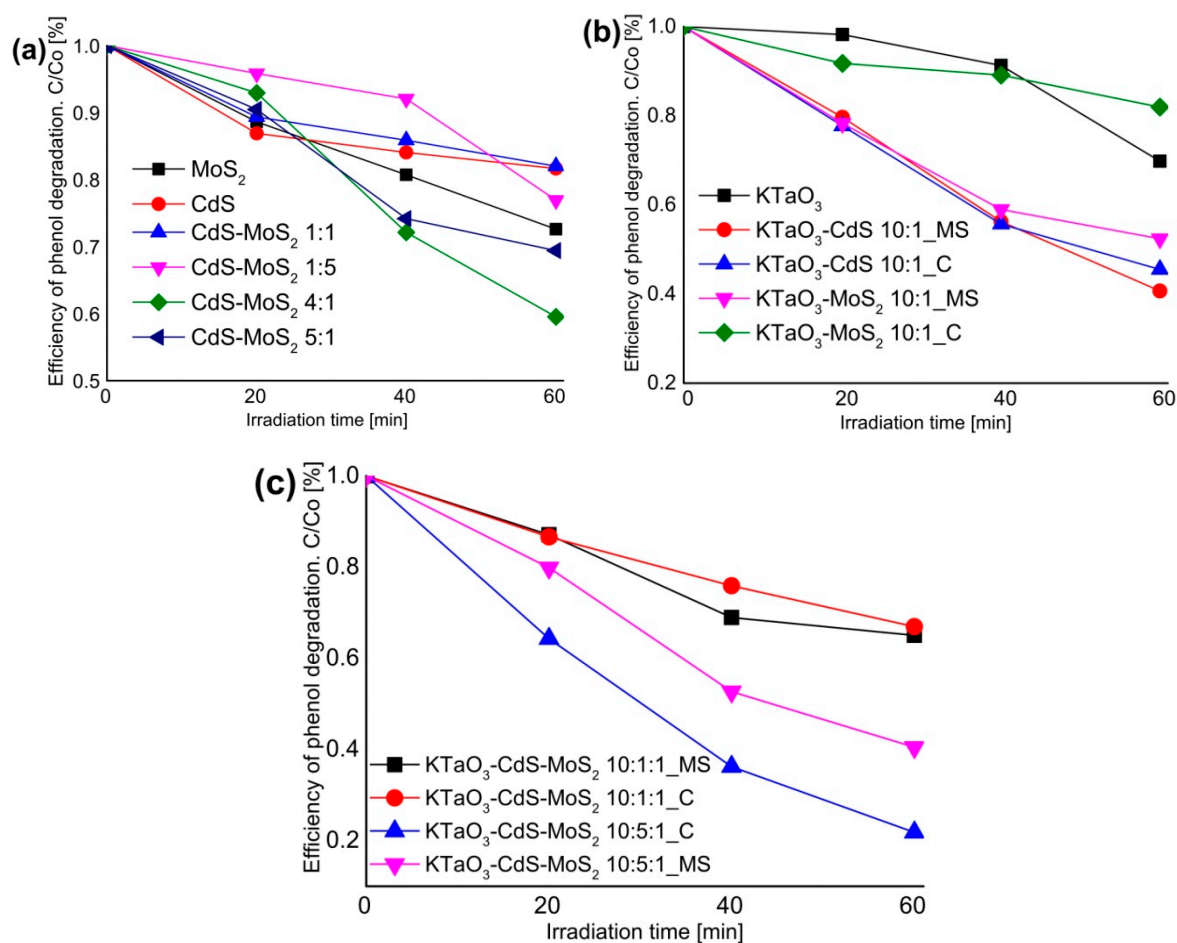


Figure 7a shows the results of phenol degradation under UV-Vis light in the presence of pure CdS and MoS₂, and their binary composites synthesized by hydro/solvothermal methods. In comparison with pure CdS and MoS₂, photocatalytic activity for degradation of phenol increased in the presence of CdS-MoS₂ nanocomposites containing excess of CdS. In the presence of CdS-MoS₂ 4:1 and CdS-MoS₂ 5:1, the percentage degradation of phenol after 60 min was about 41% and 31%, respectively, which indicates that with decreasing excess of CdS, the photocatalytic activity is relatively higher. For composites containing more or the same amount of MoS₂ as CdS, photoactivity was comparable with pure semiconductors. The highest phenol degradation rate, about $1.41 \mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$, was observed in the case of the CdS-MoS₂ 4:1 composite. For the other samples degradation rates were low and fluctuated from 0.62 to $0.90 \mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$. Zong and co-workers reported that the photocatalytic H₂ production achieved a maximum when the loading amount of MoS₂ on CdS was about 0.2 wt % [39].

Figure 7b displays the results of phenol degradation under UV-Vis light in the presence of single KTaO_3 and binary potassium tantalate-based composites containing a small amount of CdS or MoS_2 and prepared by different routes. The phenol degradation after 60 min of irradiation was only 18% in the case of the calcined $\text{KTaO}_3\text{-MoS}_2$ sample, which is lower than in the presence of single KTaO_3 (about 30%). While for the $\text{KTaO}_3\text{-MoS}_2$ sample obtained by hydrothermal method phenol degradation was more efficient (about 48%). It could be also observed that photoactivities were similar and increased to 59% and 55% for $\text{KTaO}_3\text{-CdS}$ 10-1 composites prepared by hydrothermal and calcination method, respectively. It may be suggested that loading cadmium sulfide onto KTaO_3 enhanced photoactivity, while the influence of introduction of molybdenum disulfide on the photoactivity was dependent on preparation technique. Figure 7c depicts the results of phenol degradation under UV-Vis light for ternary $\text{KTaO}_3\text{-CdS-MoS}_2$ composites containing various amounts of CdS as well as prepared by different methods. In general, more addition of CdS significantly enhanced the photocatalytic activity of ternary composites. In the presence of the $\text{KTaO}_3\text{-CdS-MoS}_2$ 10-1-1 sample the percentage degradation of phenol was low (about 35%) and quite comparable for both methods. In the case of the $\text{KTaO}_3\text{-CdS-MoS}_2$ 10-5-1 composites photoactivities were much more efficient. After 60 min of irradiation, for the sample prepared by hydro/solvothermal method phenol degradation reached 60%. At the same time in the presence of the $\text{KTaO}_3\text{-CdS-MoS}_2$ 10-5-1 sample prepared by the calcination method about 80% of phenol was degraded and it was the highest efficiency among all obtained samples. Therefore, appropriate ratio between KTaO_3 , CdS and MoS_2 semiconductors in the composites is supposed to be responsible for the highest efficiency of phenol photodegradation. This deduction coincides with the UV-Vis properties of obtained samples described in Section 3.3.

Figure 8. The percentage degradation of phenol at various time intervals under visible light in the presence of selected composites.

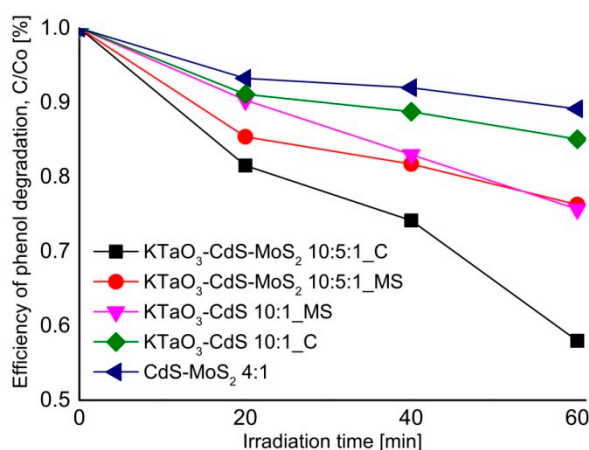


Figure 8 shows the results of phenol degradation under visible light for selected samples which exhibited the highest efficiency of phenol degradation under UV-Vis light irradiation. Among these, the highest activity (about 42%) after 60 min of visible irradiation was also exhibited by calcined ternary $\text{KTaO}_3\text{-CdS-MoS}_2$ 10-5-1 composites. In the case of the binary calcined composite containing small amount of CdS , photoactivity reached about 15%. In the presence of samples obtained by the solvothermal mixed solutions route activity was more efficient (24%). The lowest activity (about 11%) was observed for the composite containing CdS and MoS_2 at the 4:1 molar ratio.

2.6. The Photocatalytic Degradation of Toluene in the Gas Phase

The photocatalytic activity and stability of as-prepared photocatalysts were also evaluated by degradation of the toluene in the gas phase under UV light irradiation using low powered irradiation source, e.g., LEDs ($\lambda_{\max} = 375$ nm) in four subsequent measurement cycles. The efficiency of toluene photodegradation after 60 min in the presence of as-prepared semiconductor samples is given in Table 2.

It could be seen that CdS, KTaO₃ and MoS₂ semiconductors and their composites were photoactive in toluene degradation. In the case of single semiconductors, removal efficiency in the presence of CdS reached about 57% after a 60-min process and activity was stable in four subsequent cycles of irradiation. While in the presence of KTaO₃ and MoS₂ photocatalytic activity decreased from 64% and 46% (1st cycle) to 37% and 22% (4th cycle), respectively. The highest activity and stability under UV light irradiation from all among CdS-MoS₂ composites was exhibited by samples at the molar ratio 4:1 and 1:1.

Table 2. Photocatalytic activities of obtained samples for toluene photodegradation in four subsequent measurement cycles and for phenol degradation presented as phenol degradation rate.

Sample Label	Phenol Degradation Rate under UV-Vis/($\mu\text{mol}\cdot\text{dm}^{-3}\cdot\text{min}^{-1}$)	Toluene Degradation after 1 h Irradiation (LEDs, $\lambda_{\max} = 375$ nm) [%]			
		1st Cycle	2nd Cycle	3rd Cycle	4th Cycle
KTaO ₃	0.79	64	63	42	37
CdS	0.61	57	57	57	52
MoS ₂	0.90	46	23	22	22
CdS-MoS ₂ 1-5	0.77	57	53	44	27
CdS-MoS ₂ 1-1	0.62	61	53	62	52
CdS-MoS ₂ 5-1	0.81	70	60	49	48
CdS-MoS ₂ 4-1	1.41	53	56	60	62
KTaO ₃ -CdS 10-1_MS	2.08	47	45	41	40
KTaO ₃ -CdS 10-1_C	1.75	53	48	52	50
KTaO ₃ -MoS ₂ 10-1_MS	1.69	55	51	49	51
KTaO ₃ -MoS ₂ 10-1_C	0.55	46	34	37	35
KTaO ₃ -CdS-MoS ₂ 10-1-1_MS	1.15	50	52	48	39
KTaO ₃ -CdS-MoS ₂ 10-1-1_C	1.11	53	54	49	40
KTaO ₃ -CdS-MoS ₂ 10-5-1_MS	1.99	50	41	43	41
KTaO ₃ -CdS-MoS ₂ 10-5-1_C	2.81	48	48	50	46
TiO ₂ (P25)	2.87	98	96	95	95

The lowest photostability presented the CdS-MoS₂ sample when the molar ratio was 1:5. It suggests that an excess of MoS₂ caused the decrease in photostability. The CdS-MoS₂ composite at the molar ratio 5:1 exhibited the highest activity in the 1st cycle (about 70%) but this activity decreased to 48% in the 4th cycle of photoirradiation. In the case of binary KTaO₃-based composites it was observed that the photoactivity about 50% and the best stability during four cycles of irradiation was exhibited by potassium tantalate with a small amount of cadmium sulfide (KTaO₃-CdS 10-1 sample) prepared by the calcination method and potassium tantalate with molybdenum disulfide (KTaO₃-MoS₂ 10-1

sample) obtained by the hydrothermal mixed solutions route. While the photocatalytic activity of the $\text{KTaO}_3\text{-MoS}_2$ 10-1 sample prepared by calcination method after four cycles of irradiation was less by 11% as compared with the first cycle. It indicates that the activity is dependent not only on the type and content of the composite components but also on the preparation method. All of prepared ternary $\text{KTaO}_3\text{-CdS-MoS}_2$ composites exhibited about 50% efficiency degradation of toluene after the 1st cycle of irradiation, but activity didn't change after four cycles only in the case of the sample $\text{KTaO}_3\text{-CdS-MoS}_2$ 10-5-1 obtained by the calcination method.

2.7. The Origin of Photocatalytic Activity

UV and visible light induced photoactivity presented as efficiency of phenol removal after 60-min irradiation for the most active binary and ternary composites is shown in Figure 9. Highest activity under UV-Vis light of $\text{KTaO}_3\text{-CdS-MoS}_2$ (10:5:1) composite, obtained by solvothermal preparation of single semiconductors followed by calcination, could be related to the presence of heterojunctions between semiconductors. One pot reaction used for preparation of the $\text{KTaO}_3\text{-CdS-MoS}_2$ composite did not allow the formation of well-developed crystal structure of all semiconductors, as was shown in XRD analysis. However, the structure obtained by the sintering of three components could favor photogenerated charge carriers transfer between phase boundary of semiconductors resulted in higher photoactivity. The $\text{KTaO}_3\text{-CdS-MoS}_2$ nanocomposite could be excited by two photons due to utilization of a heterojunction between KTaO_3 with two low band gap semiconductors (*i.e.*, CdS and MoS_2). As shown in Figure 10, UV light could induce excitation in solid KTaO_3 ($E_g = 3.4$ eV) and generate free electrons (e^-) and holes (h^+). Since the VB position of KTaO_3 (+3.1 V) is lower than the VB band of MoS_2 (+1.8 V), h^+ transfer would then occur from KTaO_3 to MoS_2 . At the same time UV or visible light could be absorbed by CdS ($E_g = 2.5$ eV) and generate e^- and h^+ in CdS. As the CB position of CdS (−0.6 V) is higher in energy than the CB of solid MoS_2 (+0.05 V), electron transfer could occur from CdS to MoS_2 , thereby causing charge separation at the CdS- MoS_2 junction. Finally positioning the CB of KTaO_3 (−0.3 V) higher in energy than the VB of CdS (+1.8 V) causes e^- transfer from KTaO_3 to CdS and recombination of e^- in KTaO_3 with h^+ generated in CdS, thus completing the photoexcitation cycle in which the excited state of MoS_2 has been achieved via a two-photon process. Thus, organic compounds (such as phenol or toluene) could be degraded via active oxygen species generated at the surface of excited MoS_2 in two photons process.

Additionally, higher activity under UV-Vis light of the $\text{KTaO}_3\text{-CdS-MoS}_2$ 10-5-1_C sample could be also related to the presence of CdMoO_4 detected by XRD analysis (see Figure 1c). Photocatalytic activity of pure and Ag-modified CdMoO_4 under simulate solar irradiation was reported by others [44,45]. The valence band of CdMoO_4 consists of the hybrid orbitals of O 2p as well as Cd 6s and the conduction band consists of Mo 4d orbital and the band gap energies between them is about 3.4 eV. Thus, CdMoO_4 presented at the surface of composite could also adsorb UV light and enhance activity in observed photodegradation reaction. Lower UV and Vis-induced photoactivity of $\text{KTaO}_3\text{-CdS-MoS}_2$ (10:5:1) composite obtained by mixed solvothermal reaction, comparing to that one prepared by calcination step, could be related the decomposition of KTaO_3 and formation of $\text{K}_2\text{Ta}_2\text{O}_6$ and Ta_2O_5 as main component of as-prepared samples.

Figure 9. Efficiency of phenol removal under UV-Vis and visible light ($\lambda > 420$ nm) for selected binary and ternary composites.

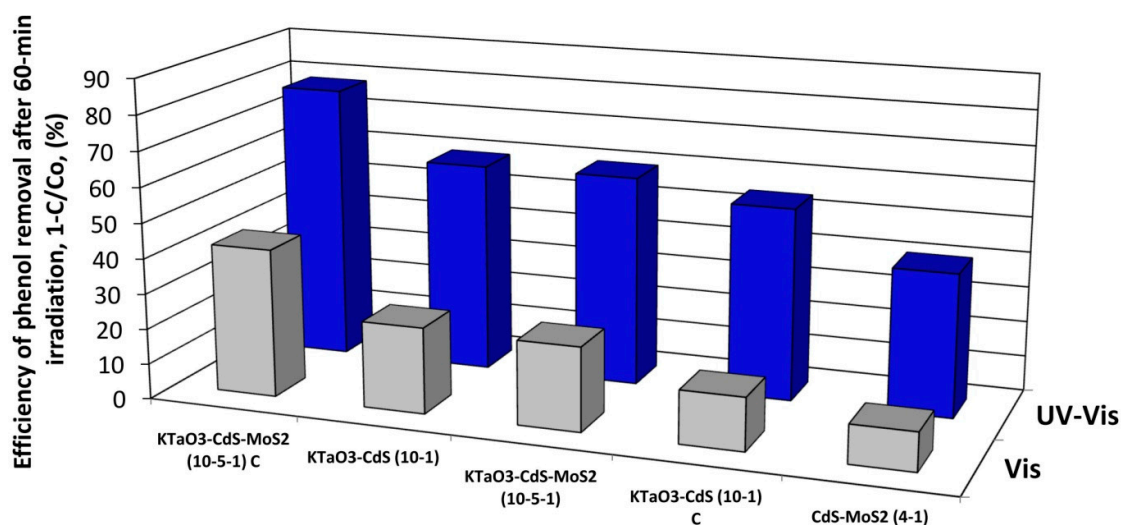
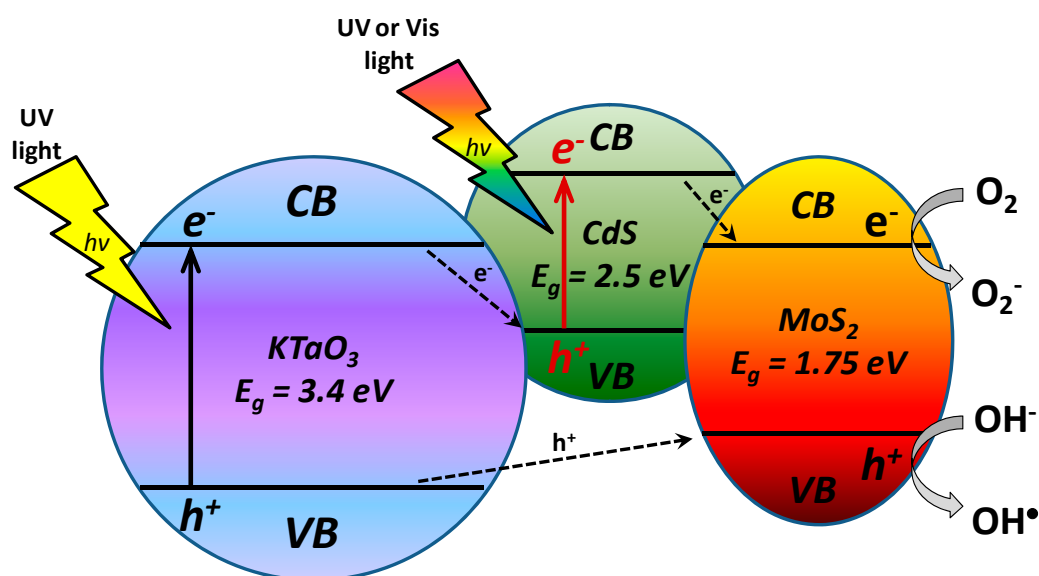


Figure 10. Probable UV-Vis two-photon excitation cycle of KTaO₃-CdS-MoS₂ composite: (1) UV induced excitation in solid KTaO₃ ($E_g = 3.4$ eV) to generate free electrons (e^-) and holes (h^+), and since the VB position of KTaO₃ is lower than the VB band of MoS₂, h^+ transfer would then occur from KTaO₃ to MoS₂; (2) UV or visible light excitation of solid CdS ($E_g = 2.5$ eV) also generates e^- and h^+ in CdS, and as the CB position of CdS is higher in energy than the CB of solid MoS₂, electron transfer could occur from CdS to MoS₂, thereby causing a charge separation at the CdS-MoS₂ junction; (3) positioning the CB of KTaO₃ higher in energy than the VB of CdS causes e^- transfer from KTaO₃ to CdS and recombination of e^- in KTaO₃ with h^+ generated in CdS, thus completing the photoexcitation cycle in which the excited state of MoS₂ has been achieved via a two-photon process.



3. Experimental

3.1. Materials and Instruments

Tantalum (V) oxide (>99% Aldrich, Poznan, Poland) and potassium hydroxide (Chempur, pure p.a.) were used as precursors for the preparation of KTaO_3 . Thiourea (Aldrich, 99%) has been chosen as a sulfur source to synthesize sulfides. $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 99\%$) and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 99.5\%$) were used as precursors of Cd and Mo, respectively. Ethanol, polyethylene glycol 400 (PEG-400), ethylene glycol (EG) were purchased from POCH S.A. (Gliwice, Poland) and used without further purification. Deionized water was used for all reactions and treatment processes. A commercial form of TiO_2 (P25, crystalline composition: 80% anatase, 20% rutile, surface area 50 g/m^2) from Evonik (Essen, Germany) was used for the comparison of the photocatalytic activity.

Nitrogen adsorption–desorption isotherms at 77 K were measured using a Micromeritics Gemini V (model 2365) physisorption analyzer (Micromeritics Instrument, Norcross, GA, USA). Specific surface areas were calculated following typical Brunauer–Emmett–Teller (BET) method using the adsorption data in the relative pressure (p/p_0) range from 0.05 to 0.3. Prior to adsorption measurements the samples were degassed under vacuum at 200 °C for 2 h.

Diffuse reflectance spectra (DRS) of the synthesized materials were characterized using the Thermo Scientific Evolution 220 UV-Visible spectrophotometer (Thermo Scientific, Waltham, MA, USA) equipped with ISA-220 integrating sphere accessory. The UV-Vis DRS spectra were recorded in the range of 200–800 nm using a barium sulfate reference.

Powder X-ray diffraction (PXRD, Philips/PANalytical X'Pert Pro MPD diffractometer, (PANalytical, Almelo, The Netherlands) with $\text{Cu K}\alpha$ radiation $\lambda = 1.5418 \text{ \AA}$) was used to determine the phase composition and calculate lattice parameters of polycrystalline samples.

The morphology of the semiconductor composites was investigated with FEI Quanta 250 FEG scanning electron microscope (SEM; FEI, Hillsboro, OR, USA) working in high vacuum mode. Energy-dispersive X-ray spectroscopy (EDS) measurements were carried out using SEM-integrated EDAX Apollo-SDD detector (EDAX Inc., Mahwah, NJ, USA). Accelerating voltage was set to 30 kV. Standardless analysis was conducted with the EDAX TEAM software with *eZAF* quantization method.

3.2. Synthesis of Single KTaO_3 , CdS and MoS_2 Semiconductors

KTaO_3 , CdS and MoS_2 semiconductors were prepared by hydro/solvothermal methods using an autoclave with a capacity of 500 mL as the reactor. In a typical procedure for the preparation of potassium tantalate, KOH (30 g) was dissolved in deionized water (60 mL), then Ta_2O_5 (11 g) and PEG-400 (3 mL) were added. This mixture (marked as *solution A*) was stirred for 1 h before it was transferred into a Teflon-lined stainless steel autoclave. The autoclave was sealed and got heated at 200 °C for 24 h. After cooling naturally to room temperature, the resulting powder was washed several times by centrifugation with distilled water and ethanol respectively and dried in an oven at 70 °C for 8 h. Finally, some white powder was obtained.

Cadmium sulfide was prepared based on the methodology presented by Zhong *et al.* [42]. In a typical procedure, CdCl_2 (18.3 g) was added into deionized water (160 mL) and EG (160 mL) under continuous stirring for 15 min. After that, thiourea (15.2 g) was added to the solution and stirring was



continued for an additional 20 min. This mixture (marked as *solution B*) was transferred into the autoclave which was sealed and maintained at 190 °C for 24 h and allowed to cool down to room temperature naturally. The crystalline powder product was washed several times by centrifugation with distilled water and ethanol, respectively and dried in the oven at 70 °C for 8 h. Finally, some yellow powder was obtained.

Molybdenum disulfide was synthesized using a method similar to reported by Wang *et al.* [46]. To prepare MoS₂, Na₂MoO₄·2H₂O (12.1 g), thiourea (15.6 g) and PEG-400 (3.5 g) were dissolved in deionized water (300 mL). The solution was stirred continuously for 15 min. The resulting mixture (marked as *solution C*) was transferred into the teflon-lined stainless autoclave which was maintained at 200 °C for 24 h, then cooled to room temperature. The precipitate was washed with deionized water and dried in the oven at 80 °C for 6 h. Finally, some black powder was obtained.

3.3. Synthesis of Binary and Ternary Semiconductor Composites

The KTaO₃, CdS and MoS₂ powders or solutions A, B, C prepared according to the methods described in Section 2.2 were combined to form semiconductor nanocomposites by the calcination or by the hydro/solvothermal mixed solutions methods, respectively. All prepared samples with different molar ratios between semiconductors are presented in Table 1.

To prepare KTaO₃-CdS, KTaO₃-MoS₂ and KTaO₃-CdS-MoS₂ composites by the calcination method, KTaO₃ and CdS or/and MoS₂ powders, respectively were mixed together sufficiently with various molar ratios. The powder mixture was calcined in the oven at 500 °C for 3 h with a heating rate of 3 °C/min. Then the heated mixture was removed from the oven and allowed to cool to room temperature naturally.

A typical hydro/solvothermal mixed solutions process for the preparation of CdS-MoS₂; KTaO₃-CdS; KTaO₃-MoS₂; KTaO₃-CdS-MoS₂ composites with various molar ratios between semiconductors was as follows: the required amounts of solutions B and C; A and B; A and C; A and B and C, respectively were mixed together and stirred continuously for 45 min using a magnetic stirrer. Then the as-prepared mixture was placed in the autoclave and heated at 200 °C for 24 h. The resulting precipitate was washed with distilled water and ethanol, respectively and dried in the oven at 70 °C for 8 h.

3.4. Measurement of Photocatalytic Activity in the Aqueous Phase

The photocatalytic activity of KTaO₃, CdS and MoS₂ single semiconductors and their nanocomposite powder in ultraviolet (UV) and visible light (Vis) was estimated by monitoring the decomposition rate of 0.21 mM phenol in the aqueous solution. Phenol was selected as a model contaminant because it is a non-volatile and common organic pollutant found in various types of industrial wastewater. Photocatalytic degradation runs were preceded by blind tests in the absence of a photocatalyst or illumination. The aqueous phase containing the photocatalyst (125 mg), deionized water (24 mL) and phenol (1 mL, C = 500 mg/dm³) was placed in a photocatalytic reactor (V = 25 cm³) equipped with a 30 mm-thick quartz window. The temperature of the aqueous phase during the experiments was maintained at 10 °C by an external circulating water bath. The prepared suspension was stirred using magnetic stirrer and aerated (V = 5 dm³/h) for 30 min in the dark to reach the adsorption equilibrium and then the content of the reactor was photoirradiated with a 1000 W Xenon lamp (Oriental Instruments,



Stratford, CT, USA) which emitted both UV and Vis irradiation. The optical path included a water filter and glass filters (GG420, Optel, Opole, Poland) to cut off IR and/or UV, respectively. GG glass filter transmitted light of wavelength greater than 420 nm. During the irradiation, 1 cm³ of suspension sample was collected at regular time periods and filtered through syringe filters ($\varnothing = 0.2 \mu\text{m}$) to remove the photocatalyst particles. Phenol concentration was estimated by colorimetric method after derivatization with diazo-*p*-nitroaniline using UV-Vis spectrophotometer (DU-7, Beckman, Warsaw, Poland).

3.5. Measurement of Photocatalytic Activity in the Gas Phase

The photocatalytic activity of the prepared semiconductors and their nanocomposite powders was also determined in the toluene degradation process. Toluene, an important volatile organic compound (VOC), was used as a model air contaminant. The photocatalysts activity tests were carried out in the flat stainless steel reactor ($V = 30 \text{ cm}^3$) equipped with a quartz window, two valves and a septa. As an irradiation source there was used an array of 25 LEDs ($\lambda_{\text{max}} = 375 \text{ nm}$, 63 mW per diode) which was described in our previous study [47]. In a typical measurement the semiconductor powder (about 0.1 g) was suspended in a small amount of water and loaded as a thick film on a glass plate (3 cm \times 3 cm) using painting technique. The obtained semiconductors coated support was dried and then placed at the bottom side of the photoreactor followed by closing the reactor with a quartz window. The gaseous mixture from a cylinder was passed through the reactor space for 1 min. The concentration of toluene in a gas mixture was about 150 ppm. After closing the valves, the reactor was kept in the dark for 15 min to reach adsorption equilibrium. A reference sample was taken just before starting irradiation. To estimate toluene concentration the samples were taken every 10 min during 60 min of irradiation. The photocatalytic stability was estimated in four subsequent cycles of toluene degradation. The analysis of toluene concentration in the gas phase was carried out using a Perkin Elmer Clarus 500 GC (Perkin Elmer, Waltham, MA, USA) equipped with a 30 m \times 0.25 mm Elite-5 MS capillary column (0.25 μm film thickness) and a flame ionization detector (FID). The samples (200 μL) were injected by using a gas-tight syringe. Helium was used as a carrier gas at a flow rate of 1 mL/min.

4. Conclusions

A series of novel binary and ternary composite photocatalysts was obtained based on the combination of potassium tantalate, cadmium sulfide and molybdenum disulfide powders as well as their hydro/solvothermal precursor solutions. It was observed that calcination is an effective method to prepare various KTaO_3 , CdS and MoS_2 semiconductor combinations, the while solvothermal mixed precursor solutions route led to obtaining other composite components. The UV-Vis DRS spectra showed that the loading MoS_2 onto CdS shifted absorbance peaks to longer wavelengths as well as loading CdS onto KTaO_3 enhanced absorption properties. On the other hand, an excess of MoS_2 in composite caused a decrease in activity both for phenol and toluene degradation. It may be suggested that the best absorption properties and the highest activity could probably be achieved for the ternary composites containing appropriate molar ratio between above semiconductors but it needs further investigation. We found that the ternary semiconductor hybrid prepared by calcination of KTaO_3 , CdS and MoS_2 powders at the 10:5:1 molar ratio exhibited very good stability during four measurement cycles in toluene degradation and excellent photocatalytic performance in phenol degradation among



all obtained photocatalysts—the activity reached 80% under UV-Vis and 42% under Vis light 60-min irradiation. This relatively high photoactivity under visible light could be related to the presence of heterojunction between semiconductors. Due to the band structure of component semiconductors, two-photon excitation together with charge carrier transfer between KTaO_3 , CdS and MoS_2 could be expected. However, ternary composite with 10:1:1 molar ratio between semiconductors exhibited relatively low activity which proved that the photocatalytic efficiency in aqueous phase reaction strictly depends on amount of composite components and need further investigation. In general, this work demonstrates that novel composites based on KTaO_3 , CdS and MoS_2 are promising as photocatalysts for the degradation of organic pollutants in both the gas and aqueous phases.

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Author Contributions

AZ designed research; BB, AC, MJW, TK and AZ performed research and analyzed the data; BB, AC, TK and AZ wrote the paper. All authors read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37–38.
2. Chen, X.B.; Mao, S.S. Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications. *Chem. Rev.* **2007**, *107*, 2891–2959.
3. Tong, H.; Ouyang, S.X.; Bi, Y.P.; Umezawa, N.; Oshikiri, M.; Ye, J.H. Nanophotocatalytic materials: Possibilities and challenges. *Adv. Mater.* **2012**, *24*, 229–251.
4. Bahnemann, D. Photocatalytic water treatment: Solar energy applications. *Sol. Energy* **2004**, *77*, 445–459.
5. Ahmad, M.; Ahmed, E.; Zhang, Y.W.; Khalid, N.R.; Xu, J.F.; Ullah, M.; Hong, Z.L. Preparation of highly efficient Al-doped ZnO photocatalyst by combustion synthesis. *Curr. Appl. Phys.* **2013**, *4*, 697–704.
6. Liao, C.H.; Huang, C.W.; Wu, J.C.S. Hydrogen production from semiconductor-based photocatalysis via water splitting. *Catalysts* **2012**, *2*, 490–516.
7. Zhang, N.; Ciriminna, R.; Pagliaro, M.; Xu, Y.-J. Nanochemistry-derived Bi_2WO_6 nanostructures: Towards production of sustainable chemicals and fuels induced by visible light. *Chem. Soc. Rev.* **2014**, *43*, 5276–5287.

8. Zhang, N.; Zhang, Y.; Xu, Y.-J. Recent progress on graphene-based photocatalysts: Current status and future perspectives. *Nanoscale* **2012**, *4*, 5792–5813.
9. Zhang, N.; Liu, S.; Xu, Y.-J. Recent progress on metal core@semiconductor shell nanocomposites as a promising type of photocatalyst. *Nanoscale* **2012**, *4*, 2227–2238.
10. Pan, X.; Yang, M.-Q.; Fu, X.; Zhang, N.; Xu, Y.-J. Defective TiO₂ with oxygen vacancies: Synthesis, properties and photocatalytic applications. *Nanoscale* **2013**, *5*, 3601–3614.
11. Yang, M.-Q.; Xu, Y.-J. Selective photoredox using graphene-based composite photocatalysts. *Phys. Chem. Chem. Phys.* **2013**, *15*, 19102–19118.
12. Fujishima, A.; Zhang, X.; Tryk, D.A. TiO₂ photocatalysis and related surface phenomena. *Surf. Sci. Rep.* **2008**, *63*, 515–582.
13. Marschall, R. Semiconductor composites: Strategies for enhancing charge carrier separation to improve photocatalytic activity. *Adv. Funct. Mater.* **2014**, *17*, 2420–2440.
14. Yang, G.; Yan, Z.; Xiao, T. Preparation and characterization of SnO/ZnO/TiO₂ composite semiconductor with enhanced photocatalytic activity. *Appl. Surf. Sci.* **2012**, *258*, 8704–8712.
15. Emeline, A.V.; Kuznetsov, V.N.; Ryabchuk, V.K.; Serpone, N. On the way to the creation of next generation photoactive materials. *Environ. Sci. Pollut. Res.* **2012**, *19*, 3666–3675.
16. Serpone, N.; Emeline, A.V. Semiconductor photocatalysis—Past, present, and future outlook. *J. Phys. Chem. Lett.* **2012**, *3*, 673–677.
17. Zhang, Y.; Tang, Z.-R.; Fu, H.; Xu, Y.-J. TiO₂-graphene nanocomposites for gas-phase photocatalytic degradation of volatile aromatic pollutant: Is TiO₂-graphene truly different from other TiO₂-carbon composite materials? *ACS Nano* **2010**, *4*, 7303–7314.
18. Kato, H.; Kudo, A. Photocatalytic water splitting into H₂ and O₂ over various tantalate photocatalysts. *Catal. Today* **2003**, *78*, 561–569.
19. Liu, J.W.; Chen, G.; Li, Z.H.; Zhang, Z.G. Hydrothermal synthesis and photocatalytic properties of ATaO₃ and AnbO₃ (A = Na and K). *Int. J. Hydrogen Energy* **2007**, *32*, 2269–2272.
20. Kudo, A. Development of photocatalyst materials for water splitting. *Int. J. Hydrog. Energy* **2006**, *31*, 197–202.
21. Lin, W.; Chen, C.; Hu, C.; Teng, H. NaTaO₃ photocatalysts of different crystalline structures for water splitting into H₂ and O₂. *Appl. Phys. Lett.* **2006**, *89*, 211904.
22. Torres-Martínez, L.M.; Cruz-López, A.; Juárez-Ramírez, I.; Meza-de la Rosa, M.E. Methylene blue degradation by NaTaO₃ sol-gel doped with Sm and La. *J. Hazard. Mater.* **2009**, *165*, 774–779.
23. Zhu, H.; Jiang, R.; Xiao, L.; Chang, Y.; Guan, Y.; Li, X.; Zeng, G. Photocatalytic decolorization and degradation of Congo Red on innovative crosslinked chitosan/nano-CdS composite catalyst under visible light irradiation. *J. Hazard. Mater.* **2009**, *169*, 933–940.
24. Zhai, T.Y.; Fang, X.S.; Bando, Y.S.; Liao, Q.; Xu, X.J.; Zeng, H.B.; Ma, Y.; Yao, J.N.; Golberg, D. Morphology-dependent stimulated emission and field emission of ordered CdS nanostructure arrays. *ACS Nano* **2009**, *3*, 949–959.
25. Dongre, J.K.; Nogriva, V.; Ramrakhiani, M. Structural, optical and photoelectrochemical characterization of CdS nanowire synthesized by chemical bath deposition and wet chemical etching. *Appl. Surf. Sci.* **2009**, *255*, 6115–6120.
26. Zhang, H.; Zhu, Y. Significant visible photoactivity and antiphotocorrosion performance of CdS photocatalysts after monolayer polyaniline hybridization. *J. Phys. Chem. C* **2010**, *114*, 5822–5826.

27. Zhong, M.; Shi, J.; Xiong, F.; Zhang, W.; Li, C. Enhancement of photoelectrochemical activity of nanocrystalline CdS photoanode by surface modification with TiO₂ for hydrogen production and electricity generation. *Sol. Energy* **2012**, *86*, 756–763.
28. Li, X.; Xia, T.; Xu, C.; Murowchick, J.; Chen, X. Synthesis and photoactivity of nanostructured CdS–TiO₂ composite catalysts. *Catal. Today* **2014**, *225*, 64–73.
29. He, D.; Chen, M.; Teng, F.; Li, G.; Shi, H.; Wang, J.; Xu, M.; Lu, T.; Ji, X.; Lv, Y. Enhanced cyclability of CdS/TiO₂ photocatalyst by stable interface structure. *Superlattices Microstruct.* **2012**, *51*, 799–808.
30. Panigrahi, S.; Basak, D. Morphology driven ultraviolet photosensitivity in ZnO–CdS composite. *J. Colloid Interface Sci.* **2011**, *364*, 10–17.
31. Jana, T.K.; Pal, A.; Chatterjee, K. Self assembled flower like CdS–ZnO nanocomposite and its photo catalytic activity. *J. Alloys Compd.* **2014**, *583*, 510–515.
32. Liu, S.; Li, H.; Yan, L. Synthesis and photocatalytic activity of three-dimensional ZnS/CdS composites. *Mater. Res. Bull.* **2013**, *48*, 3328–3334.
33. Liu, X.; Yan, Y.; Da, Z.; Shi, W.; Ma, C.; Lv, P.; Tang, Y.; Yao, G.; Wu, Y.; Huo, P.; *et al.* Significantly enhanced photocatalytic performance of CdS coupled WO₃ nanosheets and the mechanism study. *Chem. Eng. J.* **2014**, *241*, 243–250.
34. Zhao, Y.; Zhang, Y.; Yang, Z.; Yan, Y.; Sun, K. Synthesis of MoS₂ and MoO₂ for their applications in H₂ generation and lithium ion batteries: A review. *Sci. Technol. Adv. Mater.* **2013**, *14*, 043501.
35. Zong, X.; Wu, G.; Yan, H.; Ma, G.; Shi, J.; Wen, F.; Wang, L.; Li, C. Photocatalytic H₂ Evolution on MoS₂/CdS Catalysts under Visible Light Irradiation. *J. Phys. Chem. C* **2010**, *114*, 1963–1968.
36. Chen, G.; Li, D.; Li, F.; Fan, Y.; Zhao, H.; Luo, Y.; Yu, R.; Meng, O. Ball-milling combined calcination synthesis of MoS₂/CdS photocatalysts for high photocatalytic H₂ evolution activity under visible light irradiation. *Appl. Cat. A* **2012**, *443–444*, 138–144.
37. Liu, Y.; Yu, Y.X.; Zhang, W.D. MoS₂/CdS Heterojunction with high photoelectrochemical activity for H₂ evolution under visible light: The Role of MoS₂. *J. Phys. Chem. C* **2013**, *117*, 12949–12957.
38. Liu, Y.; Yu, H.; Quan, X.; Chen, S. Green synthesis of feather-shaped MoS₂/CdS photocatalyst for effective hydrogen production. *Int. J. Photoenergy* **2013**, *2013*, 247516–247520.
39. Zong, X.; Yan, H.; Wu, G.; Ma, G.; Wen, F.; Wang, L.; Li, C. Enhancement of photocatalytic H₂ evolution on CdS by loading MoS₂ as cocatalyst under visible light irradiation. *J. Am. Chem. Soc.* **2008**, *130*, 7176–7177.
40. Wiedemeier, H.; Khan, A.A. Phase studies in the system manganese sulfide–cadmium sulfide. *Trans. Metall. Soc. AIME* **1968**, *242*, 1969–1972.
41. Hu, C.-C.; Yeh, T.-F.; Teng, H. Pyrochlore-like K₂Ta₂O₈ synthesized from different methods as efficient photocatalysts for water splitting. *Catal. Sci. Technol.* **2013**, *3*, 1798–1804.
42. Zhong, S.; Zhang, L.; Huang, Z.; Wang, S. Mixed-solvothermal synthesis of CdS micro/nanostructures and their optical properties. *Appl. Surf. Sci.* **2011**, *257*, 2599–2603.
43. Zou, Y.; Hu, Y.; Gu, H.; Wang, Y. Optical properties of octahedral KTaO₃ nanocrystalline. *Mater. Chem. Phys.* **2009**, *115*, 151–153.
44. Adhikari, R.; Malla, S.; Gyawali, G.; Sekino, T.; Lee, S.W. Synthesis, characterization and evaluation of the photocatalytic performance of Ag–CdMoO₄ solar light driven plasmonic photocatalysts. *Mat. Res. Bull.* **2013**, *48*, 3367–3373.

45. Wang, W.-S.; Zhen, L.; Xu, C.-Y.; Shao, W.-Z.; Chen, Z.-L. Formation of CdMO₄ porous hollow nanospheres via self-assembly accompanied with Ostwald ripening process and their photocatalytic performance. *CrystEngComm* **2013**, *15*, 8014–8021.
46. Wang, S.; Li, G.; Du, G.; Jiang, X.; Feng, C.; Guo, Z.; Kim, S. Hydrothermal synthesis of molybdenum disulfide for lithium ion battery applications. *Chin. J. Chem. Eng.* **2010**, *18*, 910–913.
47. Nischk, M.; Mazierski, P.; Gazda, M.; Zaleska, A. Ordered TiO₂ nanotubes: The effect of preparation parameters on the photocatalytic activity in air purification process. *Appl. Catal. B* **2014**, *144*, 674–685.

Sample Availability: Samples of the compounds are available from the authors.

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