Partially decomposed PVP as a surface modification of ZnO, CdO, ZnS and CdS nanostructures for enhanced stability and catalytic activity towards sulphamethoxazole degradation

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Abstract. In order to prepare stable and efficient photocatalysts, a microwave-furnace-assisted method using ethylene glycol (EG) as a solvent has been employed to obtain metal oxides and metal sulphides nanocatalysts with partial decomposition of the polyvinylpyrrolidone (PVP) cap (P-ZnO, P-CdO, P-ZnS and P-CdS); this associates the protective functionality of PVP with enhanced catalytic activity due to effective carriers transfer. The as-produced catalysts characterization revealed an extended growth of metal oxides compared with metal sulphides, which is attributed to the competition of EG as the source of oxygen with PVP to capsule metal oxides during the synthesis. Infrared spectra confirmed the PVP–metal complexation and partial decomposition of the polymer. Metal sulphides exhibited a better catalytic activity compared with metal oxides for sulphamethoxazole degradation in UVC light owing to their size and morphology impact; further, P-CdS induced 71% antibiotic degradation after 10 h of illumination with visible light compared with only 48% for P-ZnS, 29% for P-ZdO and 20% for P-CdO due to improved light absorption. Interestingly, around 86% degradation was induced by mixing P-CdS with P-ZnS in 80:20% ratio, indicating an enhanced visible light activity due to improved electron–hole pair separation and high redox potential of P-ZnS.

Keywords. Polyvinylpyrrolidone; sulphamethoxazole; photocatalyst; metal sulphide; microwave-assisted; nanostructure.

1. Introduction

In recent years, antibiotics have occupied an advanced position among environmental pollutants due to their pharmaceutical characteristics and extensive consumption that has consequently led to the presence of their residues in environmental water. This presence has been evidenced to incite mutations in the aquatic microorganisms with continuous exposure and may further induce new strains to exist [1]. A more complicated issue is the possibility of developing an antibiotic resistance among aquatic bacteria and the transfer of resistant genes to pathogenic bacteria, which pose a great risk to human health [2,3]. Sulphamethoxazole (SMX) is among the most commonly used antibiotics for human and livestock treatment. This compound is highly resistant to conventional and biological treatments owing to its antibacterial nature, and it can persist in the environment for more than 1 year, leading to the aforementioned risks [4,5]. Hence, greater consideration must be given to eliminating such an agent from domestic and industrial effluents before discharging into the environment.

In this regard, advanced oxidation procedures (AOPs) have been devised as effective methods, which involve the generation of highly reactive species such as hydroxyl (OH[•]) and

superoxide (O₂^{•-}) radicals for the oxidation and destruction of organic pollutants [6]. Among these, nanosized heterogeneous semiconductors have gained an increasing attention and are now considered as a convenient candidate to substitute conventional methods for wastewater treatment. The advantages of these photocatalysts are their possible ability to completely degrade the organic pollutants; this results from their amazing electronic and optical properties arising from quantum confinement effects and increased surface area-to-volume; in addition to being environment friendly, they may operate in solar light and diminish the cost of treatment [7,8]. There has been an exponential growth in the number of reports concerning the synthesis and applications of metal oxides and metal chalcogenides nanocatalysts of II–VI semiconductor group, such as ZnO, ZnS, CdS, CdSe, etc. Among the various methods for synthesis, the polyol-mediated method has been reported to be suitable for preparing such nanoparticles. This method involves heating the precursors in a polyalcohol medium that plays multiple roles such as a solvent, reductant, complexant and surfactant [9]. Broadly speaking, using the polyol method can give amazing characteristics for the synthesized nanoparticles, including a uniform shape, narrow size distribution and small degree of aggregation [10]. Moreover, it was confirmed that polyol method is highly

compatible with microwave heating to increase the reaction rate of the synthesis and yield homogenous particles [11,12].

Polymeric materials such as the amphiphilic polyvinylpyrrolidone (PVP) have been widely used in stabilization, controlling the growth and reducing agglomeration of nanoparticles during synthesis [13–16]. The PVP structure consists of a sequence of polyvinyl skeletons (hydrophilic) with polar pyrrolidone groups (hydrophobic). The mechanism of PVP capsulation of nanoparticles includes coordination of metal ion with nitrogen or/and oxygen atom of pyrrolidone ring to limit the growth process, while the polyvinyl motion forms the tail of composite and prevents agglomeration through the electrostatic repulsion in a steric effect [15]. However, from the viewpoint of catalyst, PVP passivation forms a barrier layer surrounding the nanoparticles that can limit light absorption and quench the mobility of carriers to the reaction medium. Consequently, the generation of oxygen-reactive species, and further, the photocatalytic activity of nanoparticles, would be decreased significantly, as supported by earlier reports [13,17,18].

In our present work, we managed to benefit from the protecting properties of PVP and solve the carriers quenching issue by partially decomposing the PVP shield in microwave and calcination steps following the first nucleation. The method was applied to synthesize ZnS, CdS, ZnO and CdO nanostructures in order to compare the effect of different pathways of formation. We have previously utilized this method to prepare PVP–CdS nanoparticles [19] and here we extend it to prepare ZnS, the second metal sulphide (MeS), and with some modifications for metal oxides (MeO). Besides comparing the optical, structural and morphological properties of the prepared nanocatalysts, photocatalytic degradation of SMX was the decisive factor for evaluating the best product.

2. Experimental

2.1 Chemicals and materials

All materials used in our experiments were of analytical grade and used as received without any further purification. SMX powder was purchased from Virchow Laboratories Limited (India). Cadmium chloride 2.5-hydrate [$\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$] and thiourea [$\text{SC}(\text{NH}_2)_2$] were obtained from Scharlau (Spain). Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$], PVP (MW $\approx 25,000 \text{ g mol}^{-1}$), ethylene glycol (EG), hydrochloric acid (37%) and sodium hydroxide were obtained from Merck (Germany). Double distilled water was used for the preparation of all samples. SMX stock solution (500 mg l^{-1}) was prepared by dissolving 50 mg of SMX powder in 100 ml of sodium hydroxide solution (0.01 M). Working solutions were prepared by further dilution of stock solution with water to obtain the desired concentration.

2.2 Synthesis of nanocatalysts

P–ZnS and P–CdS were prepared according to our previous procedure [19]; 9 g of zinc or cadmium source and 3 g of PVP were separately dissolved in 30 and 20 ml of EG, respectively, and then heated with stirring at 75°C for 60 min. The two solutions were then mixed slowly and heated with stirring at 100°C for 40 min. Meanwhile, 3 g of thiourea was dissolved in 20 ml of EG and heated with stirring for 100 min at 75°C and then added slowly to the hot solution of (PVP–metal). The temperature of the new mixture was gradually raised to 180°C within 45 min and kept at this temperature until most of the solvent evaporated. Afterwards, the formed gel was subjected to microwave irradiation at 720 W power for 5 min. The resulting powder was then calcined for 120 min at 450°C to obtain the final product. P–ZnO and P–CdO were prepared similarly by excluding the addition of thiourea.

2.3 Characterization of nanocatalysts

The prepared nanocatalysts were characterized by powder X-ray diffraction (XRD) using a Bruker AXS D8-Advance diffractometer fitted with a Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation tube. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained by a KYKY-EM3200 and a 300 kV Philips CM30 microscope, respectively. The optical transmission spectra were measured at room temperature in the range 250–800 nm using a PG Instruments T80+ UV–Vis double-beam spectrophotometer. The direct band gap energies were calculated using Tauc plot according to the obtained spectra. Fourier transform infrared (FTIR) spectra in the range of $400\text{--}4000 \text{ cm}^{-1}$ were recorded in transmission mode using a Thermo Nicolet 8700; the powder samples were ground with KBr and compressed into a pellet prior to analysis. BET surface area analysis was performed on a Belsorp Max instrument.

2.4 Photocatalytic experiments

The experiments were conducted by illuminating the photocatalytic suspension with a 30 W UVC lamp (CH Lighting T8) as a UV light source or a 650 W halogen lamp (OSRAM 64540) as a visible light source. The lamp is fixed 10 cm above a cylindrical Pyrex container, which is in turn positioned on a magnetic stirrer to guarantee the uniformity of the mixture. Photocatalytic suspensions were prepared by dispersing different amounts of nanocatalyst (20–75 mg) in 100 ml of SMX solution (10 mg l^{-1}). The initial pH was adjusted to (3, 7 or 11) by 0.1 M of HCl or NaOH before adding the catalyst. Prior to the catalytic reaction, suspensions were stirred in dark for 60 min to achieve the adsorption equilibrium. Then, SMX photodegradation was initiated by turning on the lamp. Samples were withdrawn after different intervals of illumination followed by centrifugation to remove solid residuals. The quantitative analysis of SMX was performed by measuring the absorbance with a UV–Vis spectrophotometer at

Figure 1. XRD patterns of the prepared nanocatalysts.

Figure 2. SEM images of (a) P-ZnO, (b) P-CdO, (c) P-ZnS and (d) P-CdS; TEM images of (e, f) P-ZnS and (h, g) P-CdS.

wavenumbers 256–262 nm. The degradation efficiency was calculated by the following formula:

$$D\% = [(C_0 - C) / C_0] \times 100$$

$$= [(A_0 - A) / A_0] \times 100 \quad (1)$$

where C_0 and A_0 are the initial concentration and absorbance at $t = 0$ (equilibrium), respectively; C and A are the concentration and absorbance after an interval of illumination t .

3. Results and discussion

3.1 Characterization results

Figure 1 shows the XRD patterns of the four nanocatalysts. P-ZnO sample exhibited highly pure hexagonal wurtzite structure (JCPDS card No. 00-036-1451). This structure shows the role of EG in forming the most stable phase of these nanocatalysts (hexagonal structure) due to the high temperatures present during the synthesis process [20]. For

P-CdO, according to the obtained patterns, the sample consisted of a mixture of cubic phase CdO (JCPDS card No. 00-005-0640), cubic phase CdO₂ (00-039-1221) and monoclinic phase Cd(OH)₂ (JCPDS card No. 00-020-0179). P-ZnS exhibited cubic zinc blende structure with no phase impurities (JCPDS card No. 00-05-0566). P-CdS exhibited hexagonal structure (JCPDS No. 01-089-2944), but in the presence of monoclinic sulphur peaks (JCPDS No. 01-074-2108). Comparatively, MeO peaks were sharper and more intense than those of MeS, indicating the higher crystallinity and random orientation growth of the particles [21].

The SEM images of the four products are shown in figure 2. As can be seen, P-ZnO (figure 2a) was formed as hierarchically shaped particles nearly in the micro-range with some smaller nanograins on their surface. The particles are well separated, indicating the role of PVP in preventing the formation of agglomerates. For P-CdO (figure 2b), the image shows the formation of irregularly shaped thin plates; the presence of nanograins of about 37–49 nm in an approximate size with bright edges of the thin plates demonstrates that the plates were nanostructured. In P-ZnS image (figure 2c), spherical nanoparticles can be seen with relatively narrow size

Table 1. Average particles size obtained using microscopes, surface areas and band gap energies of the prepared nanocatalysts.

Sample	Size (nm)			Band gap energy (eV)		
	SEM	TEM	BET (m ² g ⁻¹)	Nano	Bulk	Refs
P-ZnO	39.4*	NA	NA	3.1	3.37	[23]
P-CdO	37.4**	NA	NA	2.83	2.3	[23]
P-ZnS	49.2	49	9.81	4.1	3.7	[24]
P-CdS	52.3	51.8	13.61	2.6	2.42	[14]

* Surface nanograins size.

** Nanoplates thickness.

distribution and a slight agglomeration in some places. P-ZnS TEM images (figure 2e and f) indicate that the remaining PVP shields after calcination have connected together and induced the small agglomerates. The P-CdS looks as a mixture of nanorods and nanospheres with small-diameter distributions in the SEM image (figure 2d), while its TEM images (figure 2g and h) show the spherical particles with a good monodispersity and no trace of the polymeric shield. The average particles size of each product estimated from the SEM images and TEM images (figure 2f and h) is listed in table 1.

The optical band gap energies (E_g) of the prepared nanocatalysts were estimated using the Tauc equation

$$\alpha h\nu = A (h\nu - E_g)^n, \quad (2)$$

where A is an energy-independent constant, α is the absorption coefficient and E_g is the optical band gap; n is a constant that determines the type of optical transitions and has the value $n = 1/2$ for direct transition. With the help of absorption spectra and plots of $(\alpha h\nu)^2$ vs. $h\nu$, the band gap energies were calculated by extrapolation of the straight part of each spectrum and taking the x value when $(\alpha h\nu)^2 = 0$ (table 1). The UV-Vis absorption spectra and Tauc plots of the different nanostructures at room temperature are shown in figure 3. It can be seen that P-ZnO has a sharp absorption peak at 367 nm, and an edge of about 400 nm that corresponds to the band gap energy of about 3.1 eV. Here, the high intensity of the peak suggests monodispersity of P-ZnO nanoparticles [22]. For P-CdO, the increase in band gap energy compared

with the bulk material [23] can be ascribed to the blue-shift of the optical gap due to plate thickness in the nano-regime. Both P-ZnS and P-CdS have also shown blue-shifts; P-ZnS has an absorption edge at 305 nm, which is less than 345 nm of the bulk ZnS [24]. Likewise, P-CdS has an absorption edge at about 475 nm, whereas for the bulk material it is 512 nm [14]. These blue-shifts were due to the strong quantum confinement effect as a function of decreased particle size. This optical behaviour of our nanocatalysts is in agreement with some earlier reports. For instance, Pandiyarajan and Karthikeyan [25] prepared PVP-capped ZnO and found no blue-shift ($E_g = 3.2$ eV). They attributed this result to the size of the ZnO nanoparticles, which was much greater than the exciton Bohr radius (ZnO—2.34 nm). Barve *et al* [26] prepared CdO nanoparticles using EG and cadmium chloride and obtained 3.75 eV band gap. Soltani *et al* [27] prepared ZnS by a microwave-hydrothermal method and obtained band gap energies 4.08–4.22 eV depending on microwave irradiation time. Muruganandam *et al* [28] reported that PVP-capped CdS via wet chemical method had a 2.6 eV band gap energy and 478 nm absorption edge, which then blue-shifted to 447 nm after doping with Zn^{2+} .

The FTIR spectra of the PVP-capped nanostructures were almost identical to that of pure PVP, as shown in figure 4. FTIR absorption bands positions and their functional groups explanation are listed in table 2. As can be noticed, the C–N vibration at 1016 cm⁻¹ in pure PVP separated into two peaks and the C=O vibration at 1656 cm⁻¹ shifted to a lower wavenumber in all nanocatalysts spectra, which confirms the formation of (PVP–Me²⁺) [29], while the partial decomposition of PVP was supported by the decrease in intensities of all peaks ascribed to PVP after calcination.

3.2 Mechanisms of nanostructures formation

In order to understand the variation in size and morphology of the prepared nanocatalysts, we here suggest the possible mechanism of nanostructures formation as illustrated in figure 5. In the first solution, metal salt was dissolved in EG to give Me²⁺. Upon addition of PVP solution, a coordinative complex (PVP–Me²⁺) was formed by the donation of lone pair electrons of oxygen or nitrogen atoms to the metal ions [29]. For MeS, the addition of hot thiourea (TU) solution

Figure 3. UV-Vis spectra and Tauc plots of the prepared nanocatalysts.

Figure 4. FTIR spectra of pure PVP and the prepared nanocatalysts.

resulted in the formation of $\text{PVP}[\text{Me}(\text{TU})_2]^{2+}$ complex. This complex, afterwards, underwent a thermal decomposition during the heating stage to yield PVP-capped MeS nanoparticles. During the microwave stage, the polymeric chain of PVP was broken to shorter chains and ultimately, calcination at 450°C resulted in the thermal decomposition of PVP to its oligomers or monomers or even the breaking of vinylpyrrolidone bond as reported earlier [30,31]. The acquired advantage of this partial decomposition was to expose the pyrrolidone ring to water and antibiotic molecules to then act as a mediator for carriers transfer from nanocatalyst to the

targeted molecules. For MeO, heating $\text{PVP}[\text{Me}^{2+}]$ complex at 180°C in the absence of sulphur induced the hydrolysis of the complex directly by EG to form PVP-metal glycolate. Then, the new complex was dehydrated into PVP-MeO nanoparticles with continuous heating. Similar to MeS, PVP suffered the partial decomposition under microwave and calcination. A reasonable explanation of why MeO nanoparticles grew more than MeS nanoparticles is that the complexation of $\text{PVP}[\text{Me}^{2+}]$ with EG raised the temperature needed for EG evaporation. Thus, the nuclei sites formed in the initial stage were subjected to a secondary nucleation as the time

Table 2. Functional groups and their positions in FTIR spectra for pure PVP and the prepared nanocatalysts.

Functional group	Wavenumber (cm ⁻¹)				
	P-ZnO	P-CdO	P-ZnS	P-CdS	PVP (pure)
Me-O or Me-S stretching	471	699	573	Split peak, 600–700	
O-H stretching	3445	3466	3439	3435	3517
C-H asymmetric stretching	2959	2973	2908	2973	2952
C=O stretching	1530	1589	1518	1626	1665
C-H bending	1397	1432	1379	1427	1423
C-N stretching	1122	1035	1114	1044	1016

of reaction increased, allowing for more growth. Meanwhile, PVP could not fully protect the metal core due to the competition with EG molecules that participated in the formation of the final product.

3.3 Optimum conditions for photocatalytic reaction

In order to obtain the best conditions for degradation of SMX using the prepared nanocatalysts, experiments were carried out by changing parameters such as catalyst loading and initial pH of the antibiotic solution. These two parameters are known to be the most crucial factors affecting the catalytic activity of photocatalysts. Preliminary experiments were conducted in UVC light each for 180 min and then, using optimized conditions, visible light experiments were conducted.

3.3a Effect of catalyst loading: The influence of catalyst amount on SMX degradation was studied in the range 20–75 mg with initial SMX concentration of 10 mg l⁻¹ and pH = 7 for each product. Results (figure 6) show that increase in catalyst loading has a positive effect on the SMX degradation up to 50 mg. Above this amount, SMX degradation was not considerably enhanced in the case of P-ZnO and P-CdO. However, for P-ZnS, which shows high turbidity, a slight difference in activity was obtained at all amounts and above 50 mg, activity decreased. This is because high turbidity hindered further penetration of light in the solution, which in turn decreased the generation of oxidative agents and reduced the rate of reaction. Only in the case of P-CdS, it was noticed that degradation rate was proportional to catalyst amount in the range of study. Moreover, the results indicated clearly that P-CdS possessed a superior catalytic activity over the other catalysts. The main reason behind this superiority is the smaller size compared with P-ZnO and P-CdO, which has given a higher surface area-to-volume ratio, i.e., abundant active sites on the catalyst surface to harvest more photons and adsorb more pollutant molecules. However, as regards P-ZnS, which has approximately the same particle size, the enhanced catalytic activity is credited to the larger surface area of P-CdS when compared with that of P-ZnS (table 1). Similar to size effect, increased surface area will induce more

adsorption active sites, and therefore boost redox reactions by the photogenerated electron-hole pairs. This was reflected in the high adsorption of SMX on P-CdS surface (15.6–49.1%) compared with P-ZnS (3.8–8.8%) in the range 20–75 mg after 60 min of stirring in dark. Due to the previous reasons, a 50 mg of catalyst loading was selected as the optimum amount for further experiments.

3.3b Effect of pH: Complete understanding of the influence of pH on the photocatalytic reactions remains as a difficult task. It affects a variety of properties such as surface charges of the semiconductors, which affect electrostatic interactions among the semiconductor surface, pollutant molecules, water molecules and the generated radicals [32]. Here, the role of pH in SMX degradation employing the different prepared catalysts was investigated at pH ranging from 3 to 11. Figure 7 shows the degradation of SMX (10 mg l⁻¹) as a function of solution pH. Apparently, the degradation rate shows a decrease with increasing pH for all tested catalysts and even in the absence of catalyst, revealing that SMX degradation is favoured in the acidic medium rather than in neutral and alkaline media. Also, a superiority of P-CdS was observed at all experimented pH values, resulting from the size and shape properties as mentioned before.

These results can be interpreted in a simple manner by the surface complexation reactions of the nanocatalysts and the antibiotic. Favourable pH for SMX degradation is between its two dissociation constants ($pK_{a,1} = 1.85$ and $pK_{a,2} = 5.6$) as it exists basically in its neutral molecular form. At a pH value more than $pK_{a,2}$, sulphonamide group is deprotonated and the antibiotic exists in its anionic form (SMX⁻), which is more stable and harder to be decomposed [33]. On the other hand, MeO and MeS have an amphoteric behaviour and are protonated and deprotonated at various pH values as follows:

Figure 5. Schematic of the nanocatalysts formation, pathway I for MeS and pathway II for MeO.

Figure 6. Effect of nanocatalyst amount on photodegradation of SMX (10 mg l⁻¹, pH=7) in UVC light.

Figure 7. Effect of pH on degradation of SMX (10 mg l^{-1}), catalyst amount (50 mg), in UVC light.

Hence, acidic medium is preferred for SMX adsorption and further degradation on nanocatalysts surface. Furthermore, the high efficiency of nanocatalysts in acidic medium emphasizes clearly the protective role of the PVP passivation by inhibiting nanocatalysts photocorrosion. Accordingly, the pH value of 3 was considered as the optimum value for further experiments.

3.4 Visible light studies

Utilization of UV light in photocatalytic oxidation of pollutants has some limitations such as high cost of treatment and dangerous effects of UV irradiation on human health. As a consequence, using visible light sources is preferable as it is safer and more economic. In this study, experiments were performed by exposing the catalyst–antibiotic suspension adjusted to optimum conditions, 50 mg catalyst loading and 10 mg l^{-1} SMX concentration at $\text{pH} = 3$, to a visible light source for 10 h. P-ZnO and P-CdO were not expected to show sufficient activity in visible light as they did not show in UVC light. On the other hand, P-CdS was considered a better candidate to absorb visible light than P-ZnS as it has a narrower band gap. Nevertheless, decreased band gap can lead to less photocatalytic activity due to increased probability of recombination of electrons and holes [36]. Suitably, the wider band gap P-ZnS can promote the photocatalytic activity of P-CdS by the efficient carriers separation. In view of this, a mixture of P-CdS and P-ZnS was expected to give better catalytic activity than that of the individual nanocatalysts. Earlier reports [37,38] on the degradation of methylene blue using physical mixtures of ZnS and CdS have shown that the best results were obtained at weight percentages 20:80 of ZnS:CdS. Hence,

Figure 8. Visible-light-induced degradation of SMX.

Figure 9. Schematic illustration of the electron–hole charge transfer in P-ZnS/P-CdS mixture.

a mixture of P-ZnS:P-CdS (10:40 mg) was adopted for the experiment. Figure 8 shows the results of visible light study after 10 h of illumination. P-ZdO and P-CdO presented only 29 and 20% degradations, respectively. P-CdS or P-ZnS alone were not able to totally eliminate the antibiotic with degradation percentages of 71 and 48, respectively. However, the mixture of these two nanoparticles showed remarkable degradation, which reached about 86% in the same time interval.

In order to further understand the mechanism of this enhancement, the relative potentials of conduction band (CB) and valence band (VB) of P-ZnS and P-CdS were estimated by cyclic voltammetry according to the procedure described elsewhere [39]. Results have shown that P-ZnS has a higher CB (-0.95 V) and lower VB potentials (-0.50 V) than that of P-CdS (-0.85 and -0.65 V , respectively). Here we can presume that the mixture has worked as a nanocomposite and combined the enhanced absorption of visible light of P-CdS with the high redox potential of the P-ZnS. As illustrated in figure 9, P-CdS can be effectively excited by visible light irradiation, whereas P-ZnS remains almost inactive. The

photogenerated electrons in the CB of P-CdS would contribute directly to the catalytic reaction by reducing O_2 into superoxide radical, while the holes remaining in the VB could be transferred to the localized acceptor states caused by zinc vacancies (V_{Zn}) and interstitial sulphur (I_S) above the VB of P-ZnS [40]. This transferred hole would also contribute to the generation of the powerful hydroxyl radical. Hence, the increased lifetime of charge carriers by their recombination suppression is believed to be the main reason behind the catalytic activity enhancement of the mixture.

4. Conclusions

Three steps preparation of ZnO, CdO, ZnS and CdS nanostructures capped by partially decomposed PVP was adopted. The steps included heating precursors in EG and then subjecting them to microwave irradiation and finally to a furnace calcination. XRD confirmed the formation of hexagonal structure of P-ZnO and P-CdS and cubic structure of P-CdO and P-ZnS. Optical properties showed blue-shifts of all products except P-ZnO due to increased particles size. P-ZnS and P-CdS were considered to be the best products owing to their superior catalytic degradation of SMX compared with P-ZnO and P-CdO under UVC. After optimizing the best conditions for the catalytic reaction in UVC light, a physical mixture of P-ZnS and P-CdS exhibited enhanced catalytic activity compared with the individual products when visible light was used as a source of the irradiation.

In conclusion, it seems that the method of nanoparticles preparation employed in our work is more appropriate to synthesize metal sulphides rather than metal oxides on the basis of their size, morphology and ability to degrade SMX. We finally believe that addition of another source for oxygen when synthesizing MeO in such a method may enhance their size and catalytic properties as EG will not then compete with PVP for covering the nanoparticles.

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