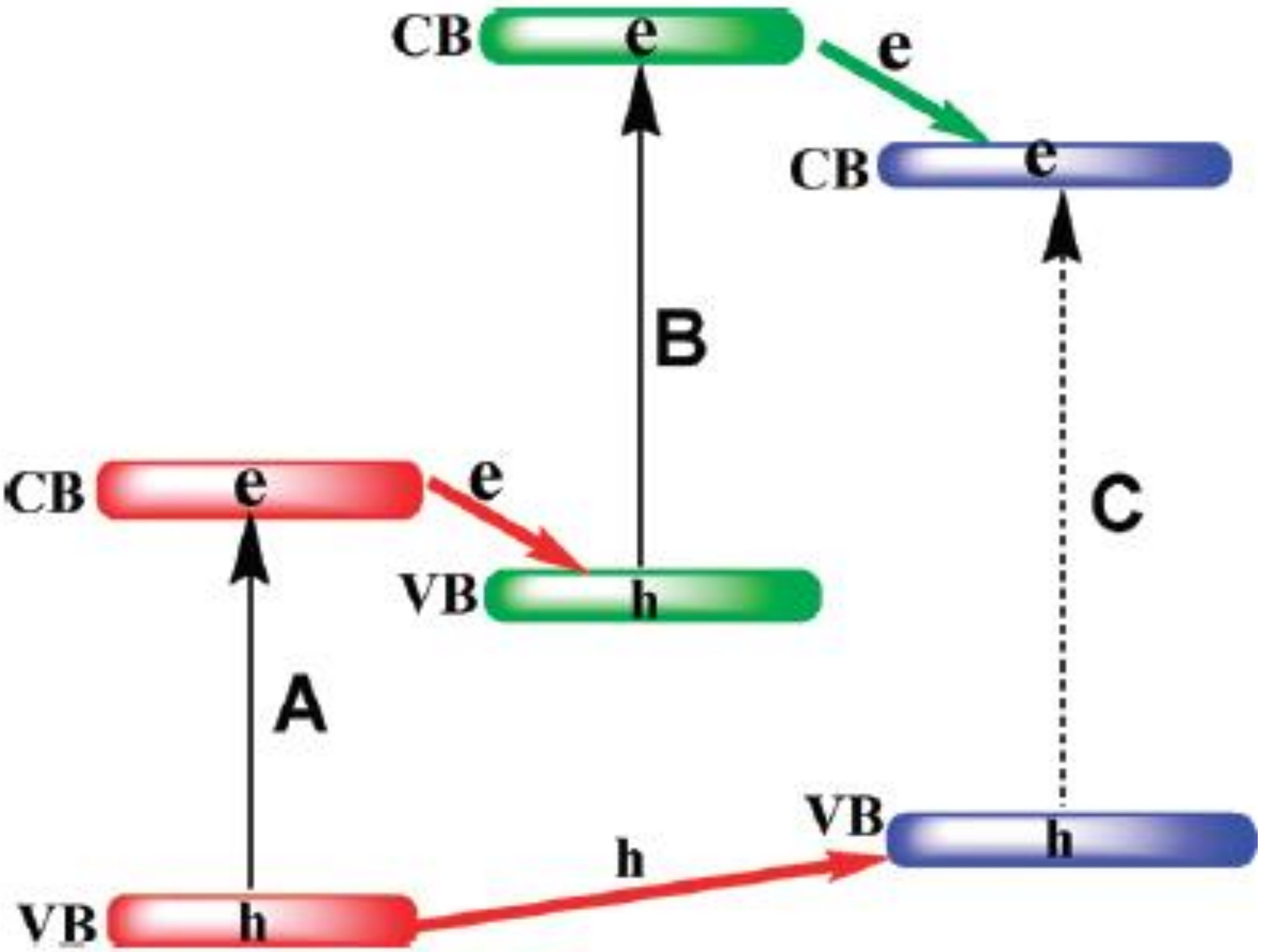
Surface properties and photocatalytic activity of semiconductor composites

Adriana Zaleska

Department of Environmental Technology

First, second and third generation of photocatalysts

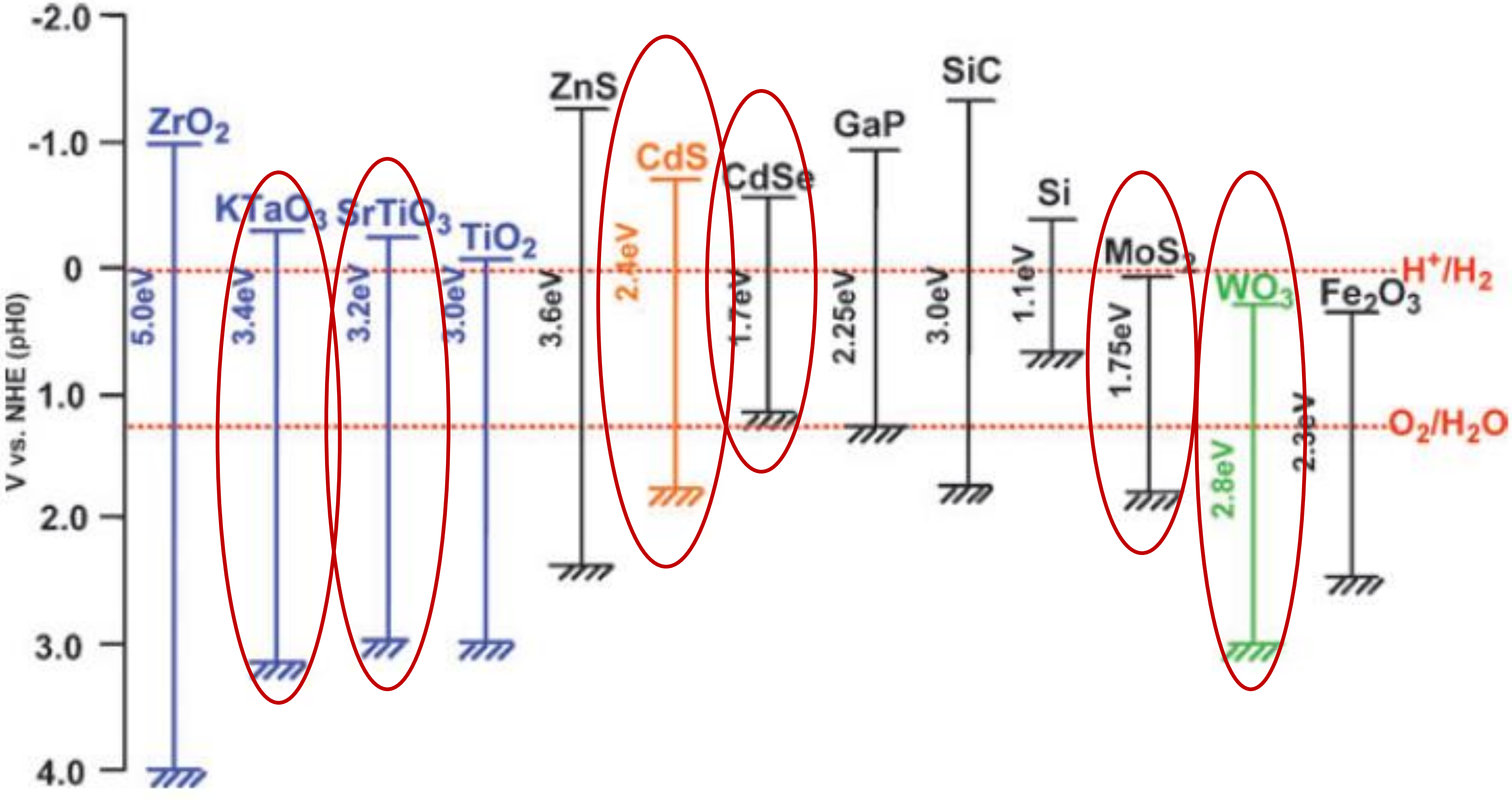


IN MARI VIA TUA

Aim

To study the influence of preparation method as well as type and amount of composite components on the surface properties and photocatalytic activity of nanocomposites materials

Semiconductors



Experimental methodology

Hydrothermal synthesis

Surface characterization

Photoactivity measurements

Experimental methodology

Hydrothermal synthesis

Surface characterization

Photoactivity measurements

- one pot synthesis
- two steps- synthesis

Autoclaving: 200°C, 24h

	Sample label and type of nanocomposite	Molar ratio of semiconductors	Preparation method
single	$KTaO_{3\ octahedral}$	-	one-step hydrothermal
	$KTaO_{3\ cubic}$	-	
	WO_3	-	
	CdS	-	
	CdSe	-	
	MoS_2	-	
	$SrTiO_3$	-	
binary	$KTaO_3$+WO_3	2:1	two-steps $KTaO_3$ + hydrothermal
	$KTaO_3$+WO_3	10:1	
	$KTaO_3$+CdSe	10:1	one-step hydrothermal
	$KTaO_3$+CdS	10:1	
ternary	$KTaO_3$+CdS+WO_3	10:1:1	two-steps $KTaO_3$ + hydrothermal
	$KTaO_3$+CdS+WO_3	20:1:1	
	$KTaO_3$+CdS+MoS_2	10:5:1	
	$KTaO_3$+CdSe+$SrTiO_3$	1:5:10	one-step hydrothermal
	$KTaO_3$+CdSe+$SrTiO_3$	10:5:10	
	$KTaO_3$+CdS+MoS_2	10:5:1	

Experimental methodology

Hydrothermal synthesis

Surface characterization

Photoactivity measurements

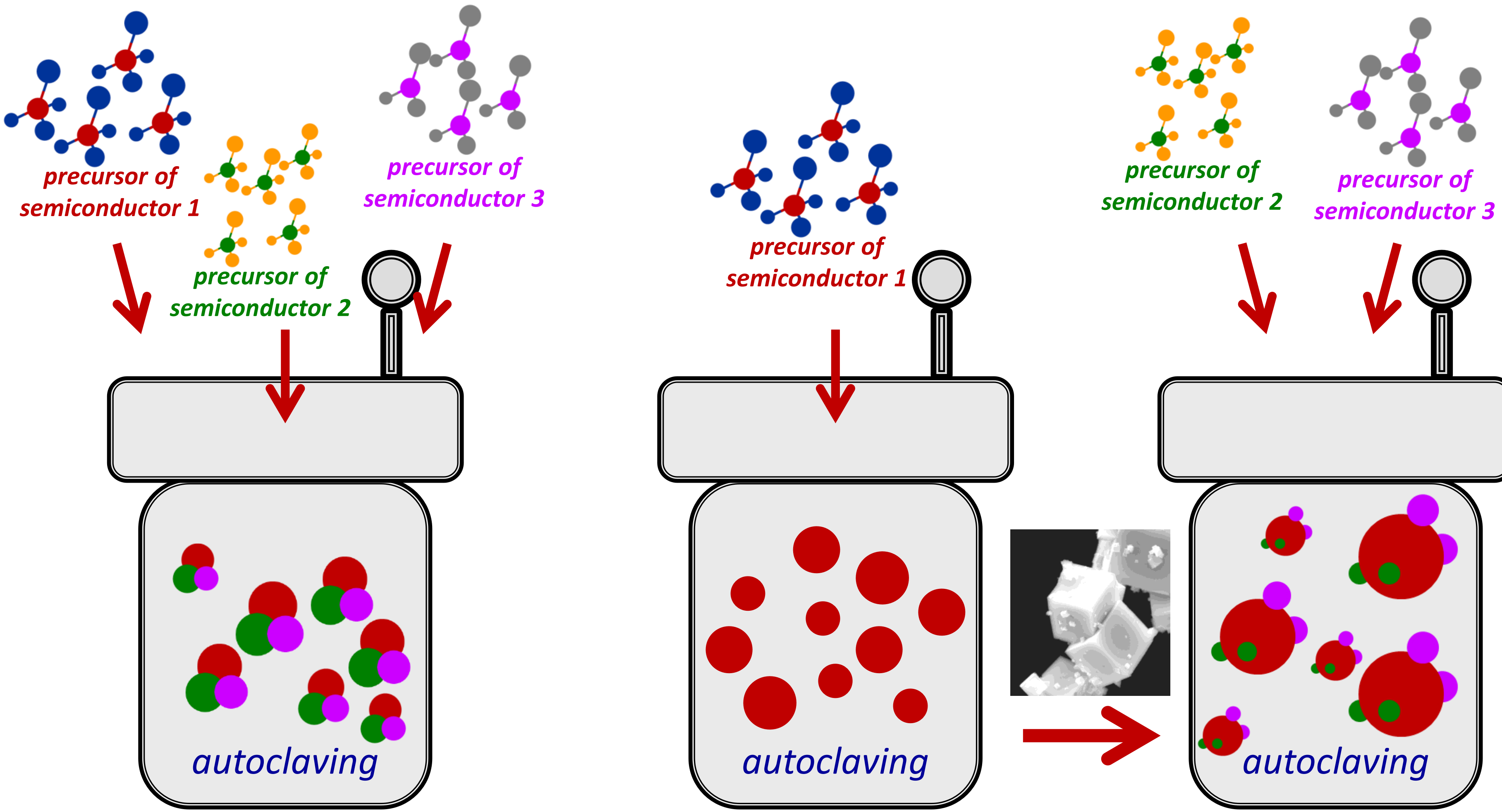
$KTaO_3$-CdS, $KTaO_3$-MoS_2 and $KTaO_3$-CdS-MoS_2

- ❑ hydrothermal synthesis of single semiconductors
- ❑ calcination step

Autoclaving: 200°C, 24h
Filtered, dried (60°C)

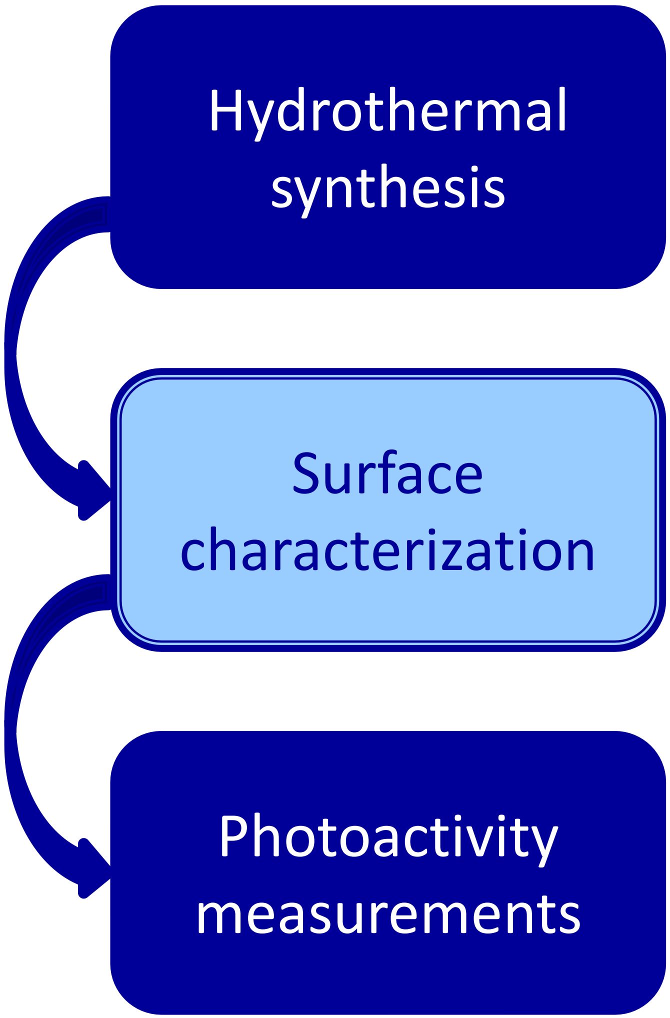
Sample label	$KTaO_3$: CdS : MoS_2 molar ratio	Preparation method
$KTaO_3$	1:0:0	hydrothermal
CdS	0:1:0	solvothermal
MoS_2	0:0:1	hydrothermal
CdS-MoS_2 5-1	0:5:1	one step solvothermal
CdS-MoS_2 4-1	0:4:1	one step solvothermal
CdS-MoS_2 1-1	0:1:1	one step solvothermal
CdS-MoS_2 1-5	0:1:5	one step solvothermal
$KTaO_3$-CdS 10-1_MS	10:1:0	one step solvothermal
$KTaO_3$-CdS 10-1_C	10:1:0	hydro/solvothermal and calcination
$KTaO_3$-MoS_2 10-1_MS	10:0:1	one step solvothermal
$KTaO_3$-MoS_2 10-1_C	10:0:1	hydro/solvothermal and calcination
$KTaO_3$-CdS-MoS_2 10-1-1_MS	10:1:1	one step solvothermal
$KTaO_3$-CdS-MoS_2 10-1-1_C	10:1:1	hydro/solvothermal and calcination
$KTaO_3$-CdS-MoS_2 10-5-1_MS	10:5:1	one step solvothermal
$KTaO_3$-CdS-MoS_2 10-5-1_C	10:5:1	hydro/solvothermal and calcination

Hydrothermal synthesis



One pot synthesis **Two steps synthesis**

Experimental methodology



- Optical properties (diffuse reflectance spectra)
- BET surface area
- Crystal structure (powder X-ray diffraction)
- Morphology (SEM microscopy)

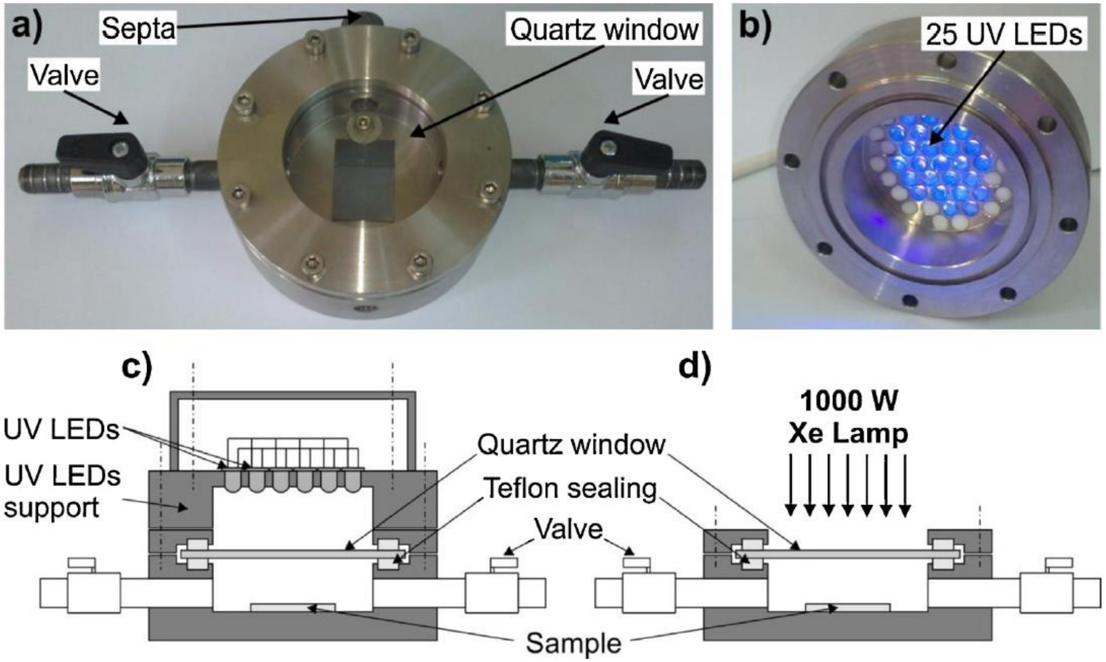
Experimental methodology

Hydrothermal synthesis

Surface characterization

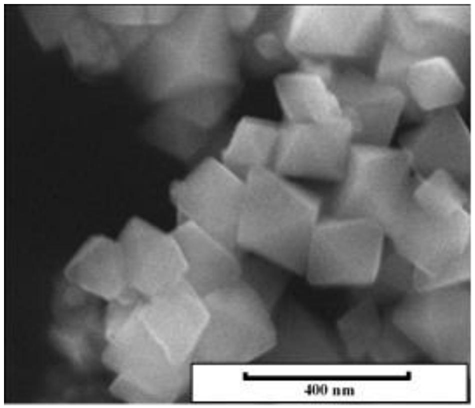
Photoactivity measurements

- Phenol degradation in the aqueous phase
- Toluene degradation in the gas phase

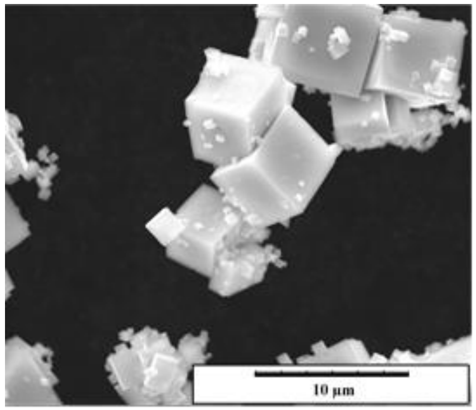


25 LEDs (λ_{max} = 375 nm, 63 mW per diode)

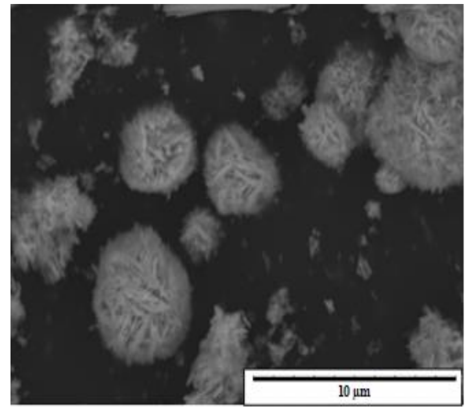
SEM images of single semiconductors



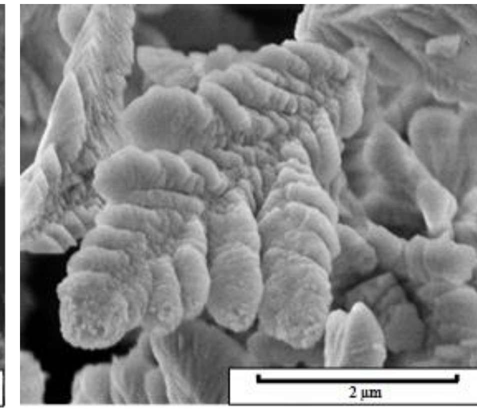
$KTaO_3$ octahedral



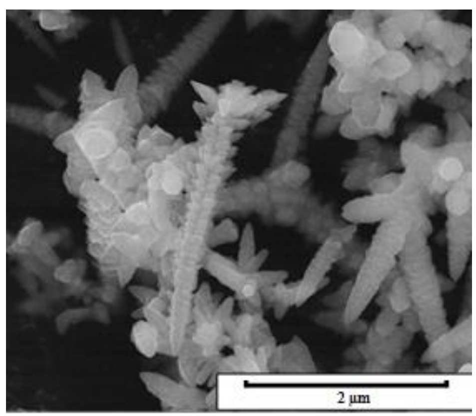
$KTaO_3$ cubic



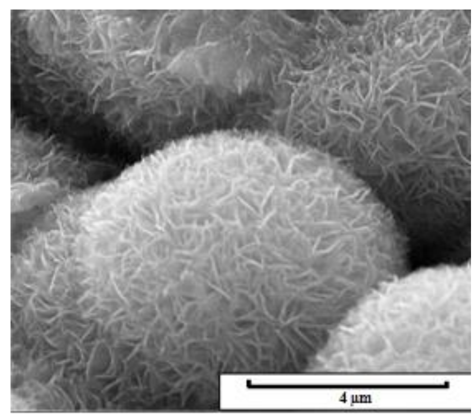
WO_3



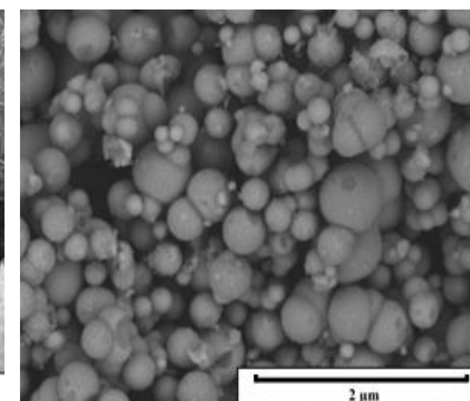
CdS



CdSe



MoS_2



$SrTiO_3$

M. Marchelek et al. / Catalysis Today (2014) – submitted

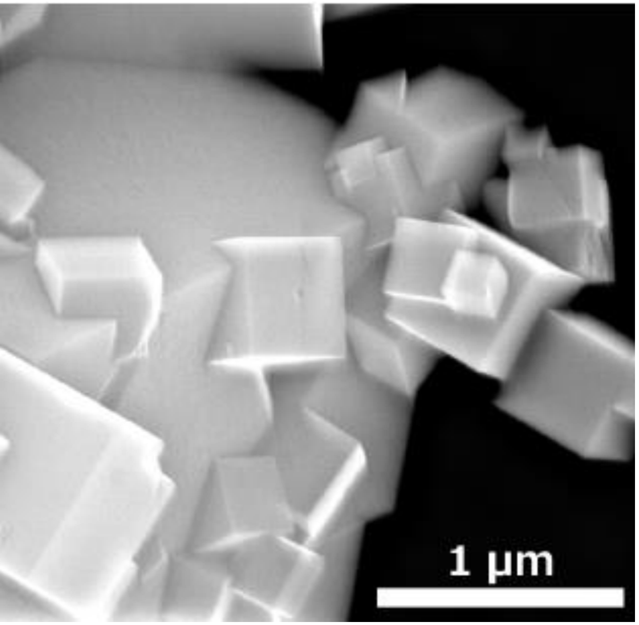
IN MARI VIA TUA

Photoactivity of single, binary and ternary semiconductors (toluene degradation in gas phase)

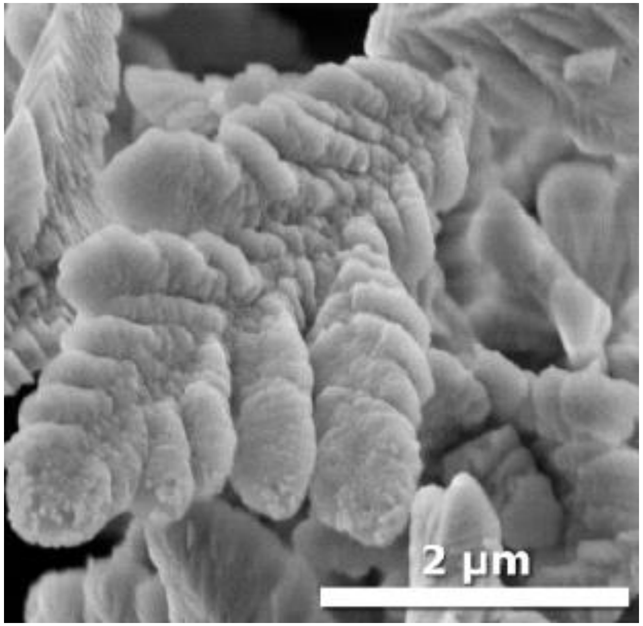
Sample label and type of nanocomposite		Molar ratio of semiconductors	Preparation method	BET surface area [$m^2 \cdot g^{-1}$]	Degradation efficiency of toluene in the gas phase after 60 min. irradiation over semiconductors in the fourth subsequent cycles (LEDs, λ_{max} = 375 min.) [%]			
					1st cycle	2nd cycle	3rd cycle	4th cycle
single	$KTaO_3$ octahedral	-	one-step hydrothermal	22.2	44	38	37	33
	$KTaO_3$ cubic	-		0.1	64	63	42	37
	WO_3	-		10.4	36	33	32	30
	CdS	-		1.2	57	57	57	52
	CdSe	-		12.7	28	27	26	19
	MoS_2	-		1.8	46	23	22	22
	$SrTiO_3$	-		17.8	41	39	35	34
binary	$KTaO_3$+WO_3	2:1	two-steps $KTaO_3$ + hydrothermal	8.1	62	28	14	13
	$KTaO_3$+WO_3	10:1		2.5	43	37	31	29
	$KTaO_3$+CdSe	10:1	one-step hydrothermal	33.9	42	38	37	33
	$KTaO_3$+CdS	10:1		17.5	47	45	41	40
ternary	$KTaO_3$+CdS+WO_3	10:1:1	two-steps $KTaO_3$ + hydrothermal	2.6	51	32	33	29
	$KTaO_3$+CdS+WO_3	20:1:1		2.2	51	39	35	31
	$KTaO_3$+CdS+MoS_2	10:5:1		4.6	59	56	56	55
	$KTaO_3$+CdSe+$SrTiO_3$	1:5:10	one-step hydrothermal	56.8	60	39	38	35
	$KTaO_3$+CdSe+$SrTiO_3$	10:5:10		58.9	60	56	50	48
	$KTaO_3$+CdS+MoS_2	10:5:1		10.3	50	41	43	42

M. Marchelek et al. / Catalysis Today (2014) – submitted

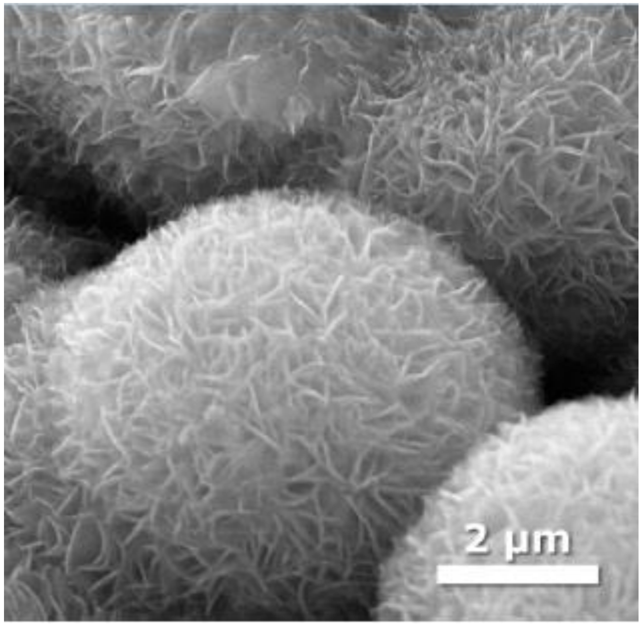
$KTaO_3$-CdS-MoS_2 nanocomposites



$KTaO_3$ cubic



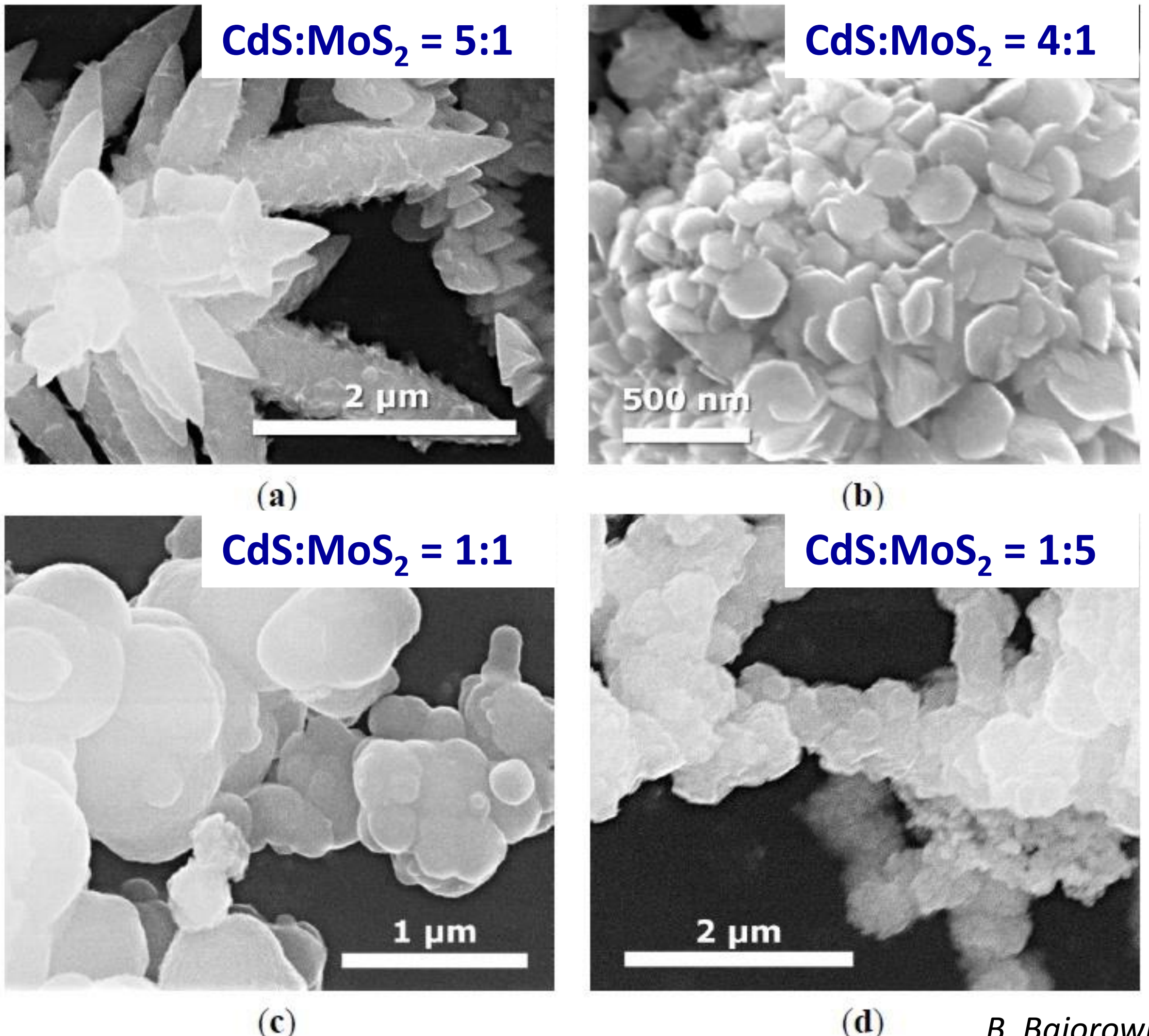
CdS



MoS_2

B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

CdS-MoS_2 binary nanocomposites



SEM images of binary CdS-MoS_2 composites obtained by solvothermal mixed solution methods with different molar ratio of CdS:

(a) CdS:MoS_2 = 5:1; (sample CdS-MoS_2 5-1);

(b) CdS:MoS_2 = 4:1 (sample CdS-MoS_2 4-1);

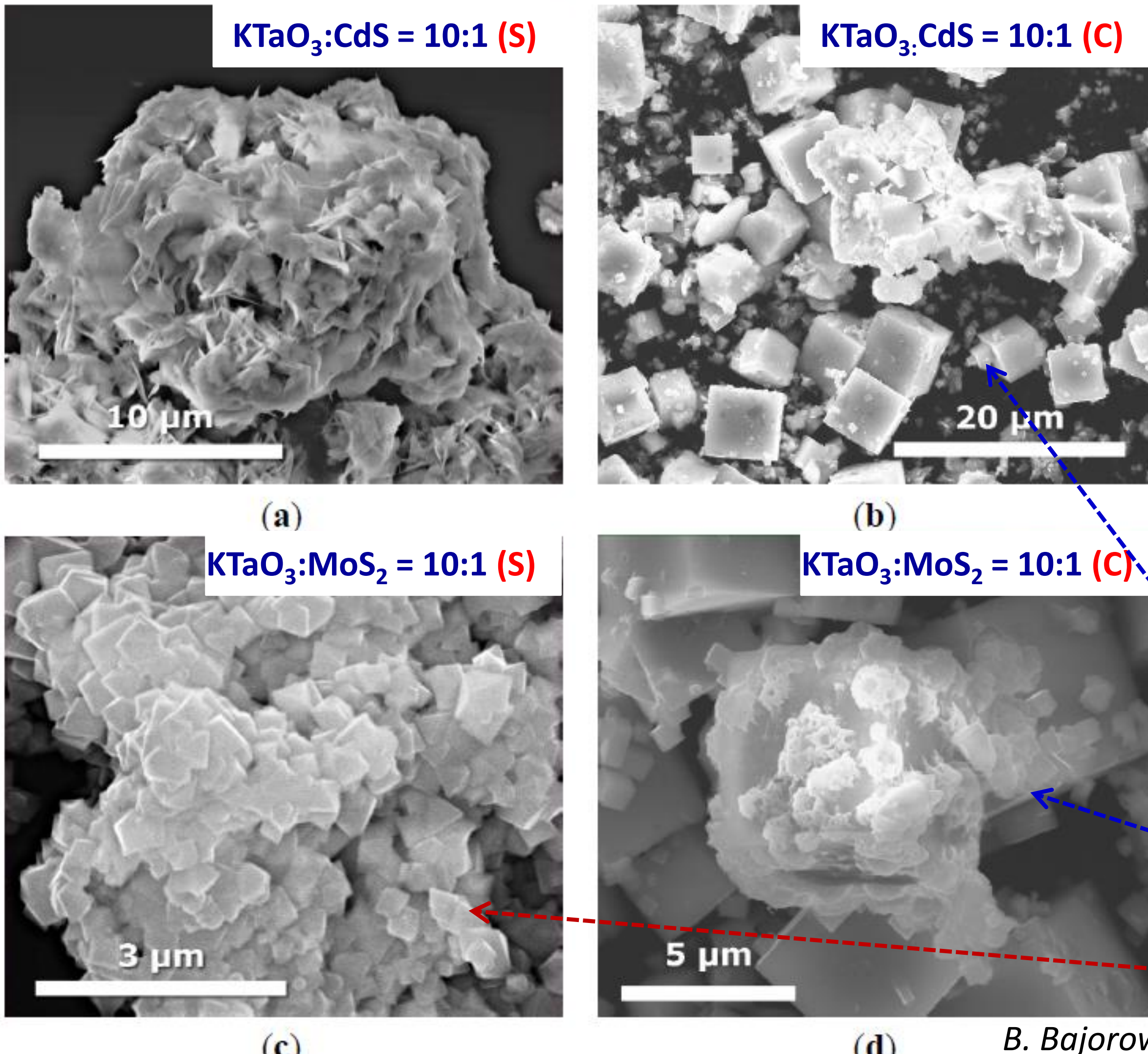
(c) CdS:MoS_2 = 1:1 (sample CdS-MoS_2 1-1);

(d) CdS:MoS_2 = 1:5 (sample CdS-MoS_2 1-5)

nanoleafs → hexagonal shaped nanostructures → bonded microspheres

B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

$KTaO_3$-CdS and $KTaO_3$-MoS_2 binary nanocomposites



(a) $KTaO_3$-CdS (10:1) obtained by solvothermal mixed solutions;

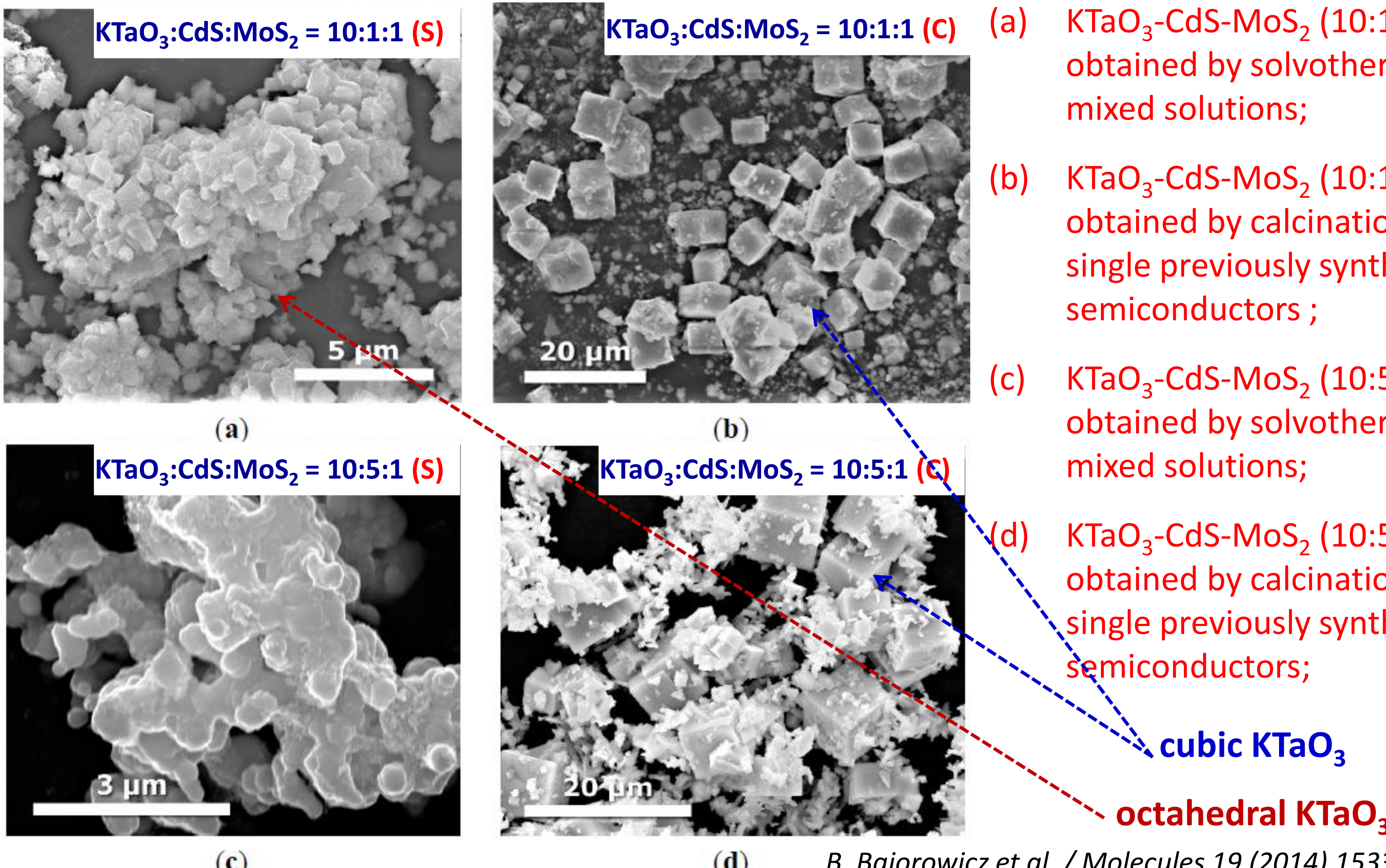
(b) $KTaO_3$-CdS (10:1) obtained by calcination of single previously synthesized semiconductors;

(c) $KTaO_3$-MoS_2 (10:1) obtained by solvothermal mixed solutions;

(d) $KTaO_3$-MoS_2 (10:1) obtained by calcination of single previously synthesized semiconductors

B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

$KTaO_3$-CdS-MoS_2 ternary nanocomposites



(a) $KTaO_3$-CdS-MoS_2 (10:1:1) obtained by solvothermal mixed solutions;

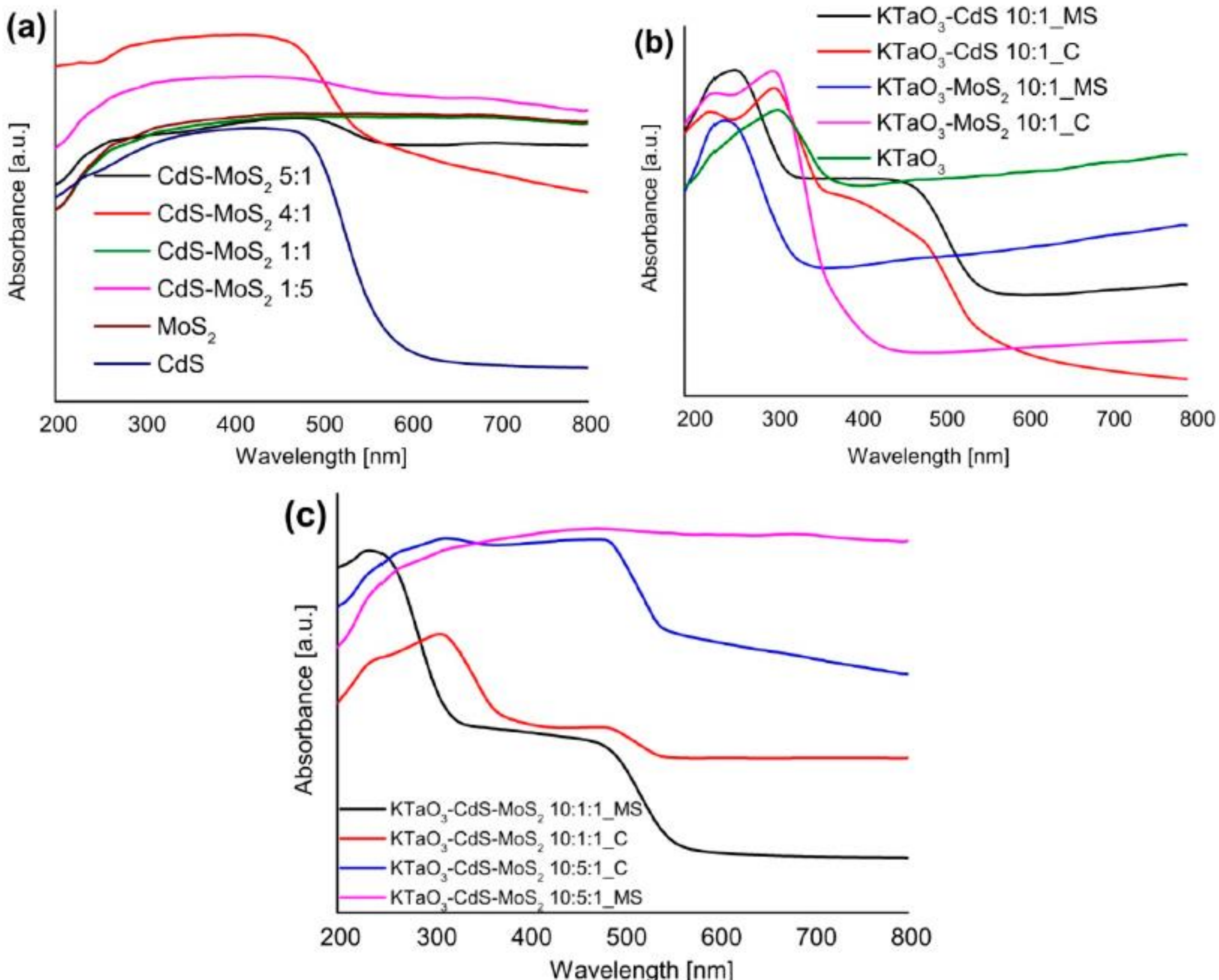
(b) $KTaO_3$-CdS-MoS_2 (10:1:1) obtained by calcination of single previously synthesized semiconductors ;

(c) $KTaO_3$-CdS-MoS_2 (10:5:1) obtained by solvothermal mixed solutions;

(d) $KTaO_3$-CdS-MoS_2 (10:5:1) obtained by calcination of single previously synthesized semiconductors;

B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

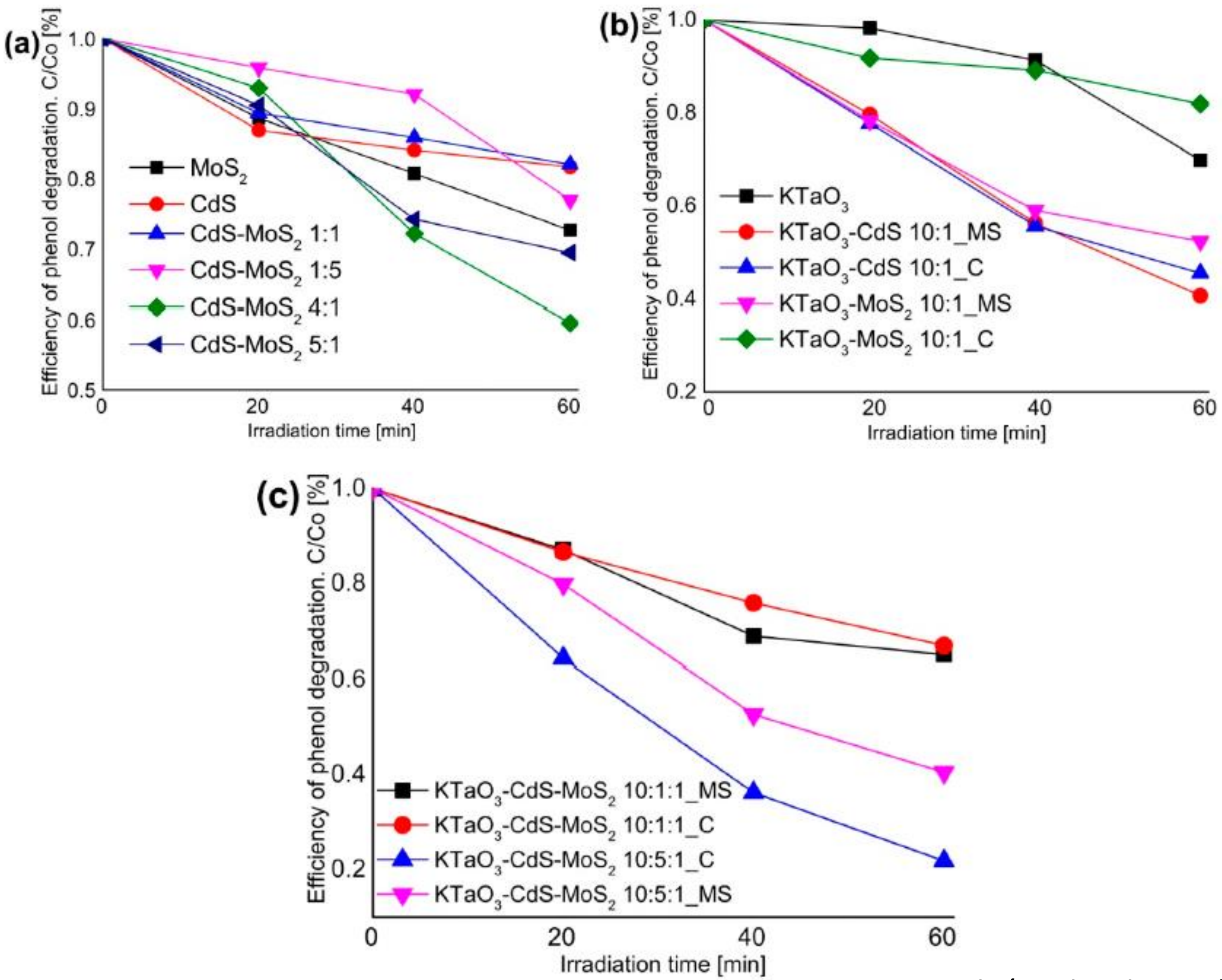
$KTaO_3$-CdS-MoS_2 based nanocomposites: optical properties



B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

$KTaO_3$-CdS-MoS_2 based nanocomposites: photoactivity

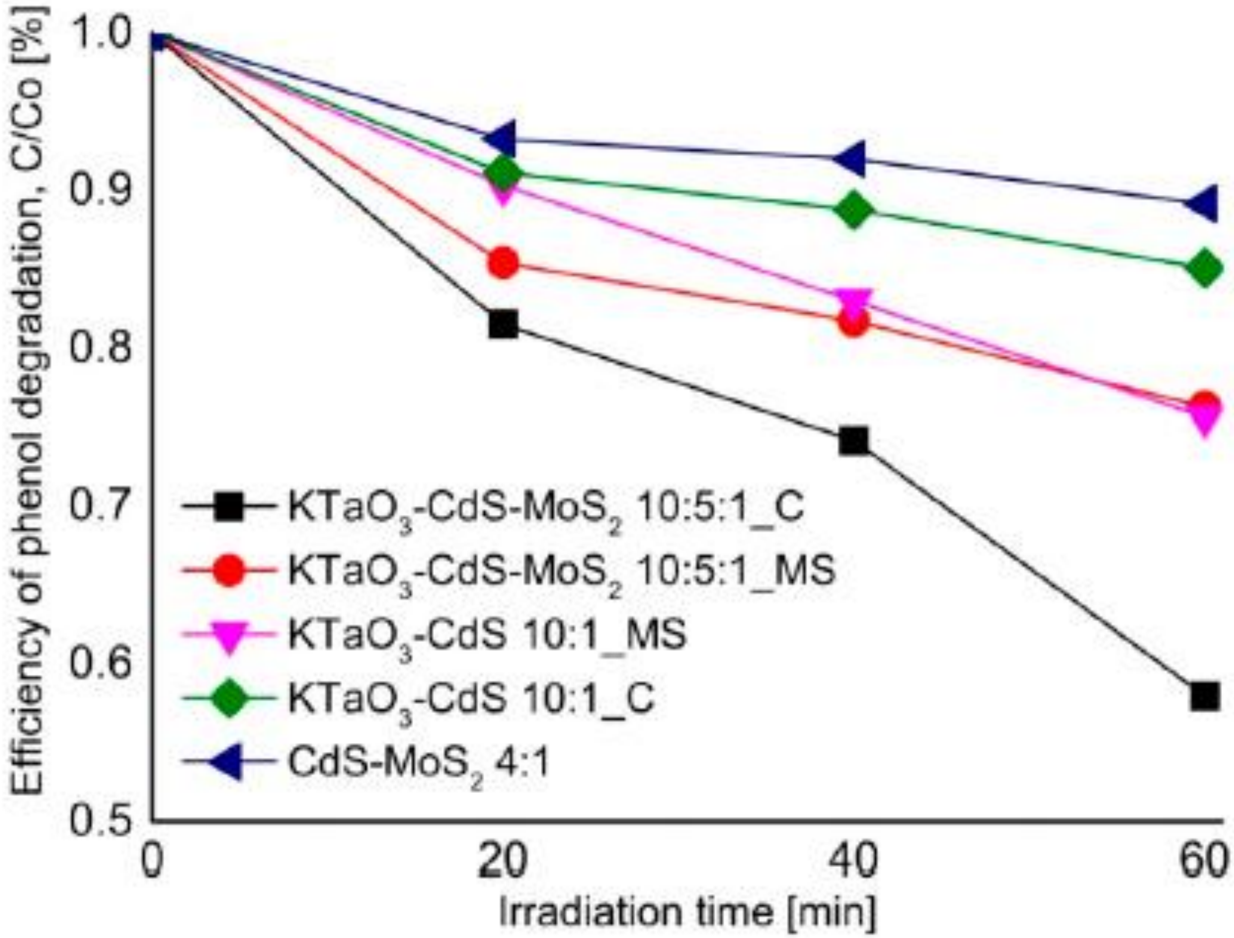
(phenol degradation in aqueous phase under UV irradiation)



B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

$KTaO_3$-CdS-MoS_2 based nanocomposites: photoactivity

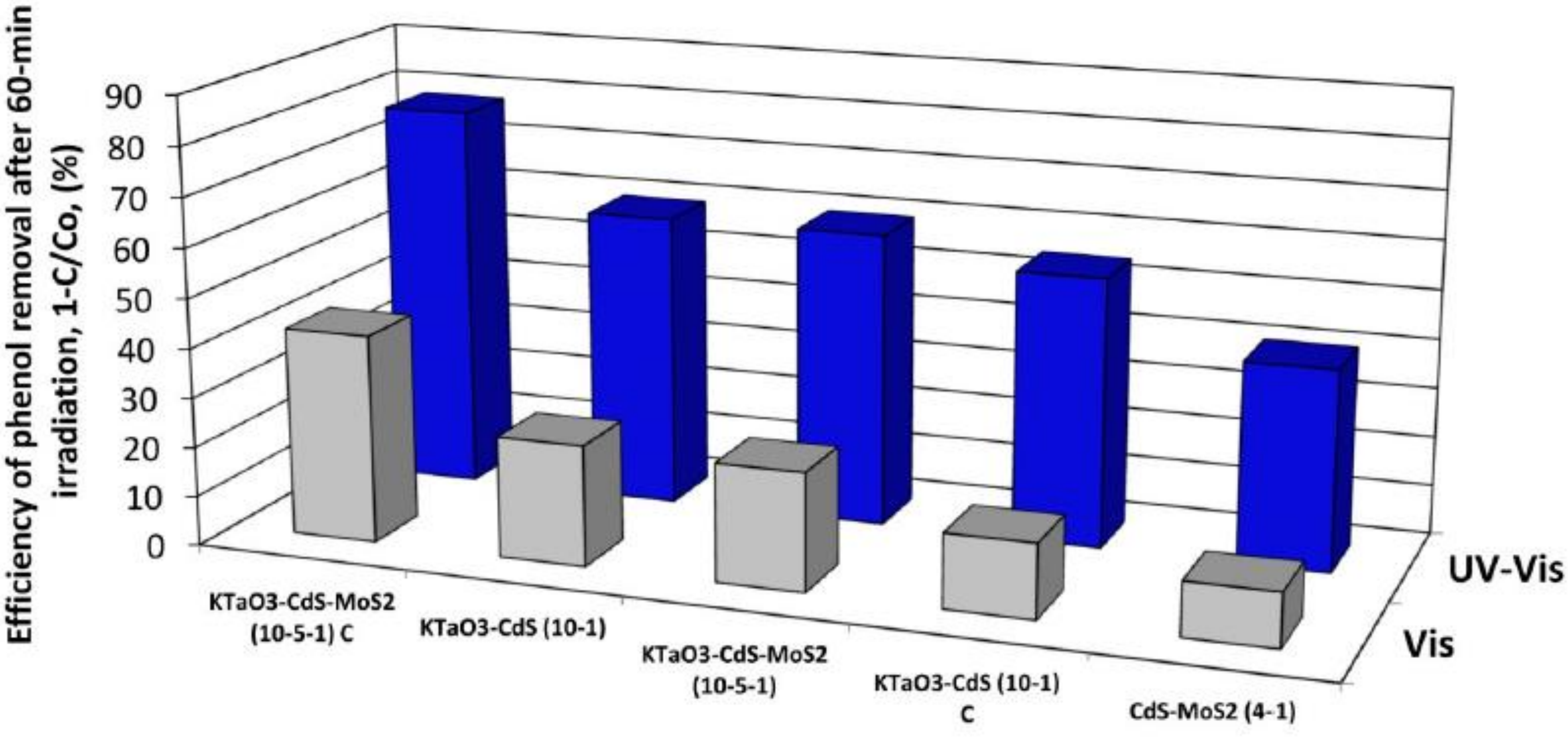
(phenol degradation in aqueous phase under visible irradiation, λ > 420 nm)



B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

$KTaO_3$-CdS-MoS_2 based nanocomposites: photoactivity

(phenol degradation in aqueous phase under UV and visible irradiation)



B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

$KTaO_3$-CdS-MoS_2 based nanocomposites: photoactivity

(phenol and toluene degradation)

Sample label	Phenol degradation rate under UV–Vis ($\mu mol \cdot dm^{-3} \cdot min^{-1}$)	Toluene degradation after 1 h irradiation (LEDs, λ_{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

B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

CdS-MoS_2 binary nanocomposites: crystal structure

Relative change of the intensity of three most dominant XRD peaks between 24 and 29 degrees

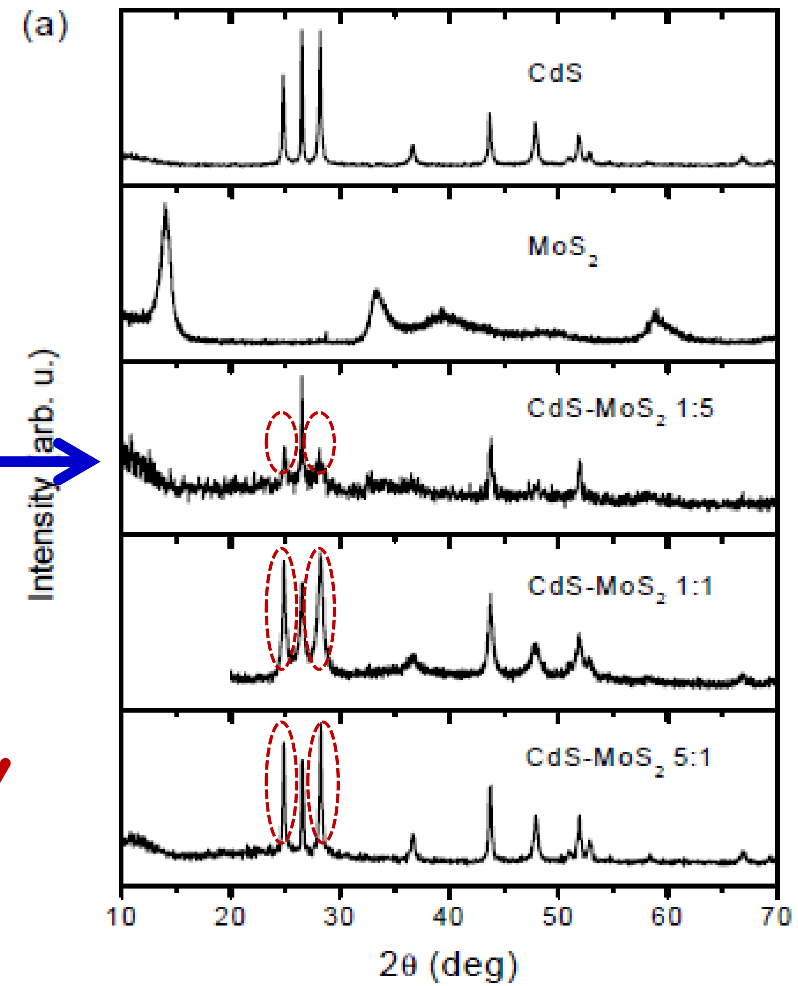
Lattice parameters refined by LeBail method:

pure CdS: a = 4.1341(8) Å ; c = 6.710(1) Å

CdS-MoS_2 (1:5): a = 4.1341(8) Å; c = 6.733(3) Å

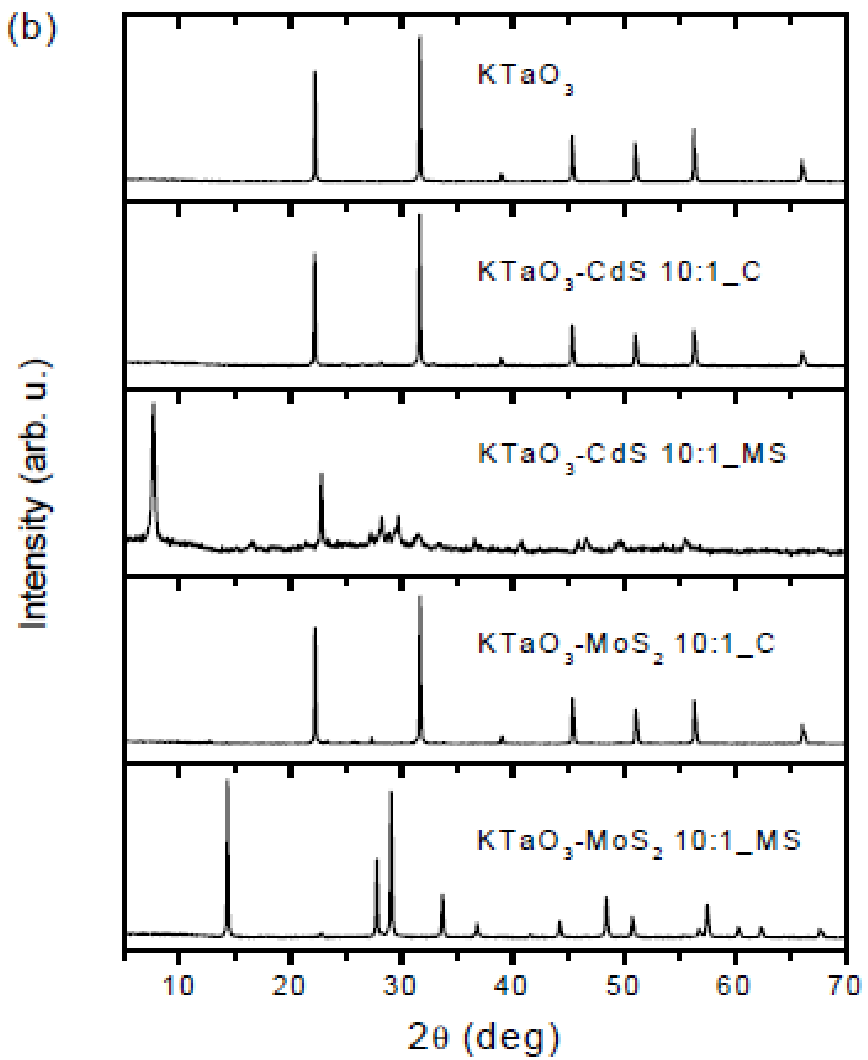
⇓

Mo atoms are incorporated into hexagonal CdS structure



B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

$KTaO_3$-CdS and $KTaO_3$-MoS_2 binary nanocomposites: crystal structure

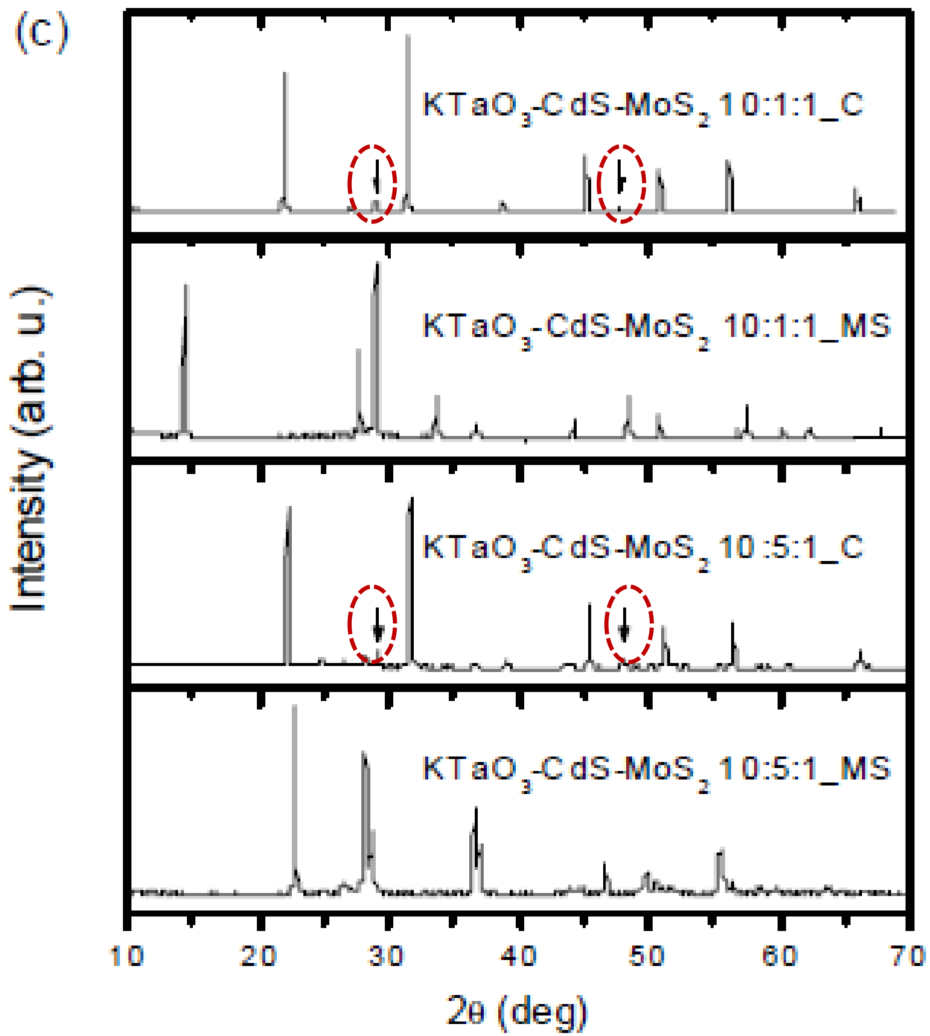


New phases:
Ta_2O_5 (majority phase)
TaS_2
$K_2Ta_{15}O_{32}$

Almost pure pyrochlore-like
$K_2Ta_2O_6$
According to literature data →
$K_2Ta_2O_6$ shows photocatalytic activity

B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

$KTaO_3$-CdS-MoS_2 ternary nanocomposites: crystal structure



New phase appeared !!

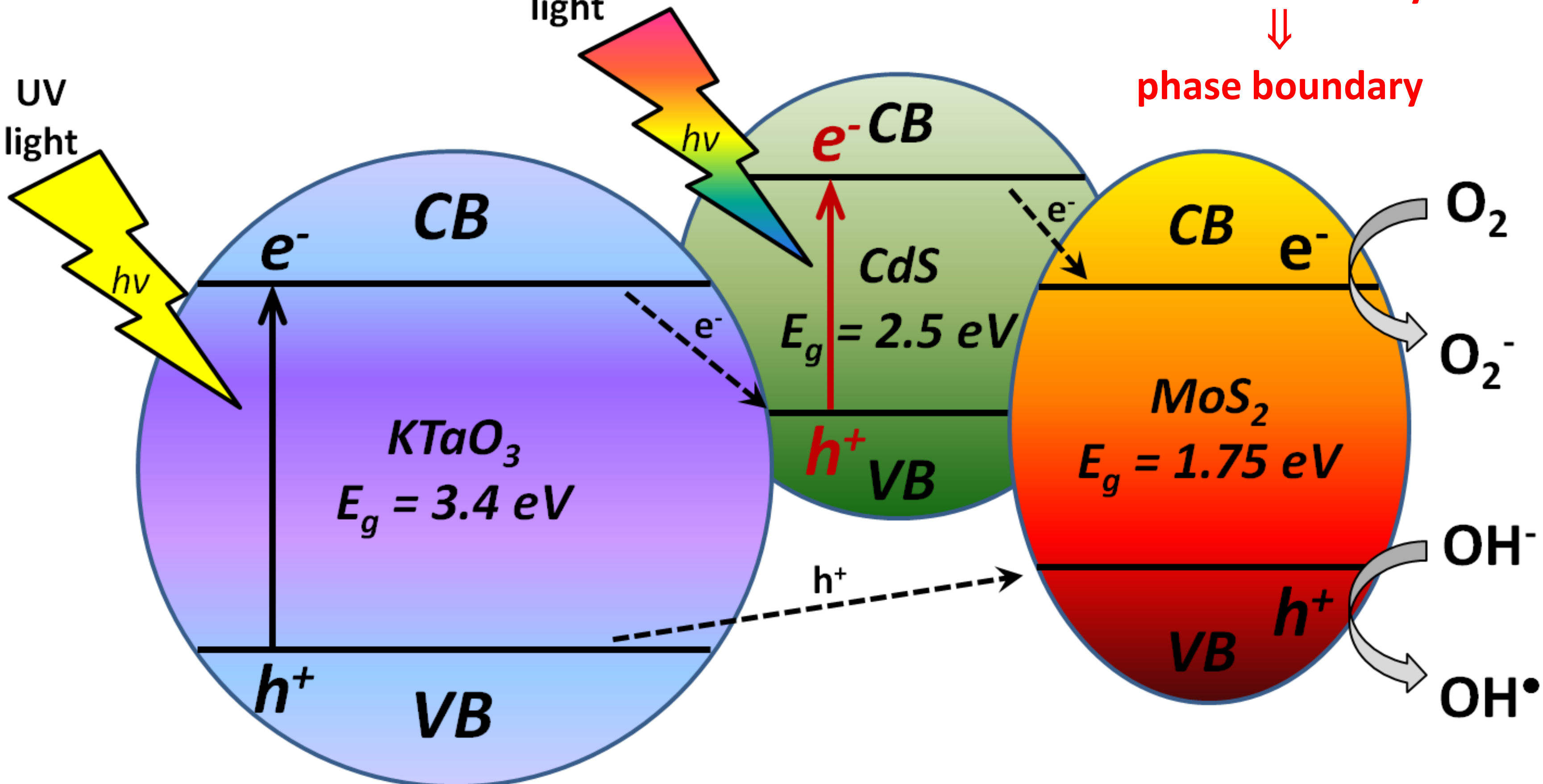
$CdMoO_4$ (↓)

Pure and Ag doped $CdMoO_4$ revealed photocatalytic activity (E_g = 3.4 eV)

B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

Possible excitation mechanism

$KTaO_3$-CdS-MoS_2 = 10:5:1
obtained by synthesis of single semiconductors followed by calcination
⇓
phase boundary



B. Bajorowicz et al. / Molecules 19 (2014) 15339-15360

Conclusions

1. Loading MoS_2 onto CdS as well as loading CdS onto $KTaO_3$ significantly enhanced absorption properties as compared with single semiconductors;

2. 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;

3. Enhanced photoactivity could be related to the two-photon excitation in $KTaO_3$-CdS-MoS_2 composite under UV-Vis and/or to additional presence of $CdMoO_4$ working as co-catalyst.

Acknowledgments

Contribution by:

B. Bajorowicz, A.Cybula, (*Faculty of Chemistry, Gdansk University of Technology*)

M. Marchelek, P. Mazierski, N. Fijałkowska (*Faculty of Chemistry, University of Gdansk*)

M. Winiarski, T. Klimczuk (*Faculty of Applied Physics and Mathematics, , Gdansk University of Technology*)

Financial support:

Polish-Norwegian Research Programme

Narodowe Centrum Badań i Rozwoju

norway grants

Thank you for your attention