Preparation, characterization, and application of bismuth oxyhalides as visible light active photocatalysts

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1. Introduction

One of the biggest social, economic, and scientific challenge of the present and the near future is to address environmental and global climate change issues. These concerns including the production of drinking water and the treatment of industrial wastewaters in a way that protects the environment and be harmless to human health. Various regulatory limits our disposal that seek to regulate pollutant emissions, unfortunately many countries persistently exceed their emission/pollution levels.

In recent decades, in addition to traditional water treatment processes, alternative processes have been developed to eliminate organic pollutants such as textile dyes, pesticides and herbicides used in agriculture. One such group of solution could be the so-called “Advanced oxidation processes (AOP)”, which includes methods that degrade organic pollutants using various redox reactions into less toxic compounds, preferably water and carbon dioxide. Among AOP/s the heterogeneous photocatalysis prominently investigated, in which a semiconductor catalyst is able to decompose contaminants in water by excitation with light of a suitable wavelength. The best-known semiconductor photocatalyst is titanium-dioxide (TiO_2), but scientific interest has long been directed to other semiconductors such as bismuth oxohalides (BiOX, X = Cl, Br, I), which are considered highly potential catalysts under UV and visible irradiation. After production, BiOX do not require further modifcations to be excitable by visible light (natural or artificial), which can greatly reduce operating costs.

2. Objective

During my doctoral studies, I joined the work of the Environmental Chemistry Research Group led by Dr. Klára Hernádi and Dr. Zsolt Pap, within which I continued my research work on the topic of the Hungarian-Indian TÉT project (TÉT_15_IN-1-2016-0013). BiOX materials are photocatalysts that are also active in visible light, so my aims included the preparation of this semiconductor materials and the study of the effect of the parameters used in solvothermal crystallization. Ethylene glycol, bismuth nitrate pentahydrate ($Bi(NO_3)_3 \cdot 5H_2O$) and potassium halides (KX) were used during the solvothermal crystallization. My doctoral dissertation main goals were:

O1: To investigate the effect of solvothermal crystallization parameters (temperature and time) on the physical and chemical properties of BiOCl, BiOBr and BiOI semiconductors like structural characteristics, and photocatalytic activity. The secondary aim was to optimize the most favorable temperature and time for photocatalytic activity among several parameters (120 ° C, 140 ° C and 160 ° C; 3 h, 24 h, 48 h).

O2: Design and investigation of the effect of additives on BiOCl, BiOBr and BiOI semiconductors' physical and chemical properties as well as on photocatalytic efficiency. To this end, I selected the most common additives in the literature (CTAB, CTAC, SDS, PVP, U and TU) and wanted to study the effect of these additives on the surface tension of the synthesis solution and their significance in the morphological, structural, optical, and photocatalytic properties of the prepared catalyst.

O3: Study of BiOCl, BiOBr, and BiOI impact on the environment. I considered how these catalysts may escape into the environment and accumulate or dilute there during industrial application. Guided by these considerations, I chose an aquatic and a terrestrial plant species (*Lemna minor*, *Lepidium Sativum*) and a terrestrial ant species (*Formica polyctena*) as indicators. Furthermore, the concentrations of the nutrient solutions were chosen considering the relevant and accepted experimental guidelines as well as the accumulation and dilution.

3. Experimental methods

Powder X-ray diffractometry (XRD) was carried out on a Rigaku Miniflex II diffractometer 2θ° = 20 – 60°, λ (CuKα) = 0.15418 nm) using 2° min^{-1} scanning speed. The primary crystallite mean size values were calculated using the Scherrer equation.

Hitachi S-4700 Type II FE-SEM scanning electron microscope (SEM) was used to record the micrographs. The microscope was equipped with a cold field emission source operating in the range of 5 – 15 kV. The samples were mounted on a conductive carbon tape, which was attached to an aluminum holder.

FEI Technai G2 X-TWIN TEM (200 kV) transmission electron microscope was used to record micrographs about the morphology of the particles. The samples were prepared as follows: a small amount of the examined material was carried out in 1.25 cm^3 of ethanol. A few drops of suspension were deposited and dried onto the surface of the grid (CF 200 Cu TEM grid).

To measure the optical properties of the samples, **diffuse reflectance spectroscopy (DRS)** was applied. The **DRS** spectra of the samples were recorded using a JASCO-V650 spectrophotometer with an integration sphere (ILV-724, λ = 250 – 800 nm). The band gap energy values were evaluated by the Kubelka-Munk approach and the Tauc plot.

The **specific surface areas** of the catalysts were determined by N_2 adsorption at 195,8 °C, using a BELCAT-A device. The specific surface area was calculated by applying the BET method.

X-ray photoelectron spectroscopy measurements were performed on a Specs Phoibos 150 MCD system employing a monochromatic Al-Kα source (1486.6 eV) at 14 kV and 20 mA and the X-ray source with a power of 200 W, while the pressure in the analyzer chamber was lower than 10^{-12} bar. Samples were mounted on double-sided carbon tape. The high-resolution O1s and Bi4f spectra were obtained using analyzer pass energy of 20 eV in steps of 0.05 eV for analyzed samples

The **surface tension** of the synthesis solution was determined by using a 3.5 mL stalagmometer and Milli-Q water as the reference. The density of the solutions was determined by using a pycnometer (10 mL) coupled on a thermometer.

Thermo Scientific DXR **Raman microscope** was used with a diode-pumped frequency-doubled Nd:YAG (10 mW) at 532.2 nm wavelength of the laser. The used confocal aperture was 50 μm pinhole. Recording the spectra autoexposure operating mode was used, within 100 signal/noise ratio. The spectra were taken by mapping method on 5 × 5 μm area.

4. Evaluation of photocatalytic efficiency

The photocatalytic decomposition of Rhodamine B (RhB) was carried out in a double-walled Pyrex® glass reactor surrounded by a thermostatic jacket (T = 25 °C) under UV ($\lambda_{max} \approx 365$ nm) and visible irradiation ($\lambda > 400$ nm). The reactor was surrounded by 6 × 6 W black light lamps (9.53 $W \cdot m^{-2}$ energy flux on the reactor position) or 4 × 24 conventional compact fluorescent lamps (Düwi 25920/R7S-24 W; 81.37 $W \cdot m^{-2}$energy flux on the reactor position). During visible light experiments, the spectrum of the lamps was slightly modified by circulating 1 M sodium nitrite (Molar Chemicals, min. 99.13%) aqueous solution in the thermostatic jacket. The $NaNO_2$ solution absorbs any UV photons below 400 nm, providing only visible light irradiation while during the UV tests, water was the thermostatic agent. The reactor ($C_{0, RhB} = 0.25$ mM; $C_{suspension} = 1.0$ $g \cdot L^{-1}$; total volume of the suspension $V_{suspension} = 130$ mL) was continuously stirred and purged with air to keep the dissolved oxygen concentration constant during the whole experiment (degradation time = 2 h). 1.5 mL sample was taken in 0, 10, 20, 30, 40, 50, 60, 80, 100 and 120 min and placed into a sample holder, centrifuged for 3 min at 13400 rpm and filtered with Filtratech 0.25 μm syringe filter. The concentration of RhB was followed by using a JASCO V-650 spectrophotometer at a detection wavelength fixed at 554 nm. The concentration of phenol was followed by HPLC (Merck-Hitachi L-7100) with a low-pressure gradient pump, equipped with a Merck-Hitachi L-4250 UV–Vis detector and a Lichrospher Rp 18 column using a methanol/water (50:50 v/v) mixture as eluent and 210 nm as the detection wavelength.

5. Summary of new scientific results

T.1. We have proved that lower temperature and shorter crystallization time are favorable for the preparation of more efficient BiOX catalysts.

1.1. By systematically changing the temperature of the solvothermal crystallization treatment, I prepared BiOX microparticles with different particle sizes. We found that with the temperature the hierarchical and primary particle size increased as well, like the samples prepared at low temperatures (120 ° C) had the smallest particle size and the highest photocatalytic efficiency.

1.2. With the time of solvothermal crystallization the primary and hierarchical particle sizes increased as well, and the specific surface area diminished or did not change. The large specific surface area is advantageous for photocatalytic decomposition processes, as the number of active centers may also increase. The shortest crystallization time (3 h) resulted the most efficient BiOI semiconductor agains methyl orange contaminants: 77.9% was removed under UV illumination and 84.1% under visible light illumination.

1.3 We have proved that elevated temperature favors the formation of metallic bismuth, which are detrimental to photocatalytic reactions. Metal precipitation was observed for samples prepared at 160 ° C crystallization temperatures. The synthesis solution was tested with the silver mirror probe to demonstrate that ethylene glycol was oxidized to carboxylic acids and aldehydes, while metallic bismuth was formed. We found that the high amount of metallic bismuth precipitate, inhibited the photocatalytic activity of BiOX by promoting the $e^- h^+$ recombination.

T.2. We have shown that the surface tension of the synthesis solution greatly influences the crystallographic, morphological, optical, and photocatalytic properties of the formed BiOX materials. The effect of the surface tension of the synthesis solutions on the crystallographic and photocatalytic properties decreases with electronegativity and ion size.

2.1. As the surface tension of the BiOCl and BiOBr synthesis solutions increased, the hierarchical particle size decreased, and the specific surface area increased as well. Furthermore, in both cases, when urea was used as an additive, the presence of cubic shaped hierarchical crystal systems were confirmed. We proved that the synthesis solution's surface tension change was the most relevant parameter which affected consistently the BiOCl structuralal and photocatalytical properties this effect was already reduced for BiOBr and no correlation was found in case of BiOI.

2.2. We found that the BiOCl, BiOBr and BiOI semiconductors produced with the additives achieved higher or at least the same photocatalytic efficiency than their crystallized version without the additive. Thus, we have demonstrated that, the additives favor the development of advantageous structural characteristics in terms of photocatalytic activity (smaller hierarchical and primary crystallite size, larger specific surface area).

2.3. We demonstrated that the additives had an effect not only on the particle size and specific surface area, but also on the amount of surface crystallographic defects. In the case of BiOCl, the formation of [Bi - * - Bi] clusters were demonstrated by Raman spectroscopy, and confirmed by XPS measurements. In the case of BiOBr semiconductor, the appearance of Bi^{4+} and Bi^{5+} were also detected by XPS measurements. In the case of BiOI, we did not find any surface correlation, proving that the effect of surface tension decreases with the KX electronegativity and ion size.

T.3. We have shown that the trend of the effect of the additives is the same for the BiOX series and that polyvinylpyrrolidone gives the best efficiency.

3.1. We found that during photocatalytic removal of RhB, degradation was aided by dye sensitization and high adsorption. BiOX semiconductors made with PVP under UV and visible light proved to be the most effective. Samples crystallized in the presence of thiourea proved to be the second most effective.

3.2. We demonstrated that all samples crystallized in the presence of PVP form smaller hierarchical microspheres than in the presence of other additives. In addition, in the presence of PVP, the primary particle size decreased, the specific surface area increased, and crystal defects appeared – that enhances the photocatalytic efficiency.

T.4. We have shown that BiOX substances increase the mortality of aquatic plants at lower concentrations and are also harmful to terrestrial plants and animal species at higher concentrations.

4.1. We found that the *Formica polyctena* had a high mortality in the presence of BiOCl and BiOBr semiconductors. In contrast, the presence of BiOI semiconductor had no negligible effect on ants.

4.2. We concluded from ecotoxicological study of Lemna minor, that the mortality rate intensified with the suspension concentration increment ($0.75\ g \cdot L^{-1}$ and $1.00\ g \cdot L^{-1}$) and BiOBr caused intense individual death already at 0.5 g · L-1 suspension concentration. We found that BiOX semiconductors also influenced the pH of the *Lemna minor* nutrient solution, as it shifted the slightly alkaline pH of the control group to neutral, which also justifies greater individual mortality.

4.3 In the case of the ecotoxicological study of *Lepidium Sativum* using BiOCl semiconductor, we found that at lower concentrations ($1.0\ g \cdot L^{-1}$ and $2.5\ g \cdot L^{-1}$) mortality did not increase compared to the control group, but at higher concentrations ($5\ g \cdot L^{-1}$) mortality has already increased. No toxicity was observed for BiOBr at any concentration. BiOI already reduced the number of individuals by $1\ g \cdot L^{-1}$ compared to the control group and increasing the amount of BiOI also increased the mortality of the individuals.

5. Scientific publications

Publications related to the scientific topic of the dissertation:

(1) **Enikő Bárdos**, Anna Krisztina Király, Zsolt Pap, Lucian Baia, Seema Garg, Klára Hernádi

The effect of the synthesis temperature and duration on the morphology and photocatalytic activity of BiOX (X = Cl, Br, I) materials

Applied Surface Science 479 (2019) 745–756

DOI.: 10.1016/j.apsusc.2019.02.136

IF.: 6.182 Citations: 17 Independent citations: 10

(2) **Enikő Bárdos**, Viktória Márta, Lucian Baia, Milica Todea, Gábor Kovács, Kornélia Baán, Seema Garg, Zsolt Pap, Klara Hernadi
Hydrothermal crystallization of bismuth oxybromide (BiOBr) in the presence of different shape controlling agents
Applied Surface Science 518 (2020) 146184,
DOI.: 10.1016/j.apsusc.2020.146184
IF.: 6.182 Citations: 7 Independent citations: 5

(3) **Enikő Bárdos**, Viktória A. Márta, Szilvia Fodor, Endre-Zsolt Kedves, Klara Hernadi, Zsolt Pap
Hydrothermal crystallization of the bismuth oxychlorides (BiOCl) with different shape control reagents
Materials 2021, 14 (9), 2261;
DIO.:doi.org/10.3390/ma14092261
IF.: 3.057 Citations: 0 Independent citations: 0

∑IF=15.421

Scientific publications published in international journals not closely related to the topic of the dissertation:

(4) **Bárdos Enikő**, Kovács Gábor, Gyulavári Tamás, Németh Krisztián, Kecsenovity Egon, Berki Péter, Baia Lucian, Pap Zsolt, Hernádi Klára
Novel synthesis approaches for WO 3-TiO 2/MWCNT composite photocatalysts- problematic issues of photoactivity enhancement factors
Catalysis Today 300 (2018) 28-38
DOI.: 0.1016/j.cattod.2017.03.019
IF.: 4.887 Citations: 14 Independent citations: 13

(5) Garg Seema; Yadav Mohit; Chandra Amrish; Sapra, Sameer; Gahlawat Soniya; Ingole Pravin; Todea Milica; **Bárdos Enikő**; Pap Zsolt; Hernádi Klára

Facile green synthesis of BiOBr nanostructures with superior visible-light-driven photocatalytic activity

Materials 11, (2018) 1273

DOI.:10.3390/ma11081273

IF.: 2.972 Citations: 16 Independent citations: 6

(6) Mohit Yadav, Seema Garg, Amrish Chandra, Pravin Ingole, **Eniko Bardos**, Hernadi Klara

Quercetin-mediated 3-D hierarchical BiOI-Q and BiOI-Q-Ag nanostructures with enhanced photodegradation efficiency

Journal of Alloys and Compounds 856, (2021) 156812

DOI.: 10.1016/j.jallcom.2020.156812

IF.: 4.650 Citations: 1 Independent citations: 0

(7) Tamás Gyulavári,Kata Kovács, Zoltán Kovács, **Enikő Bárdos**, Gábor Kovács, Kornélia Baán, Klára Magyari, Gábor Veréb, Zsolt Pap, Klara Hernadi

Preparation and characterization of noble metal modified titanium dioxide hollow spheres – new insights concerning the light trapping efficiency

Applied Surface Science 534 (2020) 147327

DOI.: 0.1016/j.apsusc.2020.147327

IF.: 6.182 Citations: 0 Independent citations: 0

(8) Zsejke-Réka Tóth, Saurav Kumar Maity, Tamás Gyulavári, Enikő Bárdos, Lucian Baia, Gábor Kovács, Seema Garg, Zsolt Pap, Klara Hernadi;

Solvothermal Crystallization of Ag/AgxO-AgCl Composites: Effect of Different Chloride Sources/Shape-Tailoring Agents

Catalysts 2021, 11(3), 379
DOI.: doi.org/10.3390/catal11030379
IF.: 3.520 Citations: 0 Independent citations: 0

(9) Endre Zsolt Kedves; Enikő Bárdos; Tamás Gyulavári; Klara Hernadi; Lucian Baia. Zsol Pap
Dependence of cationic dyes' adsorption upon α-MoO3 structural properties
Submitted for publication

∑IF=37.632

Participation in international and national conferences:

Poster presentations:

(1) Nano India 2017 Conference
2017.03.15-16., Delhi, India
Enhanced Visible Light Photocatalytic Activity of Green BiOBr Using Plant Extract
Seema Garg, Sameer Sapra, Amrish Chandra, Mohit Yadav, Scrantz Krisztina, **Bárdos Enikő**, Hernádi Klára

(2) XXIII. International Conference of Chemistry
2017.10.25-28 Deva, Romania
Preparation and characterization of bizmuth-oxyhalide composites
Király Anna Krisztina, **Bárdos Enikő**, Schrantz Krisztina, Alapi Tünde, Pap Zsolt, Lucian Baia, Samir Sapra, Amrish Chandra, Seema Garg, Hernádi Klára

(3) 5th European Conference on Environmental Applications of Advanced Oxidation Processes (5-EAAOP)

2017.06. 25-29., Praha, Czech Republic

The synthesis and photocatalytic properties of novel BiOX materials

E. Bárdos, A. Király, K. Schrantz, T.Alapi, Zs. Pap, S.Sapra, A. Chandra, S. Garg, K. Hernádi

(4) 12th International Conference on Physics of Advanced Materials (ICPAM-12)

2018.09.22. – 2018.09.28. Heraklion, Greece

Synthesis and photocatalytic properties of novel BiOX nanomaterials

E. Bárdos, A. Király, Zs. Pap, K. Hernádi

(5) 6th European Conference on Environmental Applications of Advanced Oxidation Processes

2019.06.26-30. Portorose, Slovenia

Hydrothermal synthesis of bismuth oxyhalide materials using different cationic salts

E. Bárdos, S.S. Rai, Zs. Pap, L. Baia, K. Hernádi

(6) 6th European Conference on Environmental Applications of Advanced Oxidation Processes

2019.06.26-30. Portorose, Slovenia

Surfactant assisted hydrothermal synthesis of bismuth oxyhalide materials and their photocatalytic activity

E. Bárdos, V. Márta, Zs. Pap, Gábor Kovács, Lucian Baia, K. Hernádi

(7) 6th European Conference on Environmental Applications of Advanced Oxidation Processes

2019.06.26-30. Portorose, Slovenia

Photocatalytic investigation of AgBr, BiOI, Cu_2O AND ZnO semiconductors' binary composites with orthorhombic MoO_3
Ravasz, Alpár; Kedves, Endre Zsolt; Tóth, Zsejke-Réka; **Bárdos, Enikő**; Fodor, Szilvia; Kovács, Zoltán; Pap, Zsolt; Hernádi, Klára; Baia, Lucian

(8) XXII. Nemzetközi Vegyészkonferencia
2016.11. 3-6., Timisoara, Romania
Preparation, characterization, and photocatalytic activity of WO_3-TiO_2/MWCNT nanocomposites
Bárdos Enikő, Kovács Gábor, Gyulavári Tamás, Németh Krisztián, Kecsenovity Egon, Berki Péter, Baia Lucian, Pap Zsolt, Hernádi Klára

(9) XXIII. Nemzetközi Vegyészkonferencia
2017.10.25-28 Deva, Romania
Synthesis and photocatalytic properties of novel BiOX nanomaterials
Bárdos Enikő, Király Anna Krisztina1, Schrantz Krisztina, Alapi Tünde, Pap Zsolt, Lucian Baia, Samir Sapra, Amrish Chandra, Seema Garg, Hernádi Klára

(10) XXIV. Nemzetközi Vegyészkonferencia
2018.10.24-27 Sovata, Romania
The effect of the synthesis duration on the morphology and photocatalytic activity of BiOX (X = Cl, Br, I) materials
Bárdos Enikő, Király Anna Krisztina, Pap Zsolt, Lucian Baia, Seema Garg, Hernádi Klára

First author lecture in a foreign language:

(11) II. Susatainable Raw Materials, International Project Week and Scientific Conference

2019.05.06-10, Szeged, Hungary

The effect of the synthesis temperature, duration on the BiOX (X = Cl, Br, I) morphology and photocatalytic activity

E. Bárdos, A. Király, Zs. Pap, L. Baia, K. Hernádi

First author's lecture in hungarian

(12) 5. Környezetkémiai Szimpózium

2016.10.6-7., Tihany, Hungary

Degradation of organic pollutants using TiO_2-WO_3 based nanocomposites

Bárdos Enikő & Kovács Gábor, Orbán Eszter, Gyulavári Tamás, Németh Krisztián, Kecsenovity Egon, Berki Péter, Baia Lucian, Pap Zsolt, Hernádi Klára

(13) 8. Környezetkémiai Szimpózium

2019.10.10-11., Siófok, Hungary

Effect of additives on the morphology and photocatalytic activity of BiOBr materials

Bárdos Enikő, Márta Viktória, Pap Zsolt, Baia Lucian, Garg Seema, Hernádi Klára

International / Foreign language co-author lecture

(14) XXII. Nemzetközi Vegyészkonferencia

2016.11. 3-6., Timisoara, Romania

Új nanokompozitok és nanoszerkezetek a víztisztításban

Pap Zsolt, Fodor Szilvia, Gyulavári Tamás, Kovács Gábor, Tóth Zsejke-Réka, Kása Zsolt, **Bárdos Enikő**, Rózsa Georgina, Simon Gergő, Kozmér Zsuzsanna, Rusu Mihai, Hernádi Klára, Baia Lucian, Baia Monica, Székely István, Kedves Zsolt, Boga Bíborka, Ravasz Alpár, Hampel Boglárka, Kovács Zoltán, Saszet Kata, Danciu Virginia, Cosoveanu Veronica, Vajda

Krisztina, Karácsonyi Éva, Pop ş Lucian Cristian, Czekes Zsolt, Nagy Zsuzsanna, Magyari Klára, Todea Milica, Vulpoi Adriana, Veréb Gábor, Orbán Eszter, Dombi András

(15) XXIII. Nemzetközi Vegyészkonferencia
2017.10.25-28 Deva, Romania
Synthesis and stability investigations of bismuth oxide containing mixed oxides
Kása Zsolt, **Bárdos Enikő**, Pap Zsolt, Hernádi Klára, Baia Lucian

(16) New Photocatalytic Materials for Environment, Energy and Sustainability (NPM-4)
2019.04.23-25. Antwerpen, Belgium
BiOX – the visible light photocatalyst
Klara Hernadi, **Enikő Bárdos**, Nikita Sharma, Zsolt Kása, Zsolt Pap, Seema Garg