Summary of the Ph.D. Thesis

Synthesis, characterization and photocatalytic activity of BiOX (X = Cl, I, Br) and their composites with carbon nanotubes (CNT)

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1. Introduction and objectives

The abundance of solar energy points to the potential applications of fuel generation and environmental remediation by photocatalytic materials. For long, this has been a hot topic for researchers across the globe. Among different Advanced Oxidation Processes (AOPs), heterogeneous photocatalysis stands out and is among the advanced technologies capable of degrading partially or totally a wider section of contaminants without the need of strong oxidants or harsh operating conditions. Heterogeneous photocatalysis is a process based on the activation of a semiconductor material by the use of light which upon irradiation leads to the generation of electron/hole pairs. These photogenerated charge carriers further participate in the oxidation-reduction reaction with the adsorbed pollutants and therefore, result in total mineralization of the compound. However, substantial challenges are still on the way. Among those, the major one is to find the practical use of such photocatalyst in industries, thus, cutting down the overall cost in comparison to the existing technology.

For my PhD dissertation, the main goal was to synthesize bismuth oxyhalides (BiOX) and its composites with carbon nanotubes. Carbon nanotubes (CNT) have excellent electronic and adsorption properties, therefore, they are reported to show enhanced photocatalytic activity when combined with a photocatalyst. For a better understanding of their role in the field of wastewater treatment, the composites were prepared with different amount of carbon nanotubes and at different synthesis conditions. Next, I studied the impact of such variables on the structural, morphological and optical properties of the prepared composites. My other main concern was to study the photocatalytic activity of the composites towards the removal of phenol as model pollutant and investigate the parameters behind an enhanced photocatalytic activity. For this reason, I have

made several noteworthy correlations that reveals the dependence of photocatalytic performance of the composites on parameters like synthesis time, temperature conditions and amount of carbon nanotube (CNT).

2. Experimental method and characterization

For my study, I synthesized composites of BiOX with CNT (with different compositions) *via* **hydrothermal crystallization**. For the comparison, their appropriate reference samples (without CNT) were also prepared. I investigated certain factors, namely, synthesis conditions and amount of CNT that influenced the structural, morphological, optical properties and photocatalytic activity of the composites.

A *Rigaku Miniflex II* diffractometer was used for **X-Ray Diffraction** measurements with the following measurement conditions: $2\theta° = 10\text{-}80°$, λ (Cu Kα) = 0.15406 nm, 40 kV and 30 mA, 10 – 80 ($2\theta°$) region. The average primary crystallite size was calculated using the Scherrer equation.

Morphological and elemental compositional analysis were carried out using **Scanning Electron Microscopy (SEM)** with **Energy Dispersive X-ray (EDX)** spectrometer, *Hitachi S-4700 Type II* SEM.

N_2 adsorption-desorption measurements were carried at 77K using a *BELCAT-A* device to measure the specific surface areas of the samples and calculations were done *via* BET (Brunauer-Emmett-Teller) method.

A *Jasco-V650* spectrophotometer with an integration sphere (*ILV-724*) was used for measuring the **diffuse reflectance spectra (DRS)** of the samples (λ = 220-800 nm). The indirect band-gap energy was calculated using the Kubelka-Munk equation, that is $[F(R).h\nu]^p = A(h\nu - E_g)$, where h is Planck constant, E_g is the band gap energy, A is constant and p is dependent on the type of optical

transition and is obtained by plotting the graph between $(\alpha h\nu)^{1/2}$ *vs* photon energy ($h\nu$). In some cases the possible electron transitions were evaluated by plotting the $dR \cdot d\lambda^{-1}$ *vs* λ, where R is the reflectance and λ is the wavelength.

The **photocatalytic test** was done to study the photodegradation of phenol under visible or UV light, or rhodamine B (RhB) under visible light. The test was carried out in a double-walled Pyrex® glass reactor, surrounded by a thermostatic jacket (T = 25°C) with either water (in case of UV) or sodium nitrate (in case of visible light to eliminate UV light portion) as the thermostatic agent. The four energy saving conventional fluorescence lamps (*Düwi 25920/R7S*, 24W) were used for the visible light measurements and 6 fluorescent tubes (*Vilber-Lourmat T-6L UV-A*, 6W) were used in case of UV light measurements. The changes in phenol and RhB concentration were measured by a *Hitachi* high-performance liquid chromatography (HPLC) system consisting *a Merck Hitachi L-7100* low-pressure pump and a *Merck-Hitachi L-4250* UV-Vis detector, and UV-Vis spectrophotometer, respectively.

3. Summary of scientific results

T1. The higher temperature and longer crystallization with increasing amount of CNT imparted higher crystallinity to BiOX (X= Cl, I , Br).

I have successfully synthesized composites of BiOX with CNT *via* hydrothermal synthesis method to study the impact of different CNT amounts (in wt.%: 0.5, 1 and 2%) on structural, morphological and optical properties of prepared BiOXs. Using XRD, I have demonstrated that higher degree of crystallinity was seen in the case of composites (BiOX/CNT) as compared to the CNT-free catalyst (BiOX). Therefore, I can ascertain that in this study CNT facilitated the formation of ordered structure and played a significant role in enhancing crystallinity of the composites. Besides CNT, the heating also facilitated the hydrothermal crystallization process since highly crystalline structures were obtained with rise in hydrothermal time and temperature conditions. Amorphous region, present in the case of samples prepared at lower temperature (120°C) and shorter time (4.5 h), started to disappear when the temperature and time was raised to 150°C and 6.5 h, respectively.

T.2 It was ascertained that the amount of CNT and hydrothermal crystallization influenced the structural and optical properties of BiOCl and hence, their photocatalytic activity.

T.2.1. I verified that among different compositions of CNT with BiOCl, the one with the highest CNT amount (2%) showed superior photocatalytic activity for the photodegradation of phenol and RhB under UV and visible light irradiation, respectively. I further confirmed the dependence of this composition (2% CNT) on the optical properties of BiOCl/CNT composites through the red-shift observed. The increase in degree of crystallization and red-shift in the case of 2%

CNT-containing BiOCl composites are the possible reasons for the enhancement in the photocatalytic activity of BiOCl samples.

T.2.2. Since no specific correlations were found with the optical property at lower amount of CNT (0, 0.5, 1 wt.%), therefore, later I correlated the composites with the structural property of BiOCl. Through XRD some relations with respect to the crystallinity was seen at lower CNT amount. I verified further that these CNT-compositions were linked to the crystallite size and hydrothermal crystallization conditions (time and temperature). When higher energy and longer time was given, larger crystallites were formed but with higher crystallinity and this is why higher photocatalytic activity was seen for these samples even though low or no CNT was present. The effect of CNTs was dictated by the hydrothermal crystallization conditions. In this way, I concluded that the CNT amount was one of the key factors in deciding the role of structural or optical properties in the photocatalytic activity of BiOCl.

T3. It was proven that the iodine-deficiency or defect sites affected the photocatalytic activity of BiOI and BiOI/CNT composites.

T.3.1. At first, in the BiOI and BiOI/CNT composites, the appearance of iodine-deficient BiOIs was confirmed by XRD. The diffraction peaks showed a slight shift to the lower diffraction angle which indicated changes in BiOI crystal lattice. It was ascertained that these shifted signals were the characteristic fingerprints for other iodine-deficient BiOI, namely $Bi_4O_5I_2$, $Bi_7O_9I_3$ and Bi_5O_7I. Further, with the help of EDX analysis, I confirmed the iodine-deficiency in the samples. The atomic ratio obtained for Bi:I:O showed lower amount of iodine. With DRS results, it was also pointed out towards the iodine defects as caused by the loss of iodide ions from the BiOI crystal lattice due to the blue shift in the light absorption band edge.

T.3.2. Unlike our results for BiOCl, in the case of BiOI, it was verified that BiOI/CNT composites showed higher photodegradation efficiency than pure BiOI. Different correlations including the band gap energy, iodine deficiency and photocatalytic activity were made to study the prime factor that played a key role for this opposite trend and its dependence on other factors. It was shown that the most important one was the one with band gap and iodine deficiency in regard to the photocatalytic activity. The samples with higher band gap energy showed a decrease in photocatalytic activity and *vice versa*. This was again related to iodine-deficiency in the samples. It was shown that the samples with lower band gap exhibited higher iodine-deficiency and higher photocatalytic performance.

T.4 It was shown that morphological transformations from 2D to 3D hierarchical structures were seen with rise in temperature (from 120˚C to 150˚C) and these 3D structures resulted in higher photocatalytic activity of BiOI/CNT composites.

Through SEM investigation, morphological changes were confirmed in the samples. The transition from 2D-structure to hierarchical structure took place. At higher temperature (150°C) microflower-type morphology was obtained while at 120°C nanoplates were seen. It was proved that the samples with hierarchical morphology showed higher photocatalytic activity than the ones with nanoplate morphology. It is ascertained that the self-assembly of sheets occurred at higher temperature conditions and the 3D-morphology is also a reason for enhanced photocatalytic response of BiOI/CNT composites.

T5. It was demonstrated that the appearance of a crystallization side product ($Bi_6O_6(OH)_3(NO_3)_3{\cdot}1.5H_2O$) enhanced the photocatalytic properties of BiOBr/CNT composites and is also considered as a "photocatalytic" material in the literature.

T5.1. During the synthesis, I proved the appearance of unexpected by-product (formed during the hydrolysis step of synthesis) which was confirmed through XRD where its characteristic diffraction peak was observed in all the sample series. The amount of this product was, however, dependent on several parameters like CNT content or presence of a specific crystallographic plane.

T5.2. Through DRS results, I further confirmed its presence by analyzing its first-derivative spectra in which two transition bands were seen, out of which, one of them belongs to this newly-present compound. The disappearance of this product was detected in case of samples with higher crystallinity and thus confirming that that CNT promoted higher crystallinity in the samples.

T5.3. I have demonstrated that the band gap values can be linked with the amount of by-product. I confirmed that the presence of by-product has altered the band gap values of the samples and decreased from 8.23% to 1.52% with the increase in CNT level. Correlating the band gap with activity revealed that samples with higher band gap (low or no CNT) showed superior photocatalytic activity than the ones with lower band gap and *vice-versa*. It was highlighted that this new by-product has contributed to an enhanced photoactivity and it can be regarded as a photocatalyst.

T5.4. It was proven that the photocatalytic activity can be linked with the presence of certain crystallographic planes. It was proven that the photocatalytic performance of the samples showed dependence on the presence of (003) crystallographic plane. Lower photocatalytic activity was observed for the samples with this crystallographic plane ratio value until 0.075 beyond this a constant increase of photocatalytic activity was noticed.

4. Applicability of scientific results

In my doctoral research, I have synthesized composites of BiOX with CNTs *via* hydrothermal synthesis to enhance their photocatalytic activity. I studied the dependency of photocatalytic efficiency of the as-prepared composites on several factors that could be considered significant when determining their performance in pollutant removal. My results form a fundamental understanding on the subject concerning the issues related to the incorporation of carbon-based nanostructures to a photocatalyst-composites system and its influence on several aspects (physico-chemical). These results might also help in future for designing photocatalysts. Different factors dominate and dictate the effect on photocatalytic activity and therefore, it becomes paramount to study such factors.

5. Publications and conference participations

Hungarian Scientific Bibliography (MTMT) identifier: 10078738

Publications related to the scientific topic of the dissertation:

[1] **N. Sharma**, Z. Pap, S. Garg, K. Hernadi: *Hydrothermal synthesis of BiOBr and BiOBr/CNT composites, their photocatalytic activity and the importance of early* $Bi_6O_6(OH)_3(NO_3)_3 \cdot 1.5H_2O$ *formation*
Applied Surface Science, 495 (2019) 143536.
doi.org/10.1016/j.apsusc.2019.143536
IF = 6.182 (Q1)

[2] **N. Sharma**, Z. Pap, I. Szekely, M. Focsan, G. Karacs, Z. Nemeth, S. Garg, K. Hernadi: *Combination of iodine-deficient BiOI phases in the presence of CNT to enhance photocatalytic activity towards phenol decomposition under visible light*
Applied Surface Science, 565 (2021) 150605.
doi.org/10.1016/j.apsusc.2021.150605
IF = 6.707 (Q1)

[3] **Nikita Sharma,** Bence Veres, Pranjal Dhiman, Zsolt Pap, Kornélia Baán, Seema Garg, Klara Hernadi: *The mechanistic insight of structural and optical properties of BiOCl in presence of CNTs and investigating photodegradation of phenol by BiOCl/CNT composites.*
(Re-submitted to RSC Advances)
IF = 3.361 (Q1)

[4] **Nikita Sharma**, Pap Zsolt, Seema Garg, Klara Hernadi: *BiOI/MWCNT composites for phenol degradation under visible light.*
25th International Symposium on Analytical and Environmental Problems (2019), pp. 45-49.
ISBN: 978-963-306-702-4

[5] **N. Sharma**, Z. Pap, S. Garg, K. Hernadi: *Photocatalyst Composites from Bi-based and Carbon Materials for Visible Light Photodegradation.*
Springer Nature Switzerland AG (2022), pp. 145-178., 34 p.
ISBN: 978-303-077-371-7

ΣIF = 12.89 (+3.361)

Σ Citations = 16 (Independent: 13)

Other publications:

[1] Bilal El Mrabate, Emma Szőri-Dorogházi, Mohammed Ahmed Shehab, Tanya Chauhan, Gábor Muránszky, Emőke Sikora, Ádám Filep, **Nikita Sharma**, Lilla Nánai, Klara Hernadi, Zoltán Németh: *Widespread applicability of bacterial cellulose ZnO-MWCNT hybrid membranes.*
Arabian Journal of Chemistry, 14 (2021), 103232.
doi.org/10.1016/j.arabjc.2021.103232
IF = 5.165

[2] Mohammed Ahmed Shehab, Gábor Karacs, Tamás Koós, **Nikita Sharma**, Klara Hernadi, Zoltán Németh: *Adsorptive removal of methylene blue by TiO_2 nanowire/Fe_2O_3 nanocomposite.*
Circular Economy and Environmental Protection

[3] **N. Sharma,** Zsolt Pap, Baán Kornélia, Seema Garg, Klara Hernadi: *Effective removal of phenol by combined adsorption and phtocatalytic activity of BiOCl/Activated Charcoal Photocatalyst*
(Submitted to the special issue of Journal of Molecular Structure)

ΣIF = 5.165

ΣCitations = 0 (Independent: 0)

ΣΣIF = 18.05 (+3.361)

ΣΣCitations = 16 (Independent: 13)

National and international conference participations:

(1) **N. Sharma**, Z. Pap, S. Garg, K. Hernadi: *In-situ synthesis of BiOBr and its composites with Carbon Nanotubes (CNT) and their characterization*
12th International Conference on Physics of Advanced Materials
Heraklion, Greece (2018) – poster presentation

(2) **N. Sharma**, Z. Pap, S. Garg, K. Hernadi: *In-situ synthesis of BiOBr and its composites with Carbon Nanotubes (CNT) and their characterization*
XXIV. International Conference on Chemistry
Sovata, Romania – poster presentation

(3) **N. Sharma**, Z. Pap, S. Garg, K. Hernadi: *Hydrothermal synthesis of BiOBr/MWCNT composites and significance of early formation of $Bi_6O_6(OH)(NO_3)_3 \cdot 1.5H_2O$ as an intermediate compound*
II. Sustainable Raw Materials International Project Week and Scientific Conference
Szeged, Hungary (2019) – oral presentation

(4) **N. Sharma**, Z. Pap, S. Garg, K. Hernadi: *Investigating role of $Bi_6O_6(OH)(NO_3)_3 \cdot 1.5H_2O$ as intermediate compound in BiOBr/MWCNT composites with (003) facet favoring phenol degradation under visible light*
6th European Conference on Environmental Applications of Advanced Oxidation Processes
Portorož-Portorose, Slovenia (2019) – poster presentation

(5) **N. Sharma**, Z. Pap, S. Garg, K. Hernadi: *Structural and Morphological changes with different hydrothermal temperature conditions for BiOI/MWCNT photocatalyst*
XXV International Conference on Chemistry
Cluj-Napoca, Romania (2019) – oral presentation

(6) **N. Sharma**, Z. Pap, S. Garg, K. Hernadi: *BiOI/MWCNT composites for phenol degradation under visible light*
25th International Symposium on Analytical and Environmental Problems
Szeged, Hungary – oral presentation

(7) **N. Sharma**, Z. Pap, S. Garg, K. Hernadi: *Investigation of Photocatalytic Activity of BiOI/MWCNTs composites for phenol under visible light*
Siofok, Hungary – oral presentation