

## Photocatalytic activity of liquid-phase exfoliated gallium selenide flakes

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In this work, the photocatalytic activity of layered GaSe flakes obtained by liquid-phase exfoliation of bulk crystals was tested on the photodegradation of an organic dye under UV irradiation. The initial bulk GaSe crystals were synthesized by stoichiometric fusion method. Investigation of the structure and composition showed that as-grown crystal corresponds to  $\beta$ -polytype of GaSe. Analysis of the kinetics of the decomposition MB molecules showed that the obtained flakes demonstrate good photocatalytic activity in the UV range. The efficiency of the dye photodegradation was 86% within 3 hours under UV irradiation.

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*Keywords:* Gallium selenide crystal, Stoichiometric fusion, Liquid-phase exfoliation, Photo-degradation of dye

### 1. Introduction

Today, there is a growing interest in the liquid-phase exfoliation (LPE) of layered mono- and dichalcogenide crystals, since there is a possibility of making pastes and inks of 2D nanomaterials which can be easily deposited to any surfaces using spray coating technique or printer devices [1-4]. This technology has promising applications and opens an opportunity for commercial production of composite coatings for different applications like parts of solar cells and light-sensitive detectors [5-8]. Moreover, solution processed 2D nanomaterials have a large value of specific surface area which is important for photoelectrochemical application, gas sensing and energy storage applications [9-12]. Several papers have already reported the photoelectrochemical (PEC) application of GaSe, GaTe and GaS flakes obtained by LPE, particularly in water splitting reaction, PEC-type photodetectors, hydrogen evolution electrocatalysts [13-15]. The energy band-gap is equal to 2.55, 2 and 1.65 eV for GaS, GaSe and GaTe, respectively. At the same time, GaS is an n-type indirect semiconductor, while GaSe and GaTe are p-type semiconductors with a direct transition at room temperature [16].

In this contribution, photocatalytic activity of liquid-phase exfoliated GaSe crystals was investigated by mean of decomposition of Methylene Blue (MB) dye under UV irradiation. It was shown that the presence of GaSe flakes at 0.1 mg/ml concentration accelerated the degradation of dye for 5 times comparing with the degradation rate of reference MB aqueous solution without photocatalytic admixtures.

### 2. Experimental

The synthesis of layered GaSe crystals was done by stoichiometric fusion of mixed gallium (Ga, 4N) and selenium (Se, 4N) particles in quartz ampoule sealed at a high vacuum. The fusion was carried out in a single zone vertical furnace. The Ga and Se particles were melted at 980 °C for 60 minutes. Then ampoule was cooled at the rate of 1°C/min until 550°C, further cooling down was natural.

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Liquid exfoliation of GaSe crystals was carried out in 2-propanol (IPA) solvent in an ultrasonic bath. To obtain the colloid solution with 1 mg/ml concentration, the 20 mg of GaSe crystals were mixed with 20 ml of 2-propanol and sonicated with 150 W power for 3.5 hours.

The verification of the elemental composition and microstructure of as-grown GaSe crystal and LPE GaSe flakes was carried out using energy-dispersive analysis on a scanning electron microscope (SEM) Quanta 3D 200i with EDAX device. The structure of crystals was investigated using X-ray diffraction analysis (Rigaku) and Raman spectroscopy (NT-MDT). The thicknesses of GaSe flakes were measured by atomic force microscope (NT-MDT) in tapping mode.

Photocatalytic activity of GaSe flakes was examined utilizing Methylene blue (MB, 16 mg/L) dye degradation under UV irradiation using a mercury lamp with a peak at 254 nm and a power of 14 W. UV-Vis spectrophotometer (Lambda-35) was used for the recording of absorbance spectra of MB solution.

### 3. Results and discussions

Synthesized GaSe crystals were investigated by several methods. Figure 1a shows SEM image of GaSe crystal cross-section. As can be seen from the figure the as-grown GaSe crystal has a layered structure. The values of the atomic ratios according to the energy-dispersive analyses (EDS) of the elements was 48.91 at.% and 51.09 at.% of gallium and selenium, respectively. The analysis of XRD pattern represented in Figure 1b shows that this crystal belongs to the space group 174:P-6, and has a hexagonal lattice with parameters  $a=b=3.749 \text{ \AA}$ ,  $c=15.987 \text{ \AA}$  (PDF Card No.: 00-037-0931). Figure 1c shows photoluminescence spectrum of GaSe crystal. The GaSe photoluminescence peak at 624 nm corresponds to the direct transition which is close to the energy band-gap of the crystal. These results of materials characterization indicate that the grown crystals of gallium selenide have rather high quality.

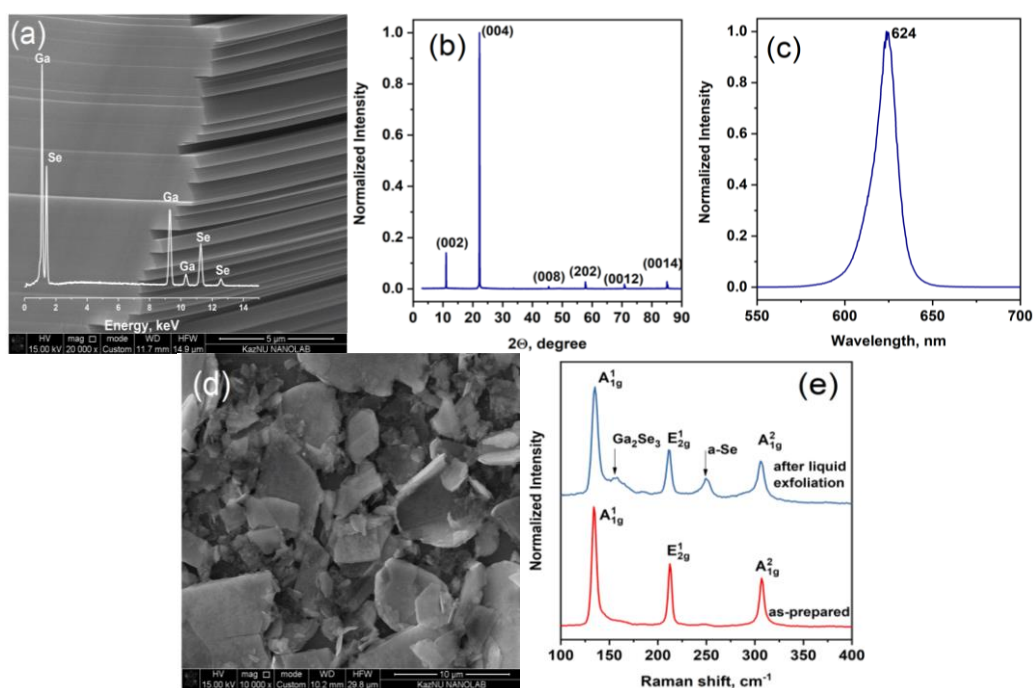


Fig. 1. SEM image of crystal cross-section and EDS spectrum (a), X-ray diffraction (XRD) pattern (b) and micro-photoluminescence spectrum (c) of as-grown GaSe crystals; SEM image of GaSe dried dispersion (d) and Raman spectra (e) of as-grown and liquid-phase exfoliated GaSe crystal.

In the next stage, the obtained GaSe polycrystals were exfoliated by ultra-sonication in IPA solution. The resultant colloid (GaSe/IPA) solution has a brown colour. After that, dispersed solution was centrifuged at 3000 rpm for 20 minutes to excretion of fine fraction. Obtained transparent solution was separated from the rest bulk mass and dried at 70°C on air.

Figure 1d illustrates SEM image of dried GaSe particles. The XRD analysis of LPE flakes drop-casted on a glass substrate as well as PL signal didn't reveal any sufficient changes in position and area of characteristic peaks. The Raman spectrum of as-prepared GaSe crystal illustrated in Figure 1e demonstrates characteristic peaks at 134, 212 and 307  $\text{cm}^{-1}$ , which correspond to  $A_{1g}^1$ ,  $E_g^2$  and  $A_{1g}^1$  vibrational modes, respectively. These spectra were recorded using a 473 nm laser light. However, Raman spectra of thick LPE GaSe flakes revealed the rise of additional small peaks at about 155 and 250  $\text{cm}^{-1}$ , indicating a slight degradation as a result of liquid exfoliation process. Broad peak at  $\sim 150 \text{ cm}^{-1}$  may be induced by  $\text{Ga}_2\text{Se}_3$  structures, while peak at 250  $\text{cm}^{-1}$  corresponds to amorphous selenium. In addition, EDS mapping depicted in Figure 2a showed homogeneous distribution of Ga and Se elements. The assessment of thickness and lateral size (areas) of the flakes was performed on the basis of AFM and SEM images, the data analysis of which is depicted on the histograms in Figure 2 (b, c).

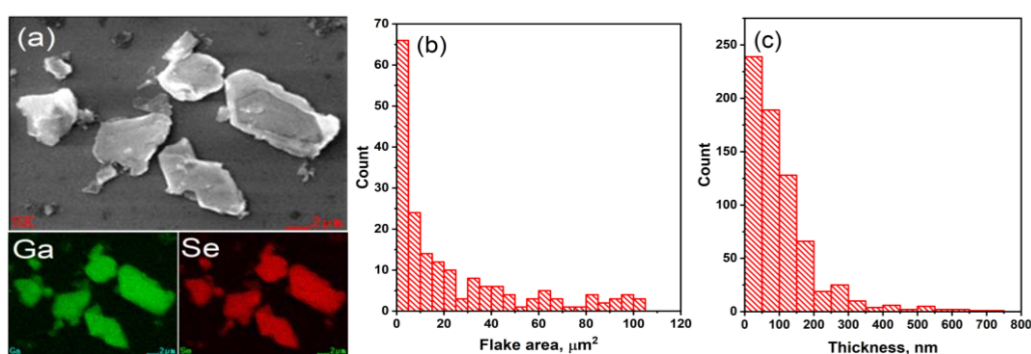


Fig. 2. SEM image and EDS mapping (a), distribution of area (b) and thickness (c) of LPE GaSe flakes.

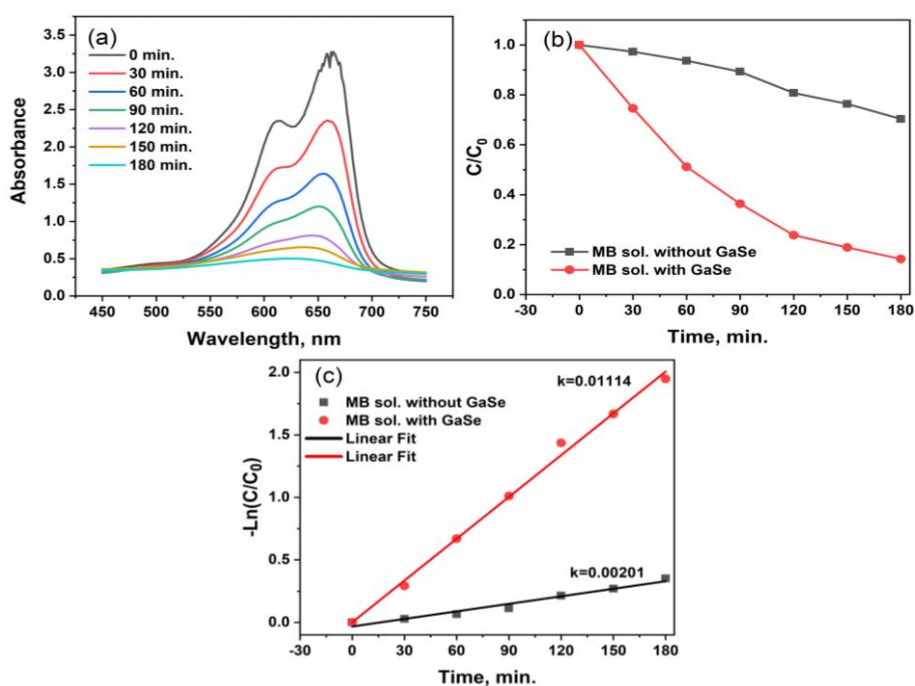
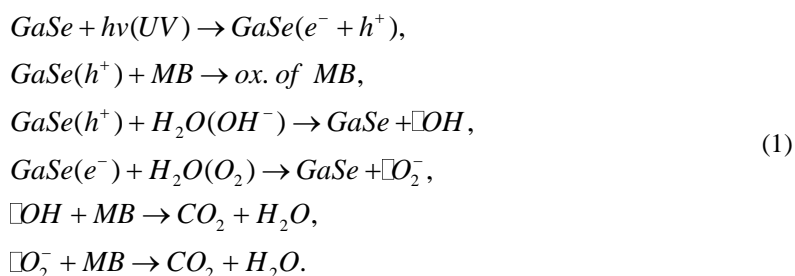


Fig. 3. Decrease in the absorbance intensity of the MB solution with GaSe flakes as a function of irradiation time (a); degradation kinetics of MB molecules under UV irradiation (b); first-order kinetic plot for the photodegradation of MB (c)

The photocatalytic activity of the obtained LPE GaSe flakes was studied on the process of photodegradation of an organic dye MB aqueous solution (16 mg/L) under the action of a UV lamp with a peak at 254 nm and a power of 14 W. Before illumination, the MB solution with GaSe flakes was placed in the dark for 30 minutes to establish thermodynamic equilibrium state. Figure 3a shows the absorption spectra of MB solution with GaSe flakes with a concentration of 0.1 mg/ml. In our experiment, the absorbance spectra of the solutions were measured each 30 minutes. Moreover, the solution was mixed each 15 minutes to avoid precipitation. The decrease of the initial concentration of MB in solution due to UV irradiation is illustrated in Figure 3b. The concentrations were determined at a peak of MB dye absorbance, i.e. on 664 nm.

The first-order kinetic plot shown in Figure 3c indicates that the presence of GaSe particles sufficiently increases the rate of MB degradation comparing to the degradation rate of the reference MB solution. The obtained values of first-order reaction rate constant  $k$  are equal to 0.01114 and 0.00201  $\text{min}^{-1}$  for MB solution with GaSe flakes and for pure reference MB solution, respectively. The mechanism of such fast degradation of MB molecules can be described by simple reactions generally written as:



In GaSe crystals an absorbed photon induces generation of electron-hole ( $e^-$ ,  $h^+$ ) pair. Photogenerated holes  $h^+$  can both directly oxidize an MB molecule on the surface and react with hydroxyl ions ( $\text{OH}^-$ ) forming, this way, highly oxidative hydroxyl radicals ( $\square\text{OH}$ ) that are also capable to decompose MB. Generated electrons ( $e^-$ ) also react with oxygen ( $\text{O}_2$ ) forming a superoxide ( $\square\text{O}_2^-$ ) which also leads to the degradation of MB molecule. Dye degradation efficiency which is defined as  $d = (C_0 - C_t) / C_0 \cdot 100\%$  equals to 86 % at 180 minutes in presence of GaSe flakes as a catalyst. It should be noted that the efficiency of the degradation depends on semiconducting properties of the flakes and also on the experiment parameters. In particular, stirring technique during irradiation process as well as sizes of the flakes at fixed mass, i.e. their specific surface area and edges crucially affect the photodegradation rate of dye.

#### 4. Conclusions

Layered GaSe crystals were synthesized using the stoichiometric fusion method. Dispersion based on GaSe flakes was obtained by liquid-phase exfoliation technique and used as a catalyst for the process of photodegradation of MB organic dye. Analysis of the obtained data showed that GaSe flakes demonstrate good photocatalytic activity increasing the photodegradation rate of MB by 5 times at the loading of 0.1 mg/ml of GaSe flakes. The dye photodegradation efficiency was 86 % within 3 hours under UV irradiation. This result indicates GaSe flakes as perspective materials for photocatalytic application.

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## References

- [1] J. Shen, Y. He, J. Wu, C. Gao, K. Keyshar, X. Zhang, Y. Yang, M. Ye, R. Vajtai, J. Lou, P. M. Ajayan, *Nano Letters* **15**(8), 5449 (2015).
- [2] F. I. Alzakia, S. C. Tan, *Advanced Science* **8**(11), 2003864 (2021).
- [3] V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, J. N. Coleman, *Science* **340**(6139), 1226419 (2013).
- [4] S. Witomska, T. Leydecker, A. Ciesielski, P. Samorì, *Advanced Functional Materials* **29**(22), 1901126 (2019).
- [5] B. Adilbekova, Y. Lin, E. Yengel, H. Faber, G. Harrison, Y. Firdaus, A. El-Labban, D. H. Anjum, V. Tung, T. D. Anthopoulos, *Journal of Materials Chemistry C* **8**, 5259 (2020).
- [6] S. K. Lee, D. Chu, J. Yoo, E. K. Kim, *Solar Energy Materials & Solar Cells* **184**, 9 (2018).
- [7] L. Wang, J. Jie, Z. Shao, Q. Zhang, X. Zhang, Y. Wang, Z. Sun, S.-T. Lee, *Advanced Functional Materials* **25**, 2910 (2015).
- [8] L. Hao, Y. Liu, W. Gao, Z. Han, Q. Xue, H. Zeng, Z. Wu, J. Zhu, W. Zhang, *Journal of Applied Physics* **117**, 114502 (2015).
- [9] L. Gao, R. Wang, A. V. Kuklin, H. Zhang, H. Ågren, *Advanced Functional Materials* **31**(17), 2010401 (2021).
- [10] G. Bianca, M. I. Zappia, S. Bellani, Z. Sofer, M. Serri, L. Najafi, R. Oropesa-Nuñez, B. Martín-García, T. Hartman, L. Leoncino, D. Sedmidubský, V. Pellegrini, G. Chiarello, F. Bonaccorso, *ACS Applied Materials & Interfaces* **12**(43), 48598 (2020).
- [11] D. Zhou, L. Zhao, B. Li, *Journal of Energy Chemistry* **62**, 27 (2021).
- [12] X. Chen, X. Chen, Y. Han, C. Su, M. Zeng, N. Hu, Y. Su, Z. Zhou, H. Wei, Z. Yang, *Nanotechnology* **30**, 445503 (2019).
- [13] M. I. Zappia, G. Bianca, S. Bellani, N. Curreli, Z. Sofer, M. Serri, L. Najafi, M. Piccinni, R. Oropesa-Nuñez, P. Marvan, V. Pellegrini, I. Kriegel, M. Prato, A. Cupolillo, F. Bonaccorso, *The Journal of Physical Chemistry C* **125**(22), 11857 (2021).
- [14] L.-C. Tien, Y.-C. Shih, *Nanomaterials* **11**, 778 (2021).
- [15] M. I. Zappia, G. Bianca, S. Bellani, M. Serri, L. Najafi, R. Oropesa-Nuñez, B. Martín-García, D. Bouša, D. Sedmidubský, V. Pellegrini, Z. Sofer, A. Cupolillo, F. Bonaccorso, *Advanced Functional Materials* **30**(10), 1909572 (2020).
- [16] W. Huang, L. Gan, H. Li, Y. Ma, T. Zhai, *CrystEngComm* **18**, 3968 (2016).