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Heterostructured AgCl/BN nanomaterials with high sorption capacity and photocatalytic activity

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In this work, the photocatalytic activity and sorption capacity of heterogeneous structures AgCl/*h*-BN obtained by the polyol method were studied in comparison with the initial micron-sized *h*-BN powder. The chemical and phase composition, as well as the surface microstructure, were analyzed by scanning electron microscopy, energy dispersive spectroscopy, X-ray phase analysis, and X-ray photoelectron spectroscopy. High photocatalytic activity and sorption ability of heterogeneous structures AgCl/BN in the reaction of the organic dye methylene blue decomposition under ultraviolet irradiation were demonstrated.

Keywords: heterogeneous materials, photocatalysis, hexagonal boron nitride, silver chloride.

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Currently, contamination of natural waters with heavy metals, industrial dyes and various organic compounds is one of the most acute environmental issues [1]. It entails detrimental consequences for human health: the development of neurological, cardiovascular and intestinal diseases [2]. That is why an urgent scientific task is to find new effective photocatalytic systems for wastewater treatment. When developing new photocatalysts, a relatively simple process of decomposition of organic dyes in aqueous solutions comes quite handy, convenient to use and practically important. Heterogeneous structures consisting of transition metal compounds and new types of two-dimensional substrates, such as graphene, molybdenum disulfide, MXenes and hexagonal boron nitride keep attracting increasing attention in recent years [3,4]. A nanocomposite containing TiO₂ and graphene/graphene oxide manifests pronounced photocatalytic properties due to its high porosity and sorption capacity of the material that is respectively higher [5]. Due to a more effective charge separation at the zinc oxide-molybdenum disulfide interfaces the MoS₂/ZnO system was shown to be a promising photocatalyst for purifying aqueous solutions of organic dyes and heavy metals [6]. Hexagonal boron nitride (*h*-BN) is of great interest as a promising substrate for catalytically active particles [7]. It is shown that the heterogeneous composite *h*-BN/TiO₂, in which TiO₂ is the carrier of *h*-BN particles, exhibits pronounced photocatalytic properties [8]. Small additions of *h*-BN have been found to increase the stability and photocatalytic activity of AgBr and AgI in the decomposition reaction of organic dyes [9]. That suggests that other silver compounds, in particular AgCl, may be promising components in a photocatalytic system based on *h*-BN. Thus, the purpose of this study is to establish the effect of AgCl nanoparticles on the *h*-BN surfaces on the photocatalytic properties of the material. Heterogeneous AgCl/BN materials were synthesized, and their structure

and photocatalytic activity in decomposing methylene blue (MB) dye in aqueous solution exposed to ultraviolet (UV) irradiation were studied.

A modified polyol synthesis [10] was used to obtain heterogeneous AgCl/BN structures. For that purpose, 100 mg of micron powder *h*-BN was dispersed in 50 ml of polyethylene glycol (PEG-400) by ultrasonic treatment with an immersion sonotrode for 3 min. 75 mg AgNO₃ was dissolved in the suspension and the resulting mixture was treated with UV light ($\lambda = 185$ nm). At the end of the synthesis, 7 ml 0.01 M HCl solution was added to the medium. The final powder was obtained washing the resulting suspension in distilled water, centrifuging it and drying the precipitate in an air stream.

Structure and composition of the obtained materials were studied by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (with a JEOL 7600F instrument). Phase composition was investigated by X-ray diffraction analysis (XRD) (D2-Phaser, Bruker). Chemical state of the surface was studied by X-ray photoelectron spectroscopy (XPS) (PHI5500VersaProbeII). The spectra were calibrated using the C 1s line (285.0 eV).

Photocatalytic activity was studied of both AgCl/BN and pure *h*-BN and AgCl. For that purpose, 50 mg of photocatalyst was added to 100 ml of MB solution of 4 mg/l concentration and dispersed by ultrasonic treatment. The resulting system was left on a magnetic stirrer in the dark for 120 min to establish sorption-desorption equilibrium under the conditions of constant stirring. Then, the system was UV irradiated for 90 min. An *U*-shaped lamp 190 mm long of 19 mm diameter was used as a source of UV radiation. The lamp power was 145 W, the UV power was 50 W; the quartz beaker with the studied solution was placed at a distance of 10 cm from the lamp. After UV treatment, the suspension was precipitated using a centrifuge, and the solution (free of precipitate now) was used as a sample

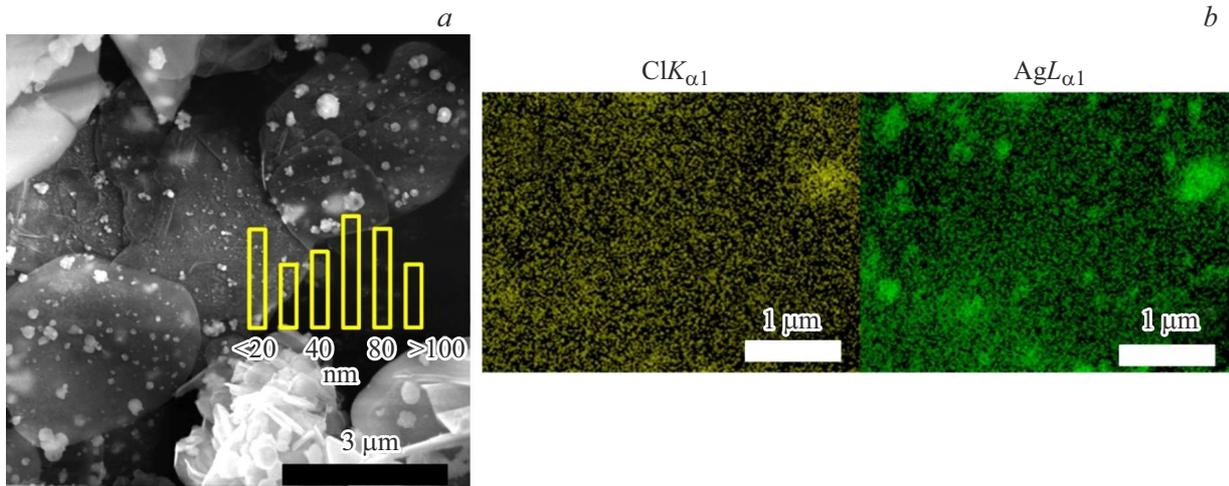


Figure 1. Electron microscopy image (a) and element distribution maps (b) of heterogeneous AgCl/BN structures.

for spectrophotometric studies in an optical spectrometer (UV-VIS-NIR Cary-5000, Variant). To study sorption capacity of the obtained materials, the same technique was used, except for exposure to the UV irradiation. Absorption intensity (optical density) was used to assess the change in concentration of dye in the solution.

Fig. 1 shows the results of SEM and EDS analysis of the obtained heterogeneous AgCl/BN structures.

A large proportion of AgCl particles (about 90%) are smaller than 100 nm, but some particles reach the size of 300 nm (Fig. 1, a). The distribution maps of Ag and Cl elements (Fig. 1, b) confirm silver chloride formation. Chemical composition of AgCl/BN was determined by EDS analysis: B — 51.1 at.%, N — 45.1 at.%, O — 2.4 at.%, Ag — 2.4 at.%, Cl — 0.4 at.%. Mass fraction of AgCl in the heterogeneous material was about 8.5%. Particles of the initial *h*-BN powder were in the form of plates, their thickness varying from 200 to 600 nm. Note that a small amount of oxygen was found in the EDS spectrum of the material, indicating the formation of BNO oxynitride on the surface of the initial *h*-BN plates, boron and nitrogen remaining in their equiatomic ratio both before and after synthesis: B — 50.5 at.%, N — 45.4 at.%, O — 4.1 at.%.

XRD results, as well as data on the chemical state of the surface, are shown in Fig. 2.

According to the obtained diffractograms, the powder *h*-BN in the initial state is represented only by hexagonal boron nitride phase, characterized by a high degree of crystallinity, without impurities in a form of B₂O₃ oxide. As a result of synthesis, AgCl nanoparticles were formed on the surface of *h*-BN; the corresponding diffraction reflexes are indicated on the X-ray pattern of the AgCl/BN sample. Weak signal observed at $2\theta = 38.1^\circ$ corresponds to the (111) silver metal line. It can be assumed that metallic silver is formed on the surface of AgCl particles as a result of their partial degradation during irradiation or incomplete reaction of silver with hydrochloric acid.

High-resolution XPS spectra (Fig. 2, b) show signals at 367.9 and 374 eV, which correspond to peaks of Ag 3d_{5/2} and Ag 3d_{3/2}. When approximating these peaks, the following components can be distinguished: Ag⁺ (367.8 and 373.8 eV), which confirms the formation of silver chloride [11], plus Ag⁰ (368.4 and 374.6 eV) of a much lower intensity, which agrees well with the results of XRD. The presence of a third peak in the spectra at high binding energies (396.5 and 375.7 eV) is caused by charging of the sample during the experiment. Two peaks can also be distinguished in the chlorine spectrum: Cl 2p_{3/2} (197.0 eV) and Cl 2p_{1/2} (198.7 eV). Also the elemental analysis of the surface of material was determined by the results of XPS: C — 23.5 at.%, N — 34.4 at.%, B — 32.2 at.%, O — 7.9 at.%, Ag — 1.0 at.%, Cl — 1.0 at.%, which agrees well with the results of EDS.

Fig. 3 shows the change of MB absorption intensity during photocatalytic tests. The initial dye intensity (MB) was taken as one.

The maximum MB absorption intensity can be observed at a wavelength of 668 nm (Fig. 3, a). Under UV irradiation, the optical density of the initial dye solution decreases slightly (by 5%, maximum), due to its partial decomposition. A significant decrease in dye concentration in the solution is observed after adding both pure boron nitride (MB BN(*s*) sample) and heterogeneous structures (MB AgCl/BN(*s*)) in it. Optical density decreases to 27% for MB AgCl/BN(*s*) and is less than 10% for MB BN(*s*) (Fig. 3, b). The observed difference in the decrease of samples optical density can be explained by the fact that AgCl has a lower sorption capacity with respect to MB compared to the *h*-BN powder. AgCl nanoparticles are located on the surface of the carrier and occupy a significant share of it, thus limiting the sorption capacity of *h*-BN. The significant sorption capacity with respect to MB, which is a cationic dye, can be explained by the presence of a negative charge on the surface of *h*-BN [12]. High adsorption

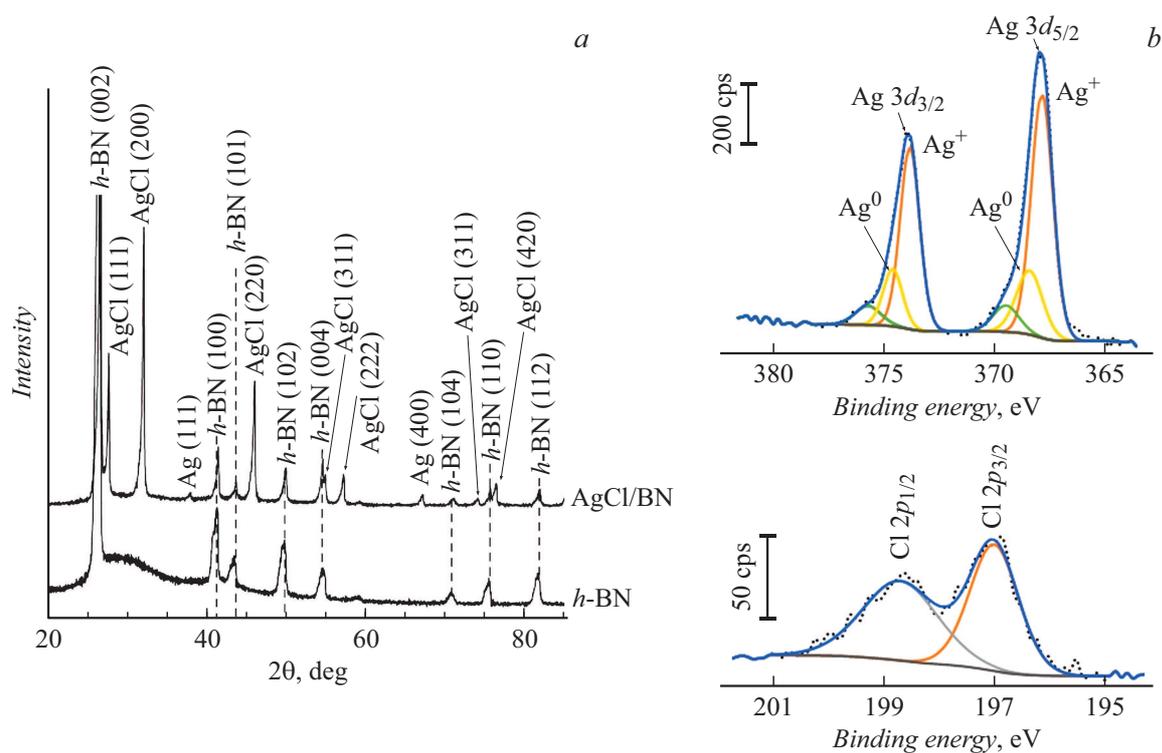


Figure 2. XRD (a) and XPS (b) spectra of heterogeneous AgCl/BN structures and the initial *h*-BN powder.

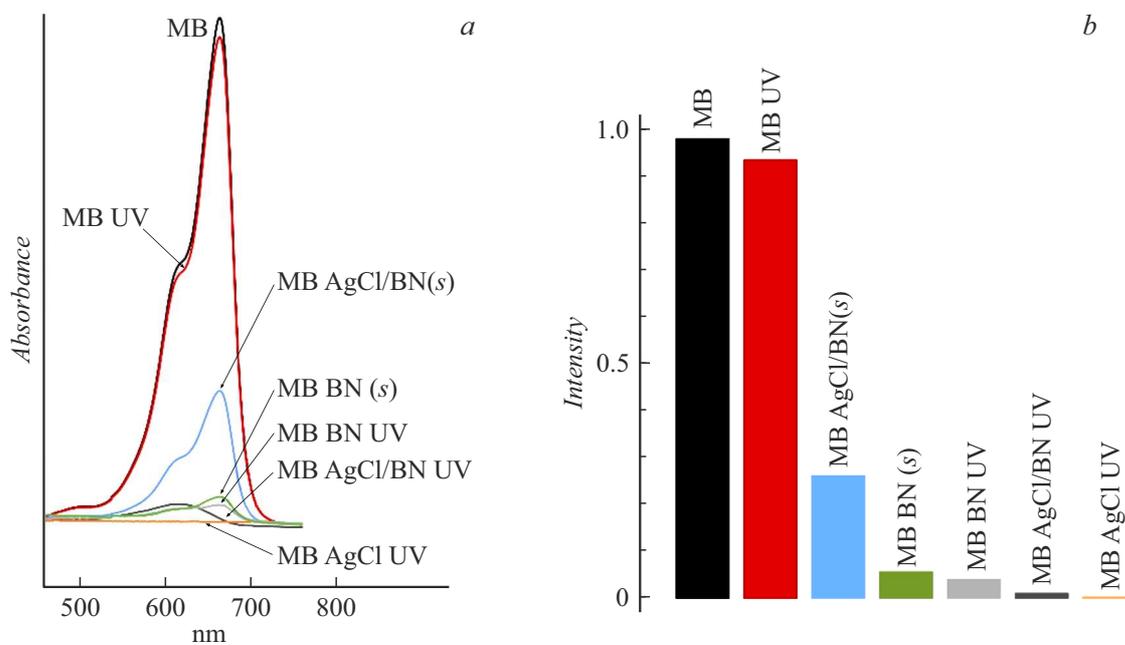


Figure 3. MB absorption spectra (a) and comparison of sample absorption intensities (b). MB is the initial MB solution; MB UV is the MB solution spectrum after UV irradiation; MB BN(s): same, after incubation in MB of the initial *h*-BN powder; MB AgCl/BN(s): same, after incubation of heterogeneous AgCl/BN structures in MB; MB BN UV: same, after photocatalytic testing with *h*-BN; MB AgCl/BN UV: same, after photocatalytic testing with AgCl/BN; MB AgCl UV: same, after photocatalytic testing with AgCl.

can also be explained by the cyclic aromatic structure of MB, which enhances the π -stacking interaction with *h*-BN. Nevertheless, photocatalytic tests of the initial *h*-BN showed no significant additional decrease in optical density of the solution (MB BN UV sample). That points to a weak photocatalytic activity of the material, explained by its wide forbidden zone E_g , its value reaching 5.7 eV according to the optical spectroscopy data. E_g decreased to 5.4 eV for AgCl/BN, indicating a chemical interaction of AgCl with BN. For that sample the value of MB optical density was close to zero, which indicates its high photocatalytic activity. The sample consisting of AgCl particles only showed complete decomposition of the dye; however, it should be noted that the AgCl content in that sample was about 10 times higher than in the AgCl/BN sample. That emphasizes the effectiveness of *h*-BN as an active substrate enhancing photocatalytic activity of AgCl. The mechanism of influence of *h*-BN on photocatalytic activity has not been sufficiently studied, but it can be assumed that the chemical interaction of AgCl and BN decreases the recombination rate of charge carriers generated during photocatalysis. Thus, we can conclude that heterogeneous materials based on *h*-BN are promising new photocatalysts.

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Conflict of interest

The authors declare that they have no conflict of interest.

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