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Photocatalytic properties of Ag-AgBr nanostructures formed by ion-exchange in photo-thermo-refractive glass for water-dye degradation

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Abstract. In this paper Ag-AgBr nanostructures photocatalytic properties were studied. Hybrid nanoparticles were grown in photo-thermo-refractive glass during the ion exchange in $AgNO_3$ solution and subsequent heat treatment. XRD study demonstrated the growth of Ag nanoparticles with increase of bromine concentration. Water-dye degradation rate shows that with increase of bromine concentration photocatalytic properties of glass are also increases.

Keywords: photocatalysis, PTR glass, silver nanoparticles, semiconductor nanoparticles

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Материалы конференции
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Фотокаталитические свойства наноструктур Ag-AgBr, сформированных методом ионного обмена в фото-термо-рефрактивном стекле, для разложения водных красителей

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Аннотация. В данной работе исследованы фотокаталитические свойства наноструктур Ag-AgBr. Гибридные наночастицы были сформированы в фото-термо-рефрактивном стекле в процессе ионного обмена в растворе $AgNO_3$ и последующей термообработки. Рентгеновское исследование продемонстрировало рост серебряных наночастиц с увеличением концентрации брома. Скорость разложения водного красителя показывает, что с увеличением концентрации брома фотокаталитические свойства стекла также возрастают.

Ключевые слова: фотокатализ, фото-термо-рефрактивное стекло, наночастицы серебра, полупроводниковые наночастицы

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Introduction

Carbon free fuel is one of the main long-term goal which humanity need to achieve as fast as possible. For that purpose, it is already done many steps, such as widespread implementation of wind power plants and solar cells, development of geothermal power plants and even fusion reactors. However, in the field of carbon-free fuel there is not much steps were done. The most promising fuel to replace the traditional petrol is hydrogen [1]. It was estimated that it is the highest clean energy carrier, which can be used in almost any energy applications such as transportation and electricity generation [2]. Notably, the sole byproduct of hydrogen combustion is water, rendering it a supreme candidate for displacing incumbent fossil fuels. The main obstacle on the way of its widespread use is the fact that hydrogen is practically never found on Earth in its pure [3]. That leads us to the main scientific field of research of development of the commercially profitable ways of extracting it from other compounds using various chemical methods. However, many of them have disadvantages like having greenhouse gases during its process. One of the possible method without significant disadvantages is to extract it from the water during photocatalysis. This is the way of water decomposition using just a semiconductor and a photon with energy higher than its energy bandgap to produce an electron – hole pair. This process can be described as following: semiconductor $+h\nu \rightarrow h\nu_{VB}^{+} + e_{CB}^{-}$, where $h\nu_{VB}^{+}$ is a hole in valence band and e_{CB}^{-} is an electron in a conductive band. Then these electron-hole pairs interact with water molecules adsorbed on its surface: $H_2O + 2h^{+} \rightarrow 2H^{+} + 1/2\ O^2$ and after that: $2H^{+} + 2e^{-} \rightarrow H^2$.

In this investigation, we delve into the characterization of Ag-AgBr hybrid nanoparticles encapsulated within a glass matrix, synthesized via an ion exchange technique.

Materials and Methods

In this research, PTR glasses with Na_2O-ZnO-Al_2O_3-SiO_2-F-Sb_2O_3-CeO_2-Ag_2O-Br matrix with different concentrations of Br were studied: GBr0.5 (Br = 0.51 mol.%), GBr0.7 (Br = 0.76 mol.%) and GBr2.1 (Br = 2.1 mol.%). Ion exchange was held in 5% $AgNO_3$ / 95% $NaNO_3$ solution. After that, thermal treatment took place for 3 hours in a muffle furnace at a temperature of 560 C°. The size of nanoparticle was calculated based on the X-ray diffraction data by the Scherrer formula [4]: $d = K\lambda / (\beta \cos\theta)$, where K is a Scherrer constant, λ is the X-ray radiation wavelength, β – peak width at half maximum and θ is the diffraction angle. To see the methyl orange dye (MO) degradation rate 405 nm laser was used. To calculate the degradation rate of MO C/C_0 first the absorption spectra of initial water dye solution was obtained using spectrophotometer Lambda 650 (PerkinElmer). Then after sample irradiation in a solution for a fixed period of time, absorption spectra were obtained again. The deference of the absorption on a 600 nm and 450 nm is C for that time interval and C_0 is for initial solution.

Results and Discussion

First, to obtain the particles size XRD method was applied. XRD spectra are shown in Figure 1. According to Scherrer formula, average Ag particle sizes are 45 nm in GBr0.5, 47 nm in GBr0.7 and 56 nm in GBr2.1.

It can be clearly seen the one peak located at 38°2θ correlated to silver 111 crystal.

It should be noted that despite the fact that XRD spectra does not show any peaks correlated to AgBr, it is reliably known from the previous studies that Ag-AgBr hybrid nanoparticles with Ag core and AgBr shell grow in this glass under these conditions [5]. Absence of any AgBr peaks can be explained by the fact that silver-core is much bigger than the AgBr-shell. For instance, the AgBr shell can be 2–5 nm while the Ag core nanoparticle is 47 nm.

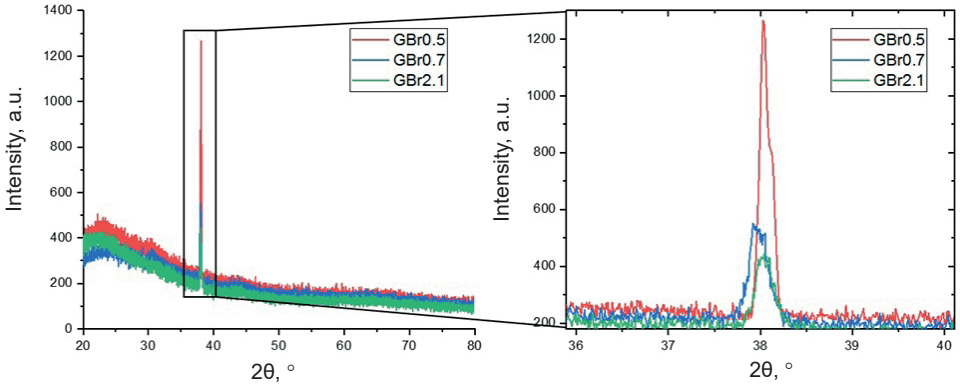

Fig. 1. XRD spectra of studied glasses

Figure 2 demonstrates different MO degradation curves using different glass samples.

Degradation of MO dye curves show that glass with the least Br concentration (GBr0.5) exhibit the worst photocatalytic MO degradation which stops at 0,14 C/C_0. While the glass with the biggest Br concentration (GBr2.1) shows the fastest MO dye degradation rate as well as the maximum degradation point of 0.08 C/C0. It can be concluded that with increase of Br concentration the photocatalytic properties are also increases. That fact can be explained by the growth of semiconductor AgBr shell on silver nanoparticle.

Last, on Figure 3 comparison of different kinds of glass samples' MO dye degradation rate is presented, where Gag contain only silver nanoparticles without any AgBr shell, GAgBr contain only semiconductor AgBr without Ag nanoparticle shell and GAg-AgBr is a sample with discussed above Ag-core and AgBr shell nanoparticles.

Degradation rate shows significant improvements in photocatalytic MO dye degradation of GAg-AgBr in comparison with samples containing only Ag or AgBr nanoparticles separately.

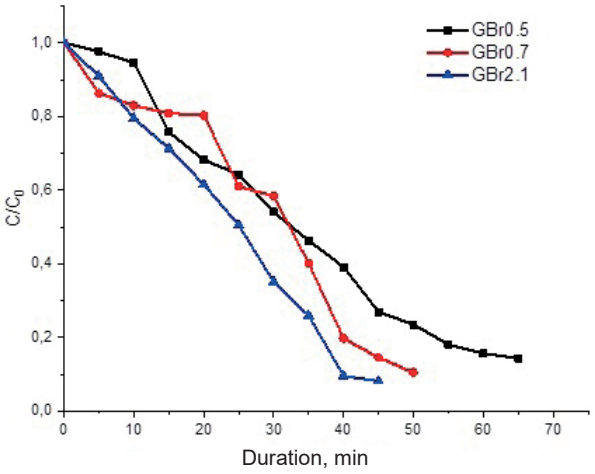

Fig. 2. Photocatalytic degradation of MO water solution with different glass samples with different Br concentration (GBr0.5 (0.51 mol.% Br), GBr0.7 (0.76 mol.% Br) and GBr2.1 (2.1 mol.% Br)

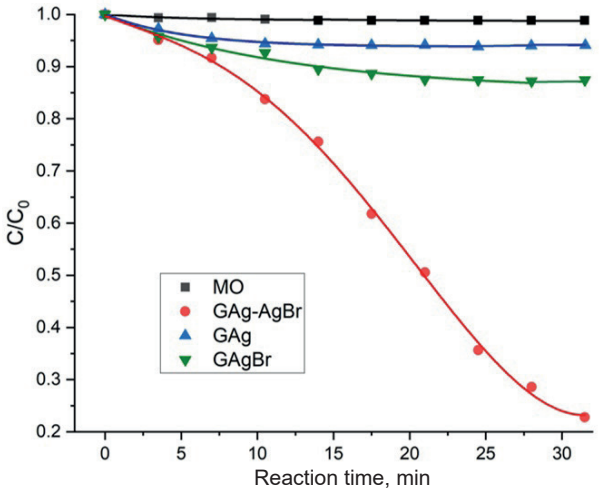

Fig.3. Photocatalytic degradation of MO water solution with different glass samples: GAg contains only Ag nanoparticles, GAgBr contains only AgBr and GAg-AgBr contains nanoparticles with Ag core and AgBr shell

Conclusion

Photocatalytic degradation of MO demonstrates that glass with Ag-AgBr nanoparticles exhibit better photocatalytic activity in comparison to samples with Ag or AgBr nanoparticles separately, which explains by the fact that AgBr shell increases electron lifetime. While higher concentration

of Br shows better dye-degradation rate. That can be explained by the growth of the nanoparticle's AgBr shell. XRD spectra also shows the increase of Ag nanoparticle, however, there is no peaks correlated to the AgBr. That can happen due to the small AgBr shell of nanoparticles which is not enough to distinguish its XRD peaks.

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