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Spectral and photocatalytic properties of Ag-AgCl nanostructures formed on surface of silicate glass by ion exchange

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Abstract. In this work, the spectral and photocatalytic properties of 3 silicate glasses with different chlorine concentrations from 0.5 to 1 mol. % were studied. Since photocatalysts require the presence of nanostructures on the glass surface, silver was introduced into silicate glass with chlorine by low-temperature Na^+-Ag^+ ion exchange. The synthesis of Ag-AgCl nanostructures occurred during heat treatment, after which a plasmonic absorption band in the visible range of the spectrum was revealed in the absorption spectra. The degree of decomposition of the aqueous solution of methyl orange dye increased from 80 to 92% with increasing chlorine concentration in the photocatalyst with Ag-AgCl nanostructures. Note that with increasing chlorine concentration, the concentration of nanostructures increases.

Keywords: ion exchange, nanostructures, nanocrystals, silver, absorption, photocatalysis

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Материалы конференции
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Спектральные и фотокаталитические свойства наноструктур Ag-AgCl, сформированных на поверхности силикатного стекла ионным обменом

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Аннотация. В данной работе были исследованы спектральные и фотокаталитические свойства 3 силикатных стекол с разной концентрацией хлора от 0,5 до 1 мол. %. Так как для фотокатализаторов необходимо наличие наноструктур на поверхности стекла серебро в силикатное стекло с хлором вводилось низкотемпературным ионным обменом Na^+-Ag^+. Синтез наноструктур Ag -AgCl происходил в процессе термической обработки, после чего на спектрах поглощения выявлена плазмонная полоса поглощения в видимом диапазоне спектра. Степень разложения водного раствора красителя метилоранжа увеличивалась с 80 до 92% с увеличением концентрации хлора в фотокатализаторе

с наноструктурами Ag-AgCl. Отметим, что при увеличении концентрации хлора концентрация наноструктур растет.

Ключевые слова: ионный обмен, наноструктуры, нанокристаллы, серебро, поглощение, фотокатализ

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Introduction

Currently, photocatalysts are being actively developed and used in various fields of science, technology and medicine. However, the quantum efficiency of modern photocatalysts is relatively low. This is mainly due to recombination processes between electrons in the conduction band and holes in the valence band, which arise under the influence of light. One of the most promising methods for suppressing recombination processes is the creation of noble metal nanoparticles in the photocatalyst matrix, which act as electron "suppressors".

The photocatalytic properties of Ag-AgBr and Ag-AgCl structures were previously studied by other authors [1–3]. Thus, according to [2], a photocatalyst with Ag-AgBr particles is capable of decomposing more than 80% of methyl orange dye in 2 minutes under solar radiation. However, the properties of Ag-AgCl photocatalyst based on sodium silicate glass have not yet been studied.

Since the presence of nanoparticles on the glass surface is important for photocatalytic applications, a promising tool for introducing silver into the glass composition is the ion exchange method. Ion exchange is a versatile and cost-effective method that allows for the precise incorporation of silver ions (Ag^+) into the glass matrix, followed by them in situ into Ag-AgCl nanostructures under controlled heat treatment conditions [4]. This method not only ensures uniform distribution of nanostructures but also enables the tuning of their size and density [5].

The aim of this paper is study of the spectral and photocatalytic properties of a photocatalyst with Ag-AgCl nanostructures in ion-exchange layers of sodium silicate glass.

Materials and Methods

The photocatalyst was created based on a matrix of sodium silicate glass Na_2O–ZnO–Al_2O_3–SiO_2–F doped with CeO_2, Sb_2O_3, Cl. The Cl concentration in the glass was 0.5, 0.75 and 1 mol. %. The 1 mm thick sample was carefully ground and polished.

The next step was to perform ion exchange on the sample in the $AgNO_3/NaNO_3$ melt (5 mol.%/95 mol.%, respectively). Ion exchange was carried out at 320 °C for 15 minutes.

The last stage of sample preparation was additional heat treatment of the sample above the glass transition temperature. The treatment temperature was 500 °C for 3 hours. After each stage, absorption spectra were measured.

The photocatalytic properties of the sample were then measured by measuring the absorption properties of an aqueous solution of methyl orange dye before and after irradiation. Its initial concentration was about 1 mg/100 ml of water. A laser with a wavelength of 405 nm was used to study the photocatalytic properties.

The solution together with the photocatalyst was subjected to broadband irradiation every 5 minutes. After each period, the absorption spectrum of the solution was measured. All spectra were measured using a Perkin-Elmer lambda 650 spectrophotometer.

The size of silver nanoparticles was calculated by Mie theory with using the following equation:

$$d = \frac{2v_F}{\Delta\omega}, \quad (1)$$

where d is the average diameter of silver nanoparticles, v_F is the Fermi velocity (1.39×10^8 cm/s for silver, $\Delta\omega$ is the half-width at half-height in the units of angular frequency.

Results and Discussion

To synthesize Ag-AgCl nanostructures, ion exchange was carried out on the surface of the sample, followed by heat treatment. Figure 1 shows the absorption spectra of the formed nanostructures. The position of this absorption peak (460 and 470 nm) of silver nanoparticles is slightly shifted to longer wavelengths relative to the spectrum of glass without chlorine from [3]. The displacement itself increases with increasing chlorine concentration to 0.75 mol.% and is caused by the growth of AgCl/NaCl shells around silver particles (Fig. 1, *a*). A further increase in concentration only leads to an increase in the absorption of nanostructures. The average diameter of the formed nanoparticles was calculated using the Mie theory (formula 1) and increased from 1.98 to 2.02 nm with increasing chlorine concentration. Note that there is a possibility of a growth in the size of the chlorine shell.

Note that during ion exchange, with increasing concentration, the depth of the layer itself increases due to the breaking of Si-O bonds by chlorine and, as a consequence, an increase in the diffusion coefficient of silver ions (Fig. 1, *b*).

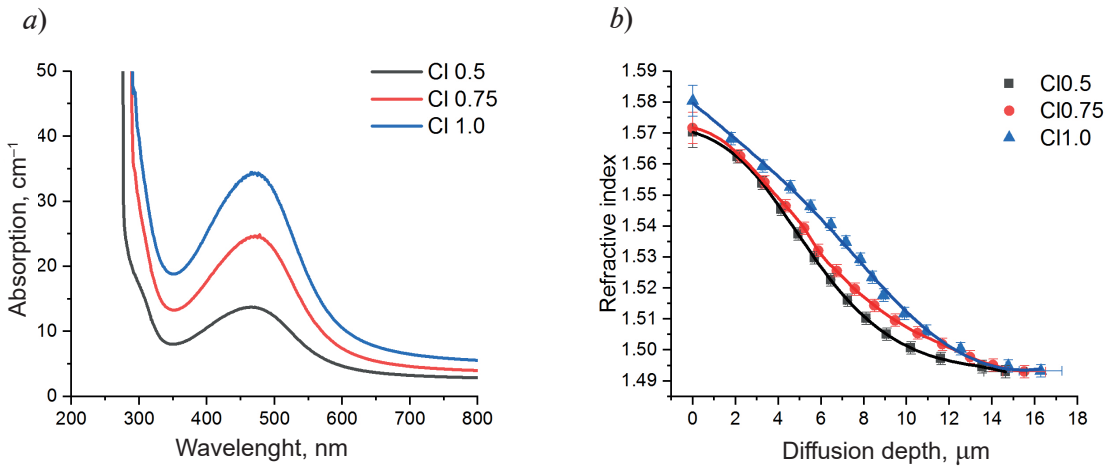

Fig. 1. Absorption spectrum for Ag-AgCl nanostructures in surface layer in silicate glass (*a*) and refractive index profiles of glasses with chlorine before heat treatment (*b*)

Figure 2 shows the dependence of the kinetics of degradation of an aqueous solution of methyl orange dye on the chlorine concentration. The amount of degradation of an aqueous solution of methyl orange dye was calculated from the ratio of the dye absorption amplitude after irradiation to the dye absorption amplitude before irradiation. The amount of degraded methyl orange dye increased with increasing chlorine concentration and amounted to 80 and 92%, respectively. The reason for the increase in the C/C_0 value is the formation of hot electrons on the surface of the sample due to the transfer of these charge carriers from silver chloride to silver nanoparticles, which enhance the effect of destruction of the dye molecule with increasing chlorine concentration. We also note that the low rate of photocatalytic reaction in samples with chlorine concentrations of 0.5 and 0.75 mol.% at the beginning of the experiment is possibly due to reabsorption of the dye on the surface. But further experiments are required to accurately interpret the data obtained.

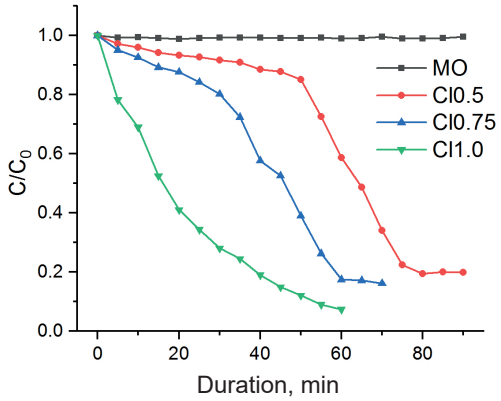

Fig. 2. The dependence of the kinetics of degradation of an aqueous solution of methyl orange dye on the chlorine concentration

Conclusion

The work assessed the photocatalytic degradation of an aqueous solution of methyl orange dye in the presence of a photocatalyst with Ag-AgCl nanostructures on the surface of silicate glass formed by the ion exchange method. It was shown that with increasing concentration of Ag-AgCl nanostructures, the C/C_0 ratio increases from 80% to 92%, associated with photocatalytic degradation of the dye.

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