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INFLUENCE OF PLASMONIC NANOPARTICLES ON THE CHARACTERISTICS OF THE PLASMA ACTIVATED PHOTOCATALYSTS

ВЛИЯНИЕ ПЛАЗМОННЫХ НАНОЧАСТИЦ НА ХАРАКТЕРИСТИКИ ПЛАЗМОАКТИВИРОВАННЫХ ФОТОКАТАЛИЗАТОРОВ

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Energy efficient plasma technologies have been successfully applied for decades in the field of material processing. In particular, low-temperature plasma has been used for catalyst synthesis. It was shown that impregnation with plasmonic silver (Ag) nanoparticles (NPs) improved the activity of plasma treated catalysts. In this study, the influence of Ag NPs was investigated on the optical characteristics of the plasma treated photocatalysts. Zinc oxide (ZnO) was chosen as a photocatalyst. The plasma treatment was performed in dielectric barrier discharge (DBD) plasma. The catalysts were characterized by photoluminescence (PL). The UV-VIS spectroscopy was used to measure the optical band gap.

Энергоэффективные плазменные технологии уже в течение нескольких десятилетий успешно применяются для обработки материалов. В частности, низкотемпературная плазма применяется для синтеза катализаторов. Было показано, что импрегнирование плазмонными наночастицами (НЧ) серебра (Ag) повышает активность катализаторов, обработанных в плазме. В настоящей работе исследовано влияние наночастиц серебра на оптические характеристики фотокатализаторов. Оксид цинка (ZnO) был выбран в качестве фотокатализатора. Плазма диэлектрического барьерного разряда (ДБР) была использована для обработки катализаторов. Катализаторы были исследованы методом фотолюминесценции (ФЛ). Для определения ширины запрещенной зоны применялась спектроскопия в УФ и видимой области.

Keywords: nanoparticles, plasmon resonance, plasma, photocatalyst, photodegradation, methyl orange, dielectric barrier discharge, plasma treatment.

Ключевые слова: наночастицы, плазмонный резонанс, плазма, фотокатализатор, фотодеградация, метиловый оранжевый, диэлектрический барьерный разряд, обработка в плазме.

Low-temperature plasma treatment has been recently proposed as an alternative method for catalysts synthesis and modification [1]. Cold plasma produced catalysts exhibited an enhanced activity, higher selectivity, and better stability compared to the catalysts prepared conventionally, e. g., by heat-treatment [2; 3]. Besides, plasma-assisted methods include environmentally friendly and energy saving processes. By plasma treatment of the materials, there is no ultimate need to use the hazard chemicals. Therefore, the disposal of the hazard chemicals can be avoided. On the other hand, plasma treatment are performed under dry conditions. It means that drying processes that require quiet a lot of energy are eliminated.

In previous work [4], a plasma treatment was successfully employed for enhancement the performance of Ag-NPs impregnated ZnO based photocatalyst. Ag-NPs impregnated ZnO catalysts were prepared by a wet impregnation method followed by plasma treatment. For this purpose, dielectric barrier discharge plasma was applied. The photocatalytic degradation of methyl orange was investigated under ultraviolet (UV) light irradiation in the presence of aqueous suspension of Ag-NPs impregnated ZnO. The performance of plasma-treated and untreated Ag-NPs impregnated ZnO-based catalysts were compared with that of commercially available catalysts. A diminished catalytic activity was observed after impregnation with Ag-NPs. A subsequent treatment by DBD-plasma lead to the enhancement of catalysts' performance. The photocatalytic activity, expressed in term of rate constants of photodegradation of methyl orange, was found to be approximately 3 times higher for synthesized samples than that for commercial catalyst.

In this paper, the Ag-NPs impregnated ZnO-based photocatalyst were investigated by optical methods. The aim of this study is to establish the relationship between the activity of the treated photocatalysts and their physic-chemical properties. The catalysts were characterized by photoluminescence (PL). The UV-VIS spectroscopy was used to measure the optical band gap.

Commercial (ECOS-1, Russia, GR pure) ZnO powder was employed as a catalyst support. The synthesis procedure can be divided into three parts. One is the preparation of colloidal suspension of silver nanoparticles in water. The second one was the impregnation of ZnO powders with silver nanoparticles. Finally the silver impregnated catalyst was treated by plasma. *Colloidal silver nanoparticles were prepared according to the method documented in reference* [5]. Aqueous solution of 50 ml of a 10^{-3} M $AgNO_3$ was heated to boiling. After that 1 ml of a 1% trisodium citrate ($C_6H_5O_7Na_3$) solution was added. The mixture was boiled for 1 hour and then was cooled down. An excess solution impregnation was chosen as a method for preparation of silver nanoparticles loaded ZnO-catalyst. Thus, a certain amount of ZnO powders was introduced in an aqueous solution containing silver nanoparticles. The silver loading was calculated to be 1 wt %. Then, the excess of solution was removed by the means of evaporation at room temperature. The product was denoted ZnO-Ag. After drying, a half amount of silver impregnated catalyst was treated by dielectric barrier discharge plasma. This catalyst was marked as ZnO-Ag-DBD. Untreated ZnO powder was used as reference catalyst (ZnO).

The plasma treatment was performed with a dielectric barrier discharge reactor, which is schematically presented in Figure1. The discharge was generated between a rod electrode (Ø: 20 mm) and a plate electrode (10x10 cm). The upper rode electrode was covered by 2.0 mm quartz glass layer and connected to a 1 kHz AC high voltage source, while the lower electrode is connected to earth through a resistor R (75 Ω) or a capacitor C (850 pF). The distance between upper electrode and treated sample was 4 mm. The applied voltage (peak-to-peak value) was of 35 kV range. The samples to be treated were located on the grounded electrode. Plasma treatment was carried out in air at atmospheric pressure for treatments times of 25 min.

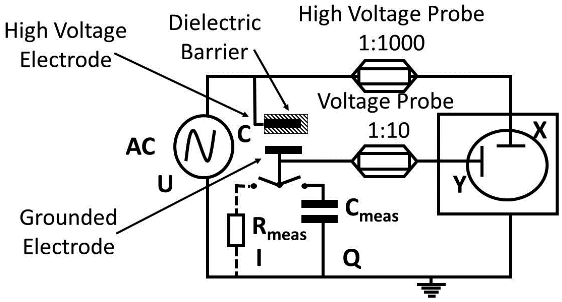

Figure 1 – Schematic representation of the DBD plasma reactor and experimental setup for voltage, current and charge transfer measurements alternatively: either current measurement (using only R_{meas}; broken line) or charge transfer measurement (using only C_{meas}; as plotted)

The electric operation parameters of DBD such as discharge voltage U, discharge current I_d, transferred charge Q, consumed electric energy (discharge energy) E_{el} were estimated as described in [4]. E_{el} was found to be of 6.5 mJ/cycle.

The photoluminescence excitation (PLE) spectra and PL spectra of the untreated and DBD-plasma treated catalysts were measured at room temperature with a fluorescence spectrophotometer (SDL-2 LOMO, F-7000), using a xenon lamp of 120 W (DKsSH-120) as light source. The PLE spectra were obtained by monitoring emission at a fixed wavelength (550 nm) while varying the excitation wavelength. In PL spectra a fixed wavelength was used to excite the samples and the intensity of emitted radiation was monitored as function of wavelength. The samples excitation was made at 330 nm. The diffuse reflection spectra of samples were measured using a UV-VIS-NIR Perkin Elmer spectrophotometer (Perkin Elmer Lambda 850 with integrated sphere).

Figure 2a shows the PLE spectra of the Ag impregnated untreated and DBD plasma treated ZnO as well as pure ZnO powders with an emission wavelength of 550 nm. Two weak peaks at 290 and 350 nm were observed for pure ZnO. For Ag impregnated samples, only one peak was observed at around 290 nm. The excitation threshold was the same for all samples. Figure 2b shows the PL spectra of the catalysts with an excitation wavelength of 330 nm. In the PL spectra of ZnO, typically there are emission bands in the UV and visible regions. The UV peak is a characteristic emission of ZnO.

It is attributed to the near-band-edge (NBE) emission through exciton-exciton collision processes. The emission in visible region are dominantly considered to be due to electron-hole recombination caused by surface or intrinsic defects, e. g. zinc interstitials and oxygen vacancies. The green PL emission at around of 530 (deep-level emission, DL) can be originated from the oxygen vacancies while the violet emission (~425 nm) can be attributed to the electronic transition from the defect level, corresponding to Zn interstitials, to the valence. As can be seen from the figure 2b, all samples exhibited two emission bands centred at 385 and 530 nm. The NBE-to-DL emission ratio was found to be of 0.6 and 0.8 for pure ZnO and for Ag impregnated ZnO, respectively. The intensity ratio of NBE emission to DL emission of the Ag NPs impregnated ZnO was not changed by DBD plasma treatment.

The increase in NBE-to-DL emission ratio can be attributed to the presence of the Ag NPs. There might be three distinct physical processes that contribute to the end edge emission enhancement. The enhancement of NBE-to-DL emission ratio might be due to electron transfer from the defect level to the Fermi level of Ag NPs followed by transfer from the Fermi level of Ag NPs to conduction band of ZnO. Consequently, increased electron density in conduction band of ZnO can lead to an increase in NBE emission intensity. In other words, the conduction band of ZnO is pumped by electrons in defect level via Ag NPs. That is possible because the energy level of defect states in ZnO (-4.99 eV with respect to the vacuum) is close to the Ag Fermi level (-4.7 eV). Besides, after the impregnation of ZnO with Ag NPs, there might surface passivation effect due to a reduction of the surface traps. The separation of holes and electrons is reduced within the passivated surface with reduced traps. That means than more electron-hole pairs can be generated. As a result, the BNE emission can be enhanced while the DL emission can be suppressed. On the other hand, there might exist surface plasmon polaritons caused by a direct exciton-plasmon coupling between excitons of ZnO and surface plasmons of Ag NPs.

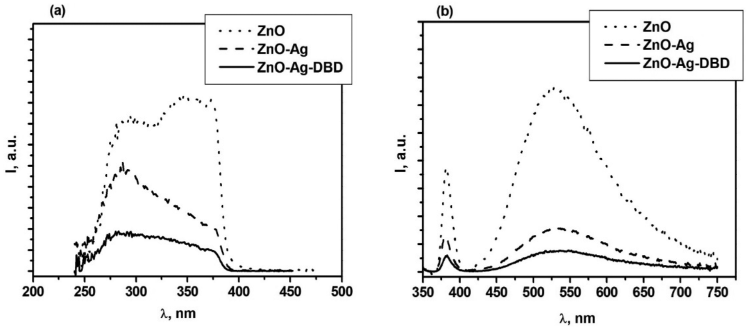

Figure 2 – PLE (a) and PL (b) spectra ZnO-based photocatalyst

Figure 3a shows the diffuse reflectance spectra of bare ZnO, untreated and plasma treated ZnO impregnated with silver NPs. The absorption in the 360–800 nm region was greater in samples impregnated with silver nanoparticles. The plasma treated sample (ZnO-Ag-DBD) showed the highest absorption. The spectra of Ag NPs impregnated ZnO had the broad weak-intensity absorption bands as arrowd in Figure 3a. This bands can be attributed to the Ag NPs plasmon absorbtio. For untreated ZnO-Ag sample, the absorption peak was at ca 420 nm. The plasmon band was red-shifted to 460 nm after plasma treatment (see the inset in figure 3a). As the band was weak, it was difficult to determine whether the band was broadened after plasma treatment. The low intensity of absorption band can be explained by the low silver concentration on the surface of samples.

The Kubelka-Munk theory was used to extract the optical band gap energy from diffuse reflectance measurements. The acquired diffuse reflectance spectra were converted to Kubelka-Munk function F(R)

$$F(R) = \frac{\alpha}{s} = \frac{(1-R)^2}{2R}, \qquad (1)$$

where R is the reflectance, α is the absorption coefficient and s is the scattering factor. The scattering factor does not depend on the wavelength and can be ignored in calculation. The McLean equation in terms of the Kubelka-Munk function was used to find the type of transition and to determine the optical band gap

$$F(R)h\nu = k\left(h\nu - E_g\right)^{1/n}, \qquad (2)$$

where k is an energy-independent constant, E_g is the optical band gap. The exponent n is determined by the type of transition: n=2 for direct allowed transitions, n=1/2 for indirect allowed transitions, n=2/3 for direct forbidden transitions, n=1/3 for indirect forbidden transitions. The value of n can be determined by plotting the $(F(R)h\nu)^n$ vs. *hν*. The best fit to the straight line gives the n. Figures 3b, 3c and 3d show McLean plots for ZnO, ZnO-Ag and ZnO-Ag-DBD. As it is clearly seen in the Figures 3b and 3c, there are certain value of n for which the plots are definitely non-linear. For the ZnO and ZnO-Ag, the best choice was n=2 which implies direct allowed transitions. From a plot $(F(R)h\nu)^n$ vs. *hν* the band gap energy can be determined by extrapolating the slope to $F(R) \rightarrow 0$. For bare ZnO, the band gap energy was found to be of 3.55 eV. The value of the band bap did not change after plasma treatment and impregnation of ZnO with Ag NPs. For ZnO-Ag-DBD catalyst, $(F(R)h\nu)^n$ can be fitted with the straight line for all values of n. Thought, no value of n gave really good straight line over the entire wavelength range (figure 3d).

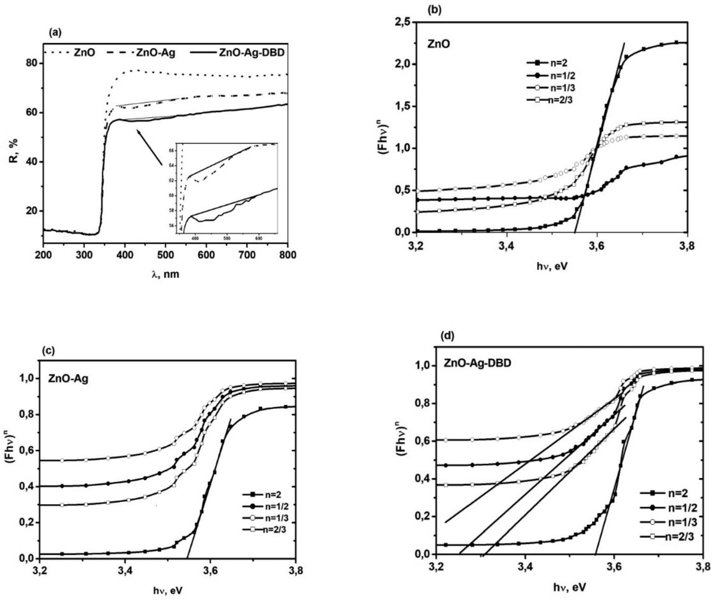

Figure 3 – Diffuse reflectance spectra (a) of bare ZnO, untreated Ag NPs impregnated ZnO, DBD-plasma treated Ag NPs impregnated ZnO and McLean plots for bare ZnO (b), untreated Ag NPs impregnated ZnO (c) and DBD-plasma treated Ag NPs impregnated ZnO (d)

Thus, for the plasma treated Ag-NPs impregnated sample, the enhancement of the catalyst performance might be due to the involvement of different type of transitions in catalytic processes.

Acknowledgements. *This work was partially financially supported by the Belorussian Republican Foundation for Fundamental Research (grant No F17-076)*.

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