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INVESTIGATION OF PHOTOCATALYTIC ACTIVITY OF TiO_2-GO NANOCOMPOSITE

Zhumabekov A.Zh., Seliverstova E.V., Ibrayev N.Kh.

Institute of molecular nanophotonics, E.A. Buketov Karaganda State University,
Karaganda, Kazakhstan, almar89-89@mail.ru

Nanocomposite based on graphene oxide and TiO_2 was synthesized by hydrothermal method. The formation of nanocomposite was confirmed by Raman spectroscopy data. Characteristic peaks of graphene oxide and TiO_2 were recorded. Energy dispersive analysis showed the presence of titanium, carbon and oxygen in the nanocomposite. The specific surface area of TiO_2-GO nanocomposite is 1.16 times more than for pure TiO_2. A study of the photocatalytic activity of synthesized material in electrolytes with different pH was carried out. It is shown that the generation of photocurrent in TiO_2–GO depends on the electrolyte and increases by 2.9, 1.3 and 1.05 times in NaOH, KOH and Na_2SO_4, respectively, compared to the pure TiO_2 films.

Keywords: graphene oxide, TiO_2–GO, nanocomposite material, titanium dioxide, photocatalysis.

Introduction

Photoelectrochemical splitting of water with semiconductors is a "green" and inexpensive way to produce hydrogen fuel. Fujishima and Honda [1] showed for the first time that photoelectrochemical water splitting occurs on the surface of titanium dioxide (TiO_2). This work marked the beginning of the study of semiconductor materials for photocatalysis.

Titanium dioxide is a well-known and most studied functional material in the field of photocatalysis [2-4]. It is widely used in the degradation of environmental pollutants, as well as for the decomposition of organic substances.

Graphene has high electron mobility, large specific surface area and high transparency [5-7]. Earlier it was shown that composites based on TiO_2 and carbon-based materials, including activated carbon, carbon nanotubes and fullerenes, are able to demonstrate higher photocatalytic characteristics than pure TiO_2 [8-10].

Preparation of TiO_2-based composites is an effective way to increase the photocatalytic activity of the material by reducing the charge recombination rate. It is assumed that there is a more efficient separation of charges – photogenerated electrons, are converted into carbon materials, and the holes remain on TiO_2 and thus slow down the recombination of electrons and holes.

At the moment, there are several methods for the synthesis of nanocomposite material based on TiO_2 and graphene oxide. For example, the sol-gel method, the hydrazine reduction method, the hydrothermal method, the solvothermal method and the UV method, and there are 2-step methods for producing a composite [11-15], which directly affect the photocatalytic activity of the obtained materials. In ref. [16-18] it was shown that the electrolyte composition and its pH affect the value of the photogenerated current, as well as the efficiency of water splitting and hydrogen generation H^+.

In this paper, nanocomposites based on TiO_2 and graphene oxide were synthesized and their structural, optical and photocatalytic properties were investigated. It is shown that the photoactivity of the nanocomposite depends on the electrolyte used.

1. Experiment

Materials

To prepare the TiO_2–GO nanocomposite, graphene oxide (GO, Cheaptubes) and TiO_2 (d>21, anatase, 99.7%, Sigma Aldrich), deionized water (purified by AquaMax water purification system), ethanol (anhydrous) were used. The films were deposited onto the surface of glass substrates coated with a conductive layer FTO (Fluorine doped tin oxide coated glass slide, ~7Ω/sq, Sigma Aldrich). Electrolytes NaOH, KOH, Na_2SO_4 were used to estimate photocatalytic properties. The pH value for them was equal to 13.4, 12.3 and 9.7, respectively. All reagents were analytically grade and used without additional purification.

The preparation and characterization of samples

Nanocomposite based on TiO_2 and graphene oxide was synthesized by hydrothermal method according to the method of [13]. The ratio of GO to TiO_2 was 1%. To measure the photocatalytic activity of the nanocomposite, a paste based on ethanol and TiO_2-GO powder with a concentration of 150 mg/ml was prepared.

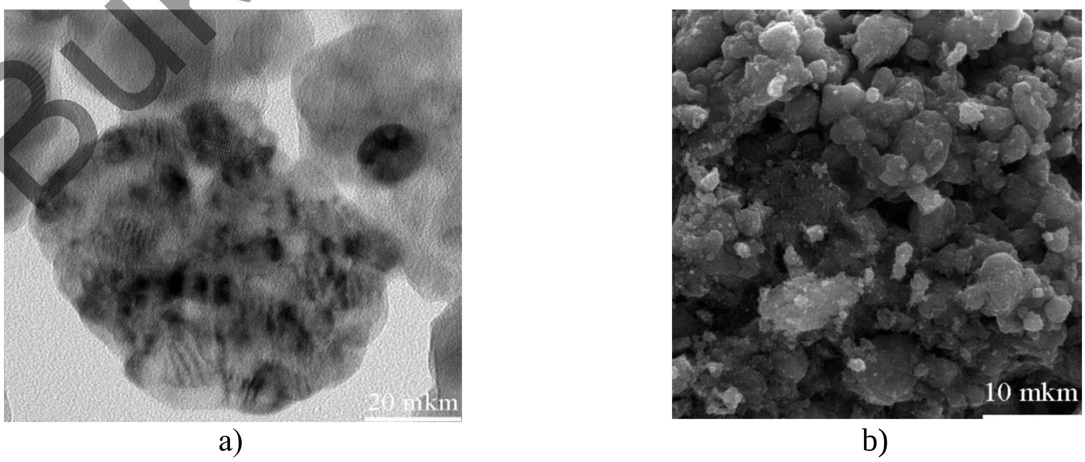
The surface morphology of the resulting nanocomposite was studied using a transmission electron microscope (TEM) JEM-1400Plus (Jeol) with an accelerating voltage of 120 kV and a scanning electron microscope (SEM) Tescan Mira-3 (Tescan). The Confotec MR520 microscope (Sol Instruments) with laser excitation at a wavelength of 632.8 nm was used to register Raman spectra.

The porous structure was studied and the specific surface area was measured by the Brunauer–Emmett–Teller (BET) method on the Sorbi–MS (META) measuring complex. Nitrogen was used as an adsorbate. Measurements were carried out at the temperature of liquid nitrogen 77 K.

The photocatalytic activity of the obtained materials was studied by recording the photoinduced current in a standard photoelectrochemical three-electrode cell with a quartz window on a potentiostate-galvanostate P-30J (Elins). Ag/AgCl was used as the reference electrode. The radiation source was a diode lamp with a power of 35 mW/cm^2. The test samples were spin-coated on the surface of substrates with FTO. Resulting films were connected to the working electrode. A platinum electrode was connected to the negative potential.

2. Results and discussion

TEM and SEM images clearly show titanium dioxide nanoparticles (Fig.1, a and b). At the same time, graphene oxide sheets are barely distinguishable since ratio of GO to TiO_2 is 1:100. Energy dispersive (EDS) analysis of the prepared samples showed that titanium, carbon and oxygen are present in the composition of the nanocomposite (Fig.2, a).



a) b)

Fig.1. TEM (a) and SEM (b) images Of TiO_2-GO nanocomposite

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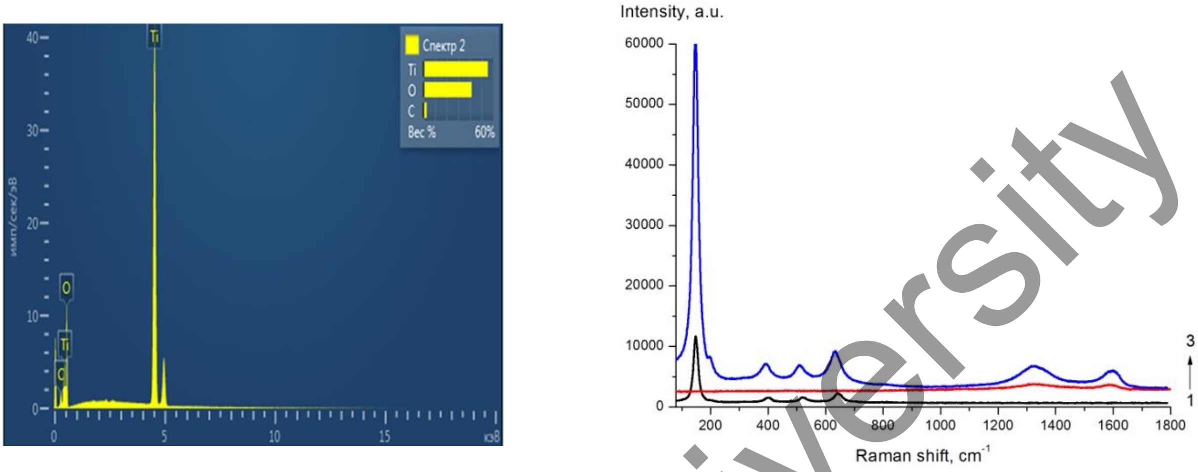
Raman spectra of the TiO_2-GO nanocomposite of the samples were also recorded (Fig.2, b). The spectra obtained are the combination of individual TiO_2 and GO curves and correlate well with the data obtained in [19, 20] for TiO_2 and graphene oxide in [21]. It was found that in the spectra of nanocomposite material the ratio of the intensities of I_D/I_G bands was increased to 1.2 from 1.05. This indicates that in graphene oxide there is occur an ordering and an increase in the number of aromatic rings in structure during the process of synthesis [21].



a) b)

Fig.2. EDS analysis (a) and Raman spectrum (a): 1 – TiO_2, 2 – GO, 3 – TiO_2-GO

Photocatalytic activity of semiconductor materials indirectly depends on its electrotransport properties and specific surface area. In the previous work [22] we investigated electrotransport and optical properties of TiO_2-GO nanocomposite and showed that nanocomposite has higher electrotransport characteristics in comparison with pure TiO_2.

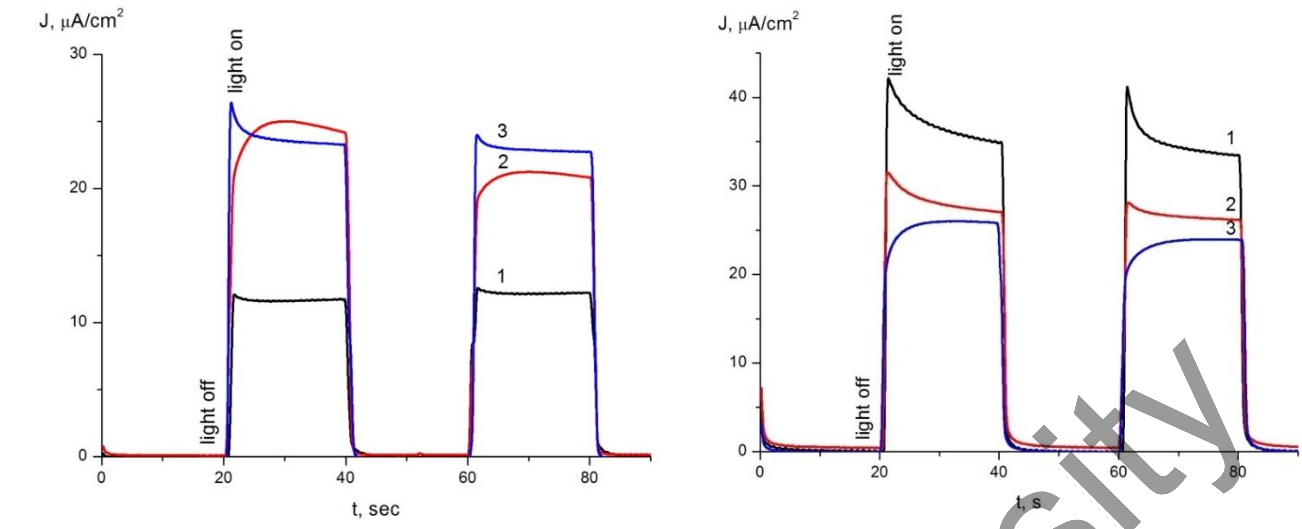
Table 1 shows the specific surface area of the TiO_2-GO nanocomposite films, as well as the titanium dioxide. It is shown the specific surface area of the semiconductor was increased by 16% after the addition of graphene oxide.

Table 1. Specific surface area of TiO_2 and nanocomposite films

Sample	**S_{BET}, m^2/g**
TiO_2	67.3
TiO_2-GO	78.0

Further, the photocatalytic activity of pure TiO_2 and TiO_2-GO nanocomposite in various electrolytes was studied. The value of the photocurrent of the samples was measured for 20 seconds with cyclic switching on and off the light. To determine the optimal conditions for the generation of electron-hole pairs in pure TiO_2 and in the nanocomposite with GO, the electrolytes of Na_2SO_4, KOH and NaOH, differing in the magnitude of the electrochemical potential, were used.

Fig.3a shows the transient characteristics of the photocurrent for samples based on pure TiO_2. It is seen that for TiO_2 the lowest values of the generated photocurrent were recorded in the electrolyte NaOH. The value of J in other electrolytes is comparable with each other. For the KOH electrolyte, a decrease in the curve profile after 60 s was registered, this indicates on acceleration of the electron recombination process in the TiO_2 film.



a) b)

Fig. 3. Transient characteristics of the TiO_2 photocurrent (a) and TiO_2-GO (b) in the electrolyte: 1 – NaOH, 2 – KOH, 3 – Na_2SO_4.

Films of TiO_2 in the Na_2SO_4 electrolyte in intensively responds to incident light interval times of 20 s. The subsequent surge in the value of the photocurrent from t=60 s shows that the film continues to generate electrons.

Thus, studies of the transient characteristics of the photocurrent showed that TiO_2 generates photocurrents in the Na_2SO_4 electrolyte (~24 $\mu A/cm^2$) about 2 and 1.04 times more than in the electrolytes NaOH and KOH, respectively.

Na_2SO_4 is not the most optimal electrolyte for TiO_2-GO nanocomposite. The most effective electrolyte in this case is NaOH solution. The measurements showed (Fig.3, b) that the value of TiO_2-GO photocurrent is in 1.25 and 1.4 times better in NaOH than in KOH and Na_2SO_4. Nevertheless, in all electrolytes under irradiation of TiO_2-GO nanocomposite there is an increase in the photocurrent by 2.9, 1.3 and 1.05 times (NaOH, KOH and Na_2SO_4 electrolytes) was registered compared to pure TiO_2.

Conclusion

Thus, studies have shown that hydrothermal synthesis forms a bond between TiO_2 particles and graphene oxide sheets, which indicates the production of nanocomposite. It was confirmed by the data of EDS analysis and Raman spectroscopy.

Studies of the transient characteristics of the photocurrent showed that the most optimal electrolyte for pure TiO_2 is Na_2SO_4, whereas for the TiO_2–GO nanocomposite – is NaOH solution. In any case, the photocatalytic activity of the nanocomposite material is in 2.9, 1.3 and 1.05 times greater in NaOH, KOH and Na_2SO_4 solutions, respectively, than in TiO_2. Since the efficiency of photocatalytic splitting of water into molecular oxygen and hydrogen will depend directly on the magnitude of the photoinduced electrons, it can be assumed that when using the NaOH electrolyte for TiO_2-GO, hydrogen generation will be higher compared to other electrolytes.

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