

Paramagnetic and Photocatalytic Properties of C-S co-Doped TiO₂ Nanocatalysts

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The paramagnetic and photocatalytic properties of C-S co-doped TiO₂ nanocatalysts were investigated. It was established, that the carbon-doped catalysts with different sulfur content show the presence of paramagnetic centers, referred to the dangling bonds in graphitized structures, intensities of this lines were drastically lowered after photocatalytic reaction. The ESR signals from Ti³⁺ centers were not detected. It was showed, that the light excitation of samples, regardless of doping (type and quantity), in the absorption band did not lead to the appearance of luminescence, so the recombination of charges occurs only in a non-radiation way, part of which reveals in photocatalysis, while the other part of the charges is captured/deactivated by defects/traps. Composite samples showed enhancement of the photocatalytic activity in the destruction of safranin T under UV irradiation as compared to pure TiO₂.

Keywords: Titanium dioxide, Carbon, Sulphur, Nanocomposites, ESR spectroscopy, Photocatalysis.

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1. INTRODUCTION

Last years, researchers pay attention to obtaining photocatalysts based on TiO₂ and different dopants [1-10]. This approach led to the appearance of visible-light-active photocatalysts due to the presence of oxygen vacancy state between the valence and the conduction bands through the formation of Ti³⁺ species, creation of new impurity levels just above the VB of TiO₂, narrowing of the band gap in case of carbon doped TiO₂ [1-4, 6]. Teruhisa et al. [9] prepared rutile doped with C⁴⁺ and S⁴⁺ which is photocatalytically active under visible light compared with pure anatase. Lei et al. [10] have prepared C, N and S co-doped anatase with photocatalytic activity under visible light irradiation, and attributed this fact to the synergic effect of the pure anatase structure, higher light absorption characteristics in visible regions, and separation efficiency of electron-hole pairs.

In our previous work [11] we have prepared and characterized nanosized C-S-TiO₂ composites photocatalytically active under UV and visible light irradiation. The aim of this work is to investigate electronic properties of these powders in more details and to obtain basic information about the nature of dopants. We used electron spin resonance (ESR) spectroscopy. This method allows one to detect and characterize paramagnetic defects which may be of significant importance for the photocatalytic properties.

2. EXPERIMENTAL

The powders were obtained by thermal hydrolysis using titanium (IV) ethoxide (3 g), thiourea (0.03, 0.07, 0.1, 0.5, and 0.7 g), citric acid (0.06 g), glycerol (2 g), and activated carbon (0.05 g), which was obtained according to technique developed in the Institute for Sorption and Problems of Endoecology NAS of Ukraine [12]. The samples were designated as 1S/C/TiO₂, 2S/C/TiO₂, 3S/C/TiO₂, 4S/C/TiO₂, 5S/C/TiO₂, respective-

ly. The photocatalysts were prepared at stepwise heating (200, 300, 400 and 500 °C) in the presence of air oxygen for 2 hours; before annealing, the mixture was thoroughly stirred up in order to obtain uniform mass. For pure titanium dioxide, the same mixture was used, but without dopants addition.

ESR spectra were recorded using X-band spectrometer Bruker Eleksys E580 at room temperature (295 K) with the following experimental parameters: frequency – 9.87 GHz; microwave power – 1 or 2 mW; modulation intensity – from 0.3 to 2 G with modulation frequency 100 kHz; scan width – 150 G; resolution – 2048 points; conversion time – 117 ms; time constant – 81 ms. Samples of Mn²⁺/MgO and diphenyl picrylhydrazyl (DPPH) were used for the spectrometer calibration. All the measurements were carried out with constant evacuation which provides pressure less than 1×10^{-2} Torr. To calculate the number of spins per gram in the samples studied, values of double integrals of their first derivative ESR spectra were compared with the double integral of the stable nitroxide radical TEMPOL (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl) spectrum (1×10^{-4} M, 10 μ L).

The luminescence of the powders was investigated using Perkin Elmer LS55.

Photocatalytic activity of the samples was evaluated by rate constants of destruction (k_d) of cationic dye Safranin T (ST) ($C = 0.03$ g/l). Before irradiation, catalyst suspension (2 g/l) in aqueous substrate solution was left in dark up to achieve adsorption equilibrium. Irradiation of dye aqueous solutions was performed at room temperature in quartz reactor in the presence of oxygen of air. A 30-W BUV-30 UV lamp with emission maximum at 254 nm and a 70-W GE Lucalox lamp with emission in the visible range at 568 nm were used as the light source.

Concentrations of the substrate were measured spectrophotometrically using Shimadzu UV-2450 spectrophotometer at $\lambda = 520$ nm. Photocatalytic rate con-

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stants were calculated using the pseudo-first-order kinetics equation.

3. RESULTS AND DISCUSSION

ESR characterization has been done for pure TiO_2 and S/C/TiO_2 samples. As far as pure TiO_2 is concerned, no intensive signal was observed; this indicates the presence of Ti(IV) cations. The ESR signals from Ti^{3+} centers were not detected.

S/C/TiO_2 samples showed intensive singlet lines, which most likely belong to unpaired electrons of dangling bonds in polyaromatic structures. These ESR lines are practically isotropic with g values of 2.0033 ± 0.0002 and line widths of 1.18, 1.41 and 1.13 G for 1S/C/TiO_2 , 4S/C/TiO_2 and 5S/C/TiO_2 catalysts, respectively. Similar lines, but much more intensive, were observed for the initial samples of carbon, which were used for the synthesis. Taking into account the difference in signal intensities for initial carbon and S/C/TiO_2 samples of approximately two orders of magnitude with maintaining of another parameters, it could be assumed with a high probability that the source of signal in the spectra of the catalysts is the same dangling bonds in graphitized carbon fragments.

Some of the previous works dedicated to the ESR investigation of activated carbon and defects in carbon-based nanomaterials as well [13-18] have clearly explained the origin of such signals. This fact, connected with the carbon doping of titanium dioxide, can also be confirmed by the presence in the initial (undoped) samples of only relatively weak asymmetric lines, which some authors [19] referred to oxygen-related centers.

The shape of ESR spectrum were unchanged for samples before and after photocatalysis (Fig. 1). The calculation of the concentrations of these centers (Table 1) were of the same order with those of similar catalysts studied in the work [20]. Such ESR signals are typical for carbon-centered radicals in both natural and activated carbon samples and in carbon nanotubes with defects as well. Such radicals can act as photosensitizers [6].

Decrease of the ESR signal intensity has been observed after photocatalysis in all cases (Fig. 1), which was due to the decrease of concentration of paramagnetic centers (Table 1). Samples with higher sulphur concentration have higher content of paramagnetic centers: thus, for 4S/C/TiO_2 it equals to 9.306×10^{17} spin/g, while for 5S/C/TiO_2 to 9.811×10^{17} spin/g in comparison with 6.849×10^{17} for 1S/C/TiO_2 (Table 1).

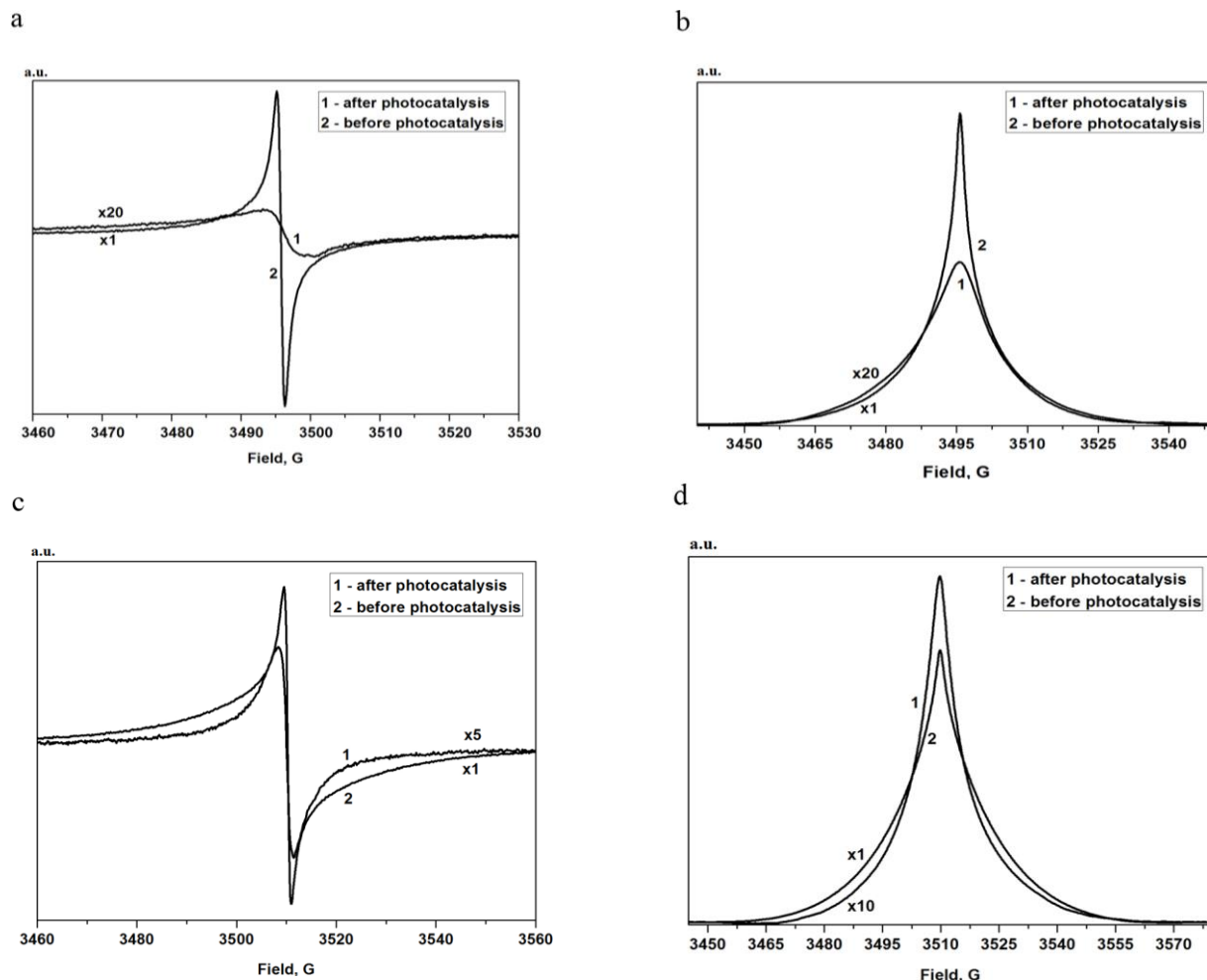
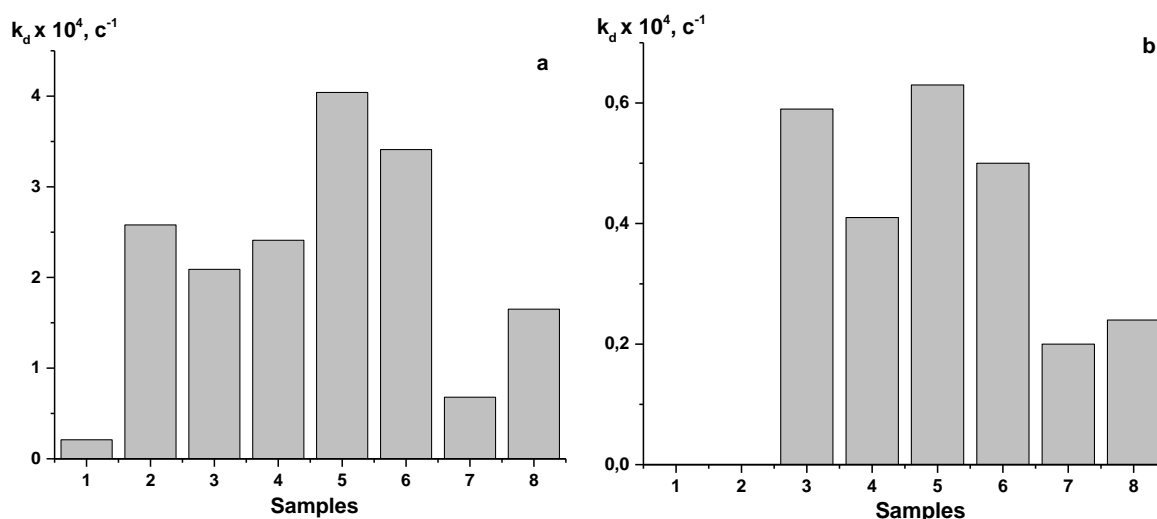


Fig. 1 – Differential (left) and integrated (right) ESR spectra of the samples: 1 – 1S/C/TiO_2 , 2 – 4S/C/TiO_2 , recorded at room temperature (295 K)

Table 1 – Parameters of ESR spectra of the samples studied and calculated values of absolute and relative spins per gram concentrations

Sample	g_{eff}	ΔH_{eff} , G	N (spin/gr.)	ΔN (spin/gr.)	$N_{\text{a.c.}}/N_{\text{b.c.}}$
1S/C/TiO ₂ before catalysis	2.0034	1.18	6.849×10^{17}	6.466×10^{17}	0.056
1S/C/TiO ₂ after catalysis	2.0031	6.38	3.838×10^{16}		
4S/C/TiO ₂ before catalysis	2.0034	1.41	9.306×10^{17}	8.499×10^{17}	0.087
4S/C/TiO ₂ after catalysis	2.0034	3.02	8.707×10^{16}		
5S/C/TiO ₂ before catalysis	2.0033	1.13	9.811×10^{17}	8.237×10^{17}	0.157
5S/C/TiO ₂ after catalysis	2.0033	3.78	1.538×10^{17}		

Here g_{eff} are effective values of g -factor; ΔH_{eff} is spectral linewidth; N and ΔN are absolute and relative concentrations of paramagnetic centers in the samples studied, respectively; $N_{\text{a.c.}}$ and $N_{\text{b.c.}}$ are their concentrations after and before catalysis.


Fig. 2 – Photocatalytic activity of samples under UV (a) and visible irradiation (b): 1 – Photolysis without catalyst, 2 – TiO₂, 3 – 1S/C/TiO₂, 4 – 2S/C/TiO₂, 5 – 3S/C/TiO₂, 6 – 4S/C/TiO₂, 7 – 5S/C/TiO₂, 8 – 6S/C/TiO₂

The samples 3S/C/TiO₂ and 4S/C/TiO₂ possess highest photocatalytic activity both under UV and visible irradiation: 4.04 and $3.41 \times 10^4 \text{ s}^{-1}$ under UV irradiation and 0.63 and $0.50 \times 10^4, \text{ s}^{-1}$ under visible light, respectively (Fig. 2).

Composites 1S/C/TiO₂, 2S/C/TiO₂ and 5S/C/TiO₂ were less photoactive: 2.09, 2.41, 0.68 (UV) and 0.39, 0.41, 0.2 (visible light), respectively.

During the study of transfer of photogenerated electrons and holes in semiconducting materials, as well as their distribution and recombination, using photoluminescent spectroscopy, it was established that the light excitation of TiO₂ samples in the absorption band, regardless of doping (type and quantity), did not lead to the appearance of luminescence. So, the recombination of charges occurs only in a non-radiation way, part of which reveals in photocatalysis, while the other part of the charges is captured/deactivated by defects/traps.

The low photocatalytic activity of the samples with higher content of dopant may be connected with higher concentration of paramagnetic centers which can act as electron-hole recombination centers [10, 21]. The enhanced UV and visible photocatalytic performance of nanocomposites compared with pure titanium dioxide is attributable to the synergistic effect of interfacial bonding, defective sites, change of band gap [11],

participation of dopants in the inhibition of electron-hole recombination, prolongation of charge lifetime, increasing of efficiency of interfacial charge separation [10, 22, 23].

4. CONCLUSIONS

The S/C/TiO₂ powders showed intensive ESR singlet lines, which belong to unpaired electrons of dangling bonds in polyaromatic structures. These ESR lines are practically isotropic with g values of 2.0033 ± 0.0002 .

ESR studies of pure titanium dioxide did not reveal an intense signal, suggesting the presence of Ti(IV) cations and signals from Ti³⁺ centers.

The light excitation of samples, regardless of doping (type and quantity), in the absorption band did not lead to the appearance of luminescence. So the recombination of charges occurs only in a non-radiation way, part of which reveals in photocatalysis, while the other part of the charges is captured/deactivated by defects/traps.

It was established that the decrease of intensity of the ESR signal after photocatalysis in all cases is due to the decrease of the concentration of paramagnetic centers.

Studies of the photocatalysts showed that an increase of sulfur content in the samples leads to an increase of the concentration of paramagnetic centers

and decrease of photocatalytic activity. At high concentrations, the paramagnetic centers act as electron-hole recombination centers.

The S/C/TiO₂ samples were more photocatalytically active under UV and visible irradiation compared with pure titanium dioxide. The enhance of photocatalytic

performance of nanocomposites is attributable to the synergistic effect of interfacial bonding, defective sites, change of band gap, participation of dopants in the inhibition of electron-hole recombination, prolongation of charge lifetime, increasing of efficiency of interfacial charge separation.

Парамагнітні та фотокаталітичні властивості нанокаталізаторів TiO₂, допованих C-S

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Досліджено парамагнітні та фотокаталітичні властивості нанокаталізаторів TiO₂, допованих C-S. Встановлено, що у вуглець-допованих каталізаторів з різним вмістом сірки наявні парамагнітні центри, що відносять до обірваних зв'язків у графітових структурах, інтенсивність їх ліній різко знижувалась після фотокаталітичної реакції. ЕПР сигнали Ti³⁺ центрів не було виявлено. Показано, що збудження світлом зразків TiO₂, незалежно від допування (типу і кількості), у смугу поглинання не призводить до появи люмінесценції, таким чином рекомбінація зарядів відбувається лише безвипромінювальним шляхом, частина якого проявляється у фотокаталізі, тоді як інша частина зарядів захоплюється/деактивується дефектами/пастками. Композитні зразки виявили підвищену фотокаталітичну активність в деструкції сафраніна Т при УФ та видимому опроміненні порівняно з чистим TiO₂.

Ключові слова: Діоксид титану, Вуглець, Сірка, Наноконтрополи, ЕПР спектроскопія, Фотокаталіза.

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