

X-ray Spectral Investigation of SiO₂/TiO₂/C Nanocomposites

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The electronic structure of SiO₂/TiO₂/C nanocomposites was investigated using the ultrasoft X-ray emission spectroscopy (USXES) method. The energy redistribution of valence electrons affected by composition of SiO₂/TiO₂/C hybrid materials was studied. The USXES SiL _{α} , CK _{α} and OK _{α} -spectra for the SiO₂/TiO₂ and SiO₂/TiO₂/C compounds were derived. It was revealed that almost all two-phase oxides penetrate to carbon pores in the ST65+C (50 wt. % C, 17.5 wt. % SiO₂, 32.5 wt. % TiO₂) nanocomposite after high-frequency vibration synthesis. It was shown that penetration of TiO₂ to highly porous carbon is higher than SiO₂. It was found that oxygen related to TiO₂ does not form bonds with carbon atoms. It was revealed that the contribution of s-states in ST20+C (50 wt. % C, 40 wt. % SiO₂, 10 wt. % TiO₂) nanocomposite increased as compared to ST20 (80 wt. % SiO₂, 20 wt. % TiO₂) owing to carbon Cs-states addition. It was shown that SiC is formed in ST65+C nanocomposite owing to substitution of oxygen atoms by carbon atoms in the presence of TiO₂ as a catalyst. Investigation of the electronic structure of SiO₂/TiO₂/C nanocomposites allows solving an important task of predicting their physical and chemical properties and synthesizing materials with necessary properties.

Keywords: Carbon, Silica, Electronic structure, Ultrasoft X-ray emission spectroscopy.

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1. INTRODUCTION

Carbon-oxide nanosystems attract attention of investigators due to the possible practical application as new catalysts and adsorbents, anode for lithium-ion batteries, high-performance supercapacitors [1-3] owing to their unique properties. Nanocomposites functionality and properties exceed those of individual oxides. The papers [4, 5] are devoted to the studies of the electronic structure of silicon dioxide. According to the results of [4], the valence band of silicon dioxide consists of two sub-bands separated by an ionic band. The lower narrow band is formed of O2s states with an admixture of Si3s and Si3p-states [4]. The works [6-9] relate to the electronic structure of titanium dioxide. According to the analysis of the density of states [8], there are predominantly O2p-like valence band states and Ti3d-like conduction band states around the band edges.

Thus, the electronic structure of individual oxides of titanium and silicon was fairly well studied in previous years. However, the electronic structure of SiO₂/TiO₂/C nanocomposites was not so far described in any works. Since properties of materials are determined by their electronic structure, it is important to investigate the electronic structure of SiO₂/TiO₂/C nanocomposites. Studies of the electronic structure of carbon-oxide nanocomposites will allow synthesizing materials with necessary properties.

In this work, a dependence of the energy redistribution of valence electrons in SiO₂/TiO₂/C hybrid materials on the composition has been elucidated. A character of the interatomic interaction in complex systems has been determined.

2. MATERIALS AND METHODS

Complex nanooxides were synthesized using a mixture of metal chlorides by flame synthesis technique [10]. Composition of nanooxide and nanooxide-carbon mixed systems is presented in Table 1.

Initial carbon materials were synthesized by MAST Carbon Technology Ltd., Guildford, UK. The average size of SiO₂ nanoparticles in A300 was 8.5 nm, and in A500, it was 5 nm.

Table 1 – The composition of nanooxide and nanooxide-carbon mixed systems

| Sample | C _{SiO₂} , wt. % | C _{TiO₂} , wt. % | C _C , wt. % |
|--------|--------------------------------------|--------------------------------------|------------------------|
| ST20 | 80 | 20 | – |
| ST65 | 35 | 65 | – |
| ST94 | 6 | 94 | – |
| ST20+C | 40 | 10 | 50 |
| ST65+C | 17.5 | 32.5 | 50 |
| ST94+C | 3 | 47 | 50 |
| A300+C | 50 | – | 50 |
| A500+C | 50 | – | 50 |

X-ray emission SiL _{α} , OK _{α} and CK _{α} -bands were obtained by means of the ultrasoft X-ray emission spectroscopy using X-ray spectrometer RSM-500 (Burevestnik, St. Petersburg, Russia). The energy resolution of RSM-500 was $\Delta E \approx 0.2-0.3$ eV for the OK _{α} -spectra, $\Delta E \approx 0.2$ eV for the CK _{α} and $\Delta E \approx 0.4$ eV for the SiL _{α} -bands. The operating conditions of the X-ray tube were: accelerating voltage, $U_a = 5$ kV and an anode current, $I_a = 2.5$ mA. X-ray quanta were registered using a scanning detector on basis of the channel electron multiplier KBL1505 (Dr. Sjuts Optotechnik GmbH, Germany). The energy

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positions of the OK_{α} , CK_{α} and SiL_{α} -bands in the samples were determined relative to that of CrL_{1} -line of the pure metal in the first order and ZrM_{ζ} -line in the second order, respectively [11]. The powder samples were rubbed directly onto the side of the distended copper anode, cooled using running water at a temperature of 10-15 °C.

3. RESULTS AND DISCUSSION

The SiO_2 and TiO_2 chemical bonds appear at synthesis as well as at electron bombardment owing to interaction between the surface layer and atoms diffused to the near-surface layer. The interaction between highly porous carbon materials and two-phase systems should be studied since some of the surface atoms that had broken bonds in individual biphasic nanoparticles are already involved in bonds. The dependence of profile change on two-phase nanoparticle composition may be defined since the OK_{α} -emission band appears in the second order with the CK_{α} -emission band of highly porous carbon. Ratio of intensity should be considered as well as dependence of the OK_{α} - and CK_{α} -bands shapes on nanooxide composition should be analyzed (Fig. 1).

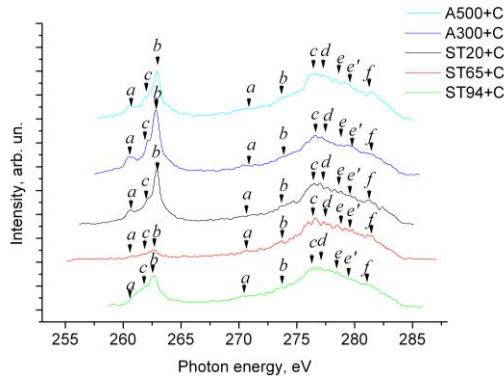


Fig. 1 – The USXES OK_{α} - and CK_{α} -bands of $SiO_2/TiO_2/C$ composites compared to A300+C and A500+C

From Fig. 1, it is clear that in the ST20 band $\frac{I_{OK_{\alpha}}^{peak}}{I_{CK_{\alpha}}^{peak}} = 1.4$ that is less than in SiO_2 (A300)+C composite, but somewhat greater than in SiO_2 (A500)+C. From the shape of the OK_{α} it is obvious that the main contribution to its intensity is made by SiO_2 , therefore the OK_{α} shape is similar to that obtained from the SiO_2 (A300)+C composite.

Intensity of the OK_{α} -band sharply decreases with an increase in the TiO_2 content in ST65+C composite and $\frac{I_{OK_{\alpha}}^{peak}}{I_{CK_{\alpha}}^{peak}} = 0.2$. The OK_{α} -emission band widens to high- and low-energy branches and becomes similar to the OK_{α} -band shape in pure TiO_2 . Increase of TiO_2 content up to 94 % leads to increasing intensity of the OK_{α} -band $\frac{I_{OK_{\alpha}}^{peak}}{I_{CK_{\alpha}}^{peak}} = 0.7$ and its shape becomes similar to TiO_2 shape. It should be mentioned that shapes of the CK_{α} -emission bands obtained from ST20+C, ST65+C and ST94+C composites are similar, because all the features in these spectra are at the same values of photon energy ($h\nu$).

A sharp decrease in the intensity of the oxygen

emission band in the ST65+C composite indicates the penetration of almost all two-phase oxides into carbon pores after high-frequency vibrational synthesis. However, after the ST94+C synthesis the three-fold increase in the intensity of the OK_{α} obviously indicates that the decrease in the SiO_2 content still leads to an increase in the intensity of the OK_{α} , apparently due to less ST94 penetration into the pores of carbon than ST65. However, the number of ST94 nanoparticles unlocked in pores is still 1.6 times less than that in the A500+C composite. This fact indicates the higher penetration of TiO_2 than SiO_2 into highly porous carbon.

The CK_{α} -emission bands of highly porous carbon and ST20+C, ST65+C and ST94+C composites should be compared on a common energy scale to determine the nature of mechanical or chemical penetration of nanoparticles into carbon pores (Fig. 2).

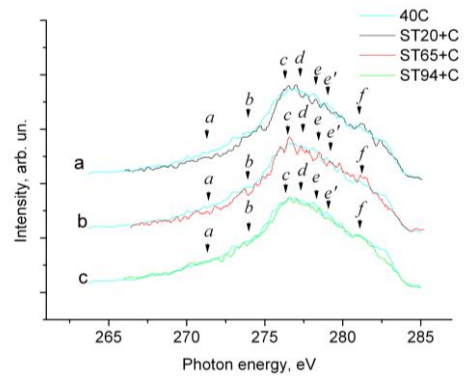


Fig. 2 – The USXES CK_{α} -bands of highly porous carbon after 40 % burning off and of $SiO_2/TiO_2/C$ composites: ST20+C (a); ST65+C (b); ST94+C (c)

Comparison of the CK_{α} -bands (Fig. 2a) shows the following result: the main changes are revealed at low-energy part, where the low-energy profile shifts to the short-wave range owing to the intensity decrease of the composite CK_{α} -band that leads to spectrum narrowing and to distinct expression of low-energy sub-band. The largest intensity decrease of the CK_{α} -band is observed in 274.5-276 eV and 271.3-273 eV energy ranges leading to narrowing of the spectrum by 0.5-0.6 eV.

The significant decrease in the intensity of the low-energy part of the CK_{α} -band was observed when going from highly porous carbon to ST65+C composite (see Fig. 2b). The CK_{α} -band intensity decrease is observed in the whole long-wave part in the energy range 267-275 eV. This effect leads to spectrum narrowing by 0.5-1.2 eV. This is in accordance with a sharp decrease of intensity of the OK_{α} -emission band. The CK_{α} -spectrum of ST65+C becomes broader due to increasing intensity of the “f” peculiarity near emission threshold corresponding to the top of valence band.

Considering the comparison of the CK_{α} -bands of highly porous carbon and ST94+C composite (Fig. 2c), one can assume that the differences between these bands are much smaller than in Fig. 2b. The profile narrowing is smaller than when comparing the CK_{α} -bands of highly porous carbon and ST65+C composite.

The shape changes of the OK_{α} -emission bands should be carried out by means of peak reduction to the same intensities for establishing shape dependence (Fig. 3).

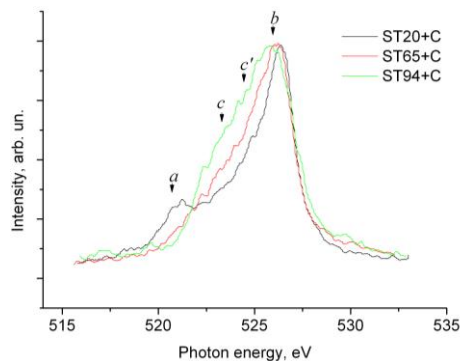


Fig. 3 – The USXES OK_α-bands of ST20+C, ST65+C, ST94+C in the second order normalized to the same intensity

Taking into account that 80 % SiO₂ is present in ST20 composite, one can assume that the main peak of its OK_α-band is the narrowest. The OK_α-band of ST65+C composite was found to be wider in both low- and high-energy range and simultaneously is narrower than the OK_α-band of ST94+C-composite. The fine structure mainly changes in the low-energy part in case of the OK_α-band widening, and its shape approaches to the OK_α-band shape in pure TiO₂ nanopowder. Such changes of the OK_α-bands of double phases indicate that oxygen related to TiO₂ may not be involved in the formation of bonds with carbon atoms. To understand the nature of the interaction of oxygen when forming composites ST+C it is worth to compare the OK_α-bands of pure ST-systems and composites (Fig. 4).

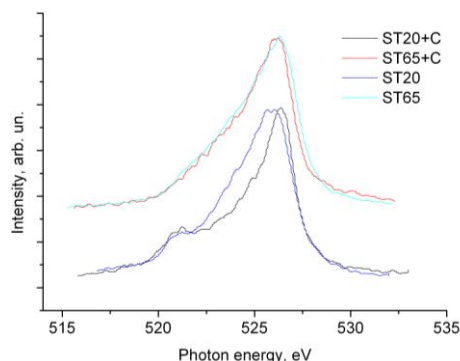


Fig. 4 – The USXES OK_α-bands of pure matrices ST20 and ST65 and SiO₂/TiO₂/C composites ST20+C; ST65+C

Intensities of the OK_α-bands of pure ST65 and composite are almost equal. Insignificant difference is observed only in the low-energy part. Such results indicate the weak interaction of oxygen in this composite with highly porous carbon.

The OK_α-band of ST20+C composite is narrower than the same band in pure ST20. Such effect may be caused by impurities present in ST20. The OK_α-band similarity of ST20+C and SiO₂ confirms above-mentioned assumption, since there is 80 % of SiO₂ in ST20. Therefore, the major changes in the OK_α-band of composite in comparison to those obtained from highly porous carbon are due to the interaction of carbon with silicon.

The comparison of the X-ray SiL_α-emission bands of pure ST20 and ST20+C composites (Fig. 5a) reveals the SiL_α-band intensity increase in the region of minimum. Above-mentioned effect indicates an increase in the

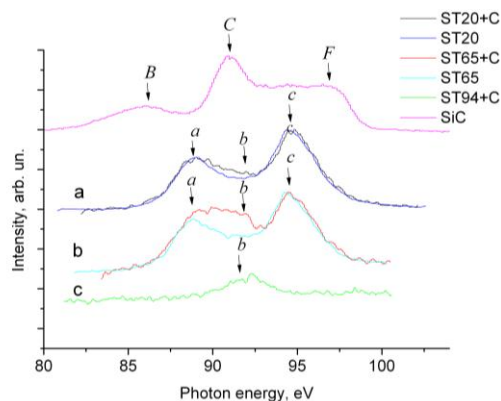


Fig. 5 – The USXES SiL_α-bands of pure matrices ST20, ST65 and SiO₂/TiO₂/C composites ST20+C; ST65+C, ST94+C and SiC

contribution of s-state in this energy region owing to carbon Cs-states addition.

When going to ST65, the shape of the SiL_α-band changes in the energy range corresponding to the minimum of this band in SiO₂. The intensity of the SiL_α-band increases in the above-mentioned range and becomes greater than “a”-peak intensity (Fig. 5b). Such intensity increase is observed in the energy range where the main maximum of the SiC SiL_α-emission band is located [12]. Such sharp increase of the SiL_α-band intensity is associated with SiC formation owing to substitution of oxygen atoms by carbon atoms in the presence of TiO₂ as a catalyst. The only one peak in the range of photon energies, which corresponds to the maximum “c” of the SiL_α-band in silicon carbide, appears in the SiL_α-spectrum of ST94+C-composite.

Since the content of SiO₂ in ST94 is very small, some background enhancements at $h\nu = 85$ eV and in the energy region $h\nu = 95$ -100 eV can be considered as the maxima “B” and “F” of the SiL_α obtained from SiC due to the fact that oxygen was replaced by carbon in 6 % of SiO₂.

4. CONCLUSIONS

To conclude, we have investigated the electronic structure of SiO₂/TiO₂/C nanocomposites using the ultrasoft X-ray emission spectroscopy (USXES) method. Our study revealed the penetration of almost all two-phase oxides into carbon pores in the ST65+C composite after high-frequency vibration synthesis. It was found that less ST94 penetrate into the pores of carbon than ST65. We also revealed the higher penetration of TiO₂ than SiO₂ into highly porous carbon. Furthermore, we found that oxygen related to TiO₂ may not be involved in the formation of bonds with carbon atoms. It was shown that the contribution of s-state in ST20+C composites increased as compared to ST20 owing to carbon Cs-states addition. The SiC formation in ST65+C owing to substitution of oxygen atoms by carbon atoms in the presence of TiO₂ as a catalyst was revealed.

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Рентгеноспектральне дослідження нанокompatитів SiO₂/TiO₂/CБ. Ільків¹, С. Петровська¹, Я. Зауличний²

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Електронна структура нанокompatитів SiO₂/TiO₂/C досліджена методом ультрам'якої рентгенівської емісійної спектроскопії (УМРЕС). Енергетичний перерозподіл валентних електронів в гібридних SiO₂/TiO₂/C матеріалах було вивчено в залежності від складу. Були отримані УМРЕС SiL_α, CK_α та ОК_α-спектри SiO₂/TiO₂ та SiO₂/TiO₂/C сполук. Було виявлено, що майже всі двофазні оксиди проникають у пори вуглецю після високочастотного вібраційного синтезу в композиті ST65+C (50 мас % C, 17.5 мас % SiO₂, 32.5 мас % TiO₂). Було показано, що проникнення TiO₂ у високопористий вуглець більше, ніж SiO₂. Було виявлено, що кисень, який відноситься до TiO₂, не утворює зв'язків з атомами вуглецю. Було встановлено, що вклад s-станів в нанокompatиті ST20+C (50 мас % C, 40 мас % SiO₂, 10 мас % TiO₂) зростає у порівнянні з ST20 (80 мас % SiO₂, 20 мас % TiO₂) завдяки додаванню Cs-станів вуглецю. Було показано, що SiC формується в нанокompatиті ST65+C завдяки заміщенню атомів кисню атомами вуглецю у присутності TiO₂, як каталізатора. Дослідження електронної структури нанокompatитів SiO₂/TiO₂/C дозволяє вирішити важливу задачу передбачення їх фізичних та хімічних властивостей та синтезувати матеріали з необхідними властивостями.

Ключові слова: Вуглець, Оксид кремнію, Електронна структура, Ультрам'яка рентгенівська емісійна спектроскопія.