

Interactions in Al₂O₃ - graphene oxide composite: XPS study

*A. I. Kukharenko^{1,2}, S. O. Cholakh¹, E. Z. Kurmaev^{1,2}, I. S. Zhidkov^{1,2}

¹ Institute of Physics and Technology, Ural Federal University,
21 Mira St., Yekaterinburg, 620002, Russian Federation

² M.N. Mikheev Institute of Metal Physics, Russian Academy of Sciences, Ural Branch,
18 S. Kovalevskaya St., Ekaterinburg, 620108, Russian Federation

*Corresponding author: Andrey I. Kukharenko, E-mail: a.i.kukharenko@urfu.ru

Submitted 30 November 2023, received in revised form 28 February 2024

The structure of an aluminum oxide/graphene oxide (GO) composite was studied using X-ray photoelectron spectroscopy (XPS). High-energy resolved XPS measurements of Al 2p-core level spectra revealed the formation of Al–O–C bonds, which indicated the occurrence of interfacial reactions between Al₂O₃ and GO in the process of composite synthesis. An increase in intensity in the near-edge region of XPS valence band (VB) spectrum was observed with increasing GO concentration, indicating possible contribution of the electronic states of carbon. Filling the electronic states on the edge of VB allows to associate GO doping with the loss of dielectric properties of the original Al₂O₃ compound. Addition of graphene oxide to Al₂O₃ ceramics changed conductive properties of the composite due to formation of new chemical bonds.

Keywords: X-ray photoelectron spectroscopy; graphene oxide; alumina oxide; composite.

INTRODUCTION

Composites are materials consisting of two or more different substances that share their properties to form a new material with new properties. As a rule, in a composite there are no chemical reactions between its constituent substances and each substance entering the composite retains own basic properties. On the other hand, formation of chemical bonds between the materials comprising the composite gives it additional strength and rigidity. This is especially true for ceramic composites where ceramic pores are filled with fillers. Alumina (Al₂O₃-based) ceramics is often used in composites because it has such useful properties as high melting point, hardness and strength, wear, and chemical resistance [1]. However, alumina-based industrial ceramics has high density and fragility. Recently, it was found that disadvantages of alumina-based ceramics can be eliminated using graphene. It turned out that inclusion of graphene improved the mechanical properties of brittle materials, and a decrease in grain size significantly increased the strength of ceramics. The composites comprised of graphene and ceramic materials have a great potential for forming additional functional properties of interest for various applications [2]. On one hand, graphene exhibits exceptional electrical, thermal, optical, and mechanical properties [3], and on the other hand, ceramic materials act as mechanically and chemically resistant matrices with synergistic dielectric or semiconductor properties [4]. Combination of these properties in one material, a ceramics/graphene composite, can result in unique conductive materials for high-temperature applications in thermoelectric devices [5] as well as electrode material

for lithium-ion batteries [6] and electrochemical capacitors [7]. Graphene oxide (GO) is very convenient to use for chemical preparation of Al₂O₃/graphene composites because GO can be easily prepared from graphite [7] and it is dispersible in water [8]. Thermal or chemical reduction of GO to reduced graphene oxide (rGO) is used to acquire electrical conductivity of the ceramics/GO composite [9]. In the present paper structure of Al₂O₃/GO composite was studied employing X-ray photoelectron spectroscopy (XPS).

XPS is a very powerful technique, suitable for characterization of elemental and chemical composition of subsurface layers (1–10 nm) of solids. The phenomenon is bombardment of a surface with X-ray photons. The monochromatic soft X-ray beam is based on the external photoelectric effect, which refers to the bombardment of a surface with X-ray photons. A monochromatic soft X-ray beam is used for excitation of electrons. Kinetic energy and quantity of the electrons knocked out from the atoms' core levels are measured using a channel detector. The difference between the photon's energy and the sum of the electrons' kinetic energy and the work function determines the electron binding energy. The resulting XPS spectrum represents the dependence of the number of photoelectrons on the binding energy. The binding energy of the electrons is a characteristic of the elements, but it is also affected by the formal oxidation state, the local bonding environment such as the nature of the nearest-neighbor atoms, their number and electronegativity, bonding hybridization etc. Therefore, XPS is sensitive to the chemical nature of the materials and provides somewhat different results for different

chemical bonds. The surface sensitivity of XPS makes it a valuable tool in the study of 2D materials such as graphene and graphene oxide (GO).

EXPERIMENTAL

Al_2O_3 /graphene powders with graphene concentrations of 0.56 % and 1.24 wt. % were prepared in the following way: Al_2O_3 (Taimei TM-DAR, > 99.99 % purity) powder for ceramic matrices with an average particle size of around 150 nm were dispersed in distilled water, then mixed with the graphene oxide dispersion and finally ball milled for 1 h. Homogeneous mixtures were spray dried and uniaxially pressed (30 MPa) prior to spark plasma sintering in an FCT-HP D25/1 (FCT Systeme GmbH) apparatus in vacuum (10^{-1} mbar) with the heating rate of 50 °C/min under applied pressure of 80 MPa, and holding time of 1 min. The final sintering temperature in case of Al_2O_3 /graphene composites was 1500 °C. Densities close to 100 % theoretically expected were found in all composites.

The dielectric properties of the samples were previously studied [10] by standard low-frequency impedance measurements (PSM1735-NumetriQ). The results are presented in the Table 1.

Table 1

The results of measuring the relative dielectric constant ϵ' at a frequency of 1 kHz and conductivity σ [10].

Sample	σ , S/cm	ϵ'
Al_2O_3	10^{-11}	10
$\text{Al}_2\text{O}_3 + 0.56\%$ GO	10^{-7}	10^2
$\text{Al}_2\text{O}_3 + 1.24\%$ GO	10^{-1}	$-2,2 \cdot 10^{4*}$

* negative value of dielectric constant as for conductors

X-ray photoelectron spectra were measured using a PHI 5000 Versa Probe XPS spectrometer (ULVAC Physical Electronics, USA) based on a classic X-ray optic scheme with a hemispherical quartz monochromator and an energy analyzer working in the range of binding energies from 0 to 1500 eV. Electrostatic focusing and magnetic screening was used to achieve the energy resolution of $\Delta E \leq 0.5$ eV for Al K_α radiation (1486.6 eV). An ion pump was used to maintain the analytical chamber at 10^{-7} Pa, and dual channel neutralization was used to compensate local surface charge generated during the measurements. The XPS spectra were recorded using Al K_α X-ray emission – the spot size was 200 mm, the X-ray power delivered to the sample was less than 50 W, and typical signal-to-noise ratios were greater than 10000:3.

RESULTS AND DISCUSSIONS

Fig. 1 presents the XPS survey spectra of Al_2O_3 and Al_2O_3 /GO composites measured at 600–0 eV binding energy range, and Table 2 shows the surface composition of the studied samples obtained from these

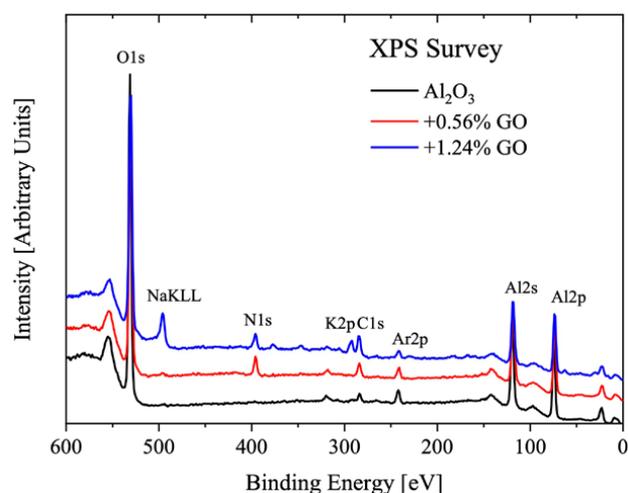


Fig. 1. XPS survey spectra of Al_2O_3 and Al_2O_3 /GO composites

measurements. The sample annealed at 1500 °C with a high content of GO showed the contamination with N, K, Ca, Na impurities. The presence of such impurities is associated with the preparation of GO. Fig. 2 shows high-energy resolved XPS Al 2p-spectra in the initial (b) and GO-doped Al_2O_3 ceramics (a). It is seen that GO-doping led to a noticeable broadening of the XPS Al 2p-spectrum and, along with the main component centered at the binding of 74.4 eV, a high-energy contribution appeared at the binding energy of 75.2 eV, which can be attributed to the formation of Al–O–C bonds [11].

The XPS valence band spectrum of Al_2O_3 (Fig. 3) shows the low-energy O 2s-subband located at 23.3 eV and upper valence band at 0–12 eV composed by mixed O 2p and Al 3p (3s)-states in full accordance with available XPS-measurements and DFT-calculations [12]. GO-doping is accompanied by appearance of C 2s-states at 17.3 eV and additional fine structure at 0–4 eV. Relative intensity of these additional bands increases with graphene oxide concentration, which undoubtedly connects their origin with the carbon electronic states. An interesting moment is filling the electronic states on the edge of VB (in the region of 0–4 eV) upon adding GO that allows to connect doping the ceramics

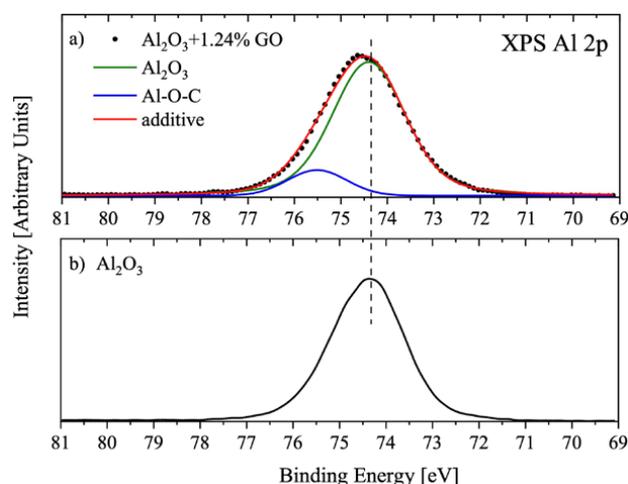


Fig. 2. XPS Al 2p of $\text{Al}_2\text{O}_3 + 1.24\%$ GO composite (a) and Al_2O_3 (b)

Table 2

Surface composition of Al_2O_3 , $\text{Al}_2\text{O}_3 + 0.56\% \text{GO}$ and $\text{Al}_2\text{O}_3 + 1.24\% \text{GO}$ 1500 °C (in at. %).

Sample	C	O	Al	N	K	Ca	Na
Al_2O_3	4	60.4	35.6	-	-	-	-
$\text{Al}_2\text{O}_3 + 0.56\% \text{GO}$	8.9	53.1	32.6	5.4	-	-	-
$\text{Al}_2\text{O}_3 + 1.24\% \text{GO}$	10.4	50.1	28.3	5	1.1	0.3	4.8

with the loss of dielectric properties of the initial Al_2O_3 compound described by Fernández-García et al. [10].

CONCLUSION

Addition of graphene oxide to Al_2O_3 ceramics led to the formation of Al–O–C bonds and the appearance of fine structure in the valence band spectrum in the region of 0–4 eV. The results are in good agreement with previous data on the study of dielectric properties and conductivity of Al_2O_3 –GO ceramic samples [10]. An increase of the relative dielectric constant and conductivity was observed in Al_2O_3 –GO ceramics at the low concentration of GO (0.56 wt. %) compared to undoped Al_2O_3 ceramics. Such changes are associated with variation in the microstructure of the composite (grain size). Addition of 1.24 wt. % GO led to a change in the electrical properties of the material resulting in a metallic type of conductivity. Our XPS studies showed that the reason for this was the interaction between the GO and Al_2O_3 phases due to formation of new chemical bonds and, as a consequence, a change in the structure of the valence band.

ACKNOWLEDGEMENTS

This work was supported by Ministry of Science and High Education of the Russian Federation: Theme “Electron” No AAAA-A18-118020190098-5 and Project FEUZ-2023-0013. We thank José Luis Menéndez and Lucía Fernández-García (Consejo Superior de Investigaciones Científicas (CSIC) – Universidad de Oviedo) for sample preparation.

REFERENCES

- Abyzov A. M. Aluminum Oxide and Alumina Ceramics (Review). Part 2. Foreign Manufacturers of Alumina Ceramics. *Technologies and Research in the Field of Alumina Ceramics, Refractories and Industrial Ceramics*, 2019, vol. 60, pp. 33–42. doi: 10.1007/s11148-019-00305-1.
- Centeno A., Rocha V. G., Alonso B., Fernández A., Gutierrez-Gonzalez C. F., Torrecillas R., Zurutuza A. Graphene for tough and electroconductive alumina ceramics *J. Eur. Ceram. Soc.*, 2013, vol. 33, pp. 3201–3210. doi: 10.1016/j.jeurceramsoc.2013.07.007.
- Porwal S., Grasso S., Reece M.J. Review of graphene–ceramic matrix composites. *Adv. Appl. Ceram.*, 2013, vol. 112, no. 8, pp. 443–454. doi: 10.1179/174367613X13764308970581.
- Jankovsky O., Simek P., Sedmidubsky D., Huber S., Pumera M., Sofer Z. Towards highly electrically conductive and thermally insulating graphene nanocomposites: Al_2O_3 –graphene. *RSC Advances*, 2014, vol. 4, no. 15, pp. 7418–7424. doi: 10.1039/C3RA45069D.

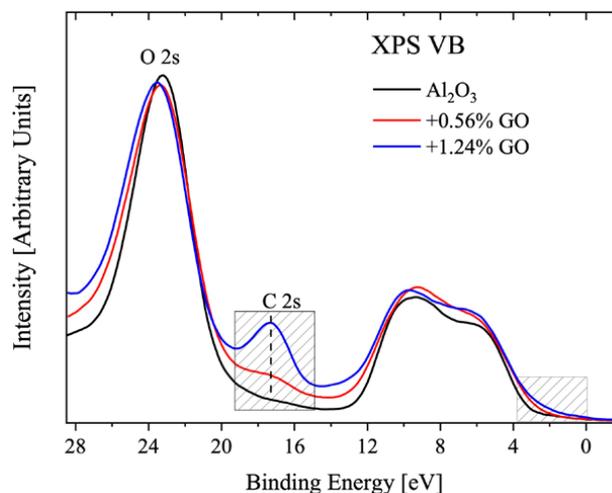


Fig. 3. XPS valence bands of Al_2O_3 and $\text{Al}_2\text{O}_3/\text{GO}$ composites

- Meng F., Li J., Cushing S. K., Bright J., Zhi M., Rowley J. D., Hong Z., Manivannan A., Bristow A. D., Wu N. Photocatalytic water oxidation by hematite/reduced graphene oxide composites. *ACS Catal.*, 2013, vol. 3, no. 4, pp. 746–751. doi: 10.1021/cs300740e.
- Wang H., Cui L.-F., Yang Y., Casalongue H.S., Robinson J. T., Liang Y., Cui Y., Dai H. Mn_3O_4 –graphene hybrid as a high-capacity anode material for lithium ion batteries. *J. Am. Chem. Soc.* 2010. vol. 132, no. 40, pp. 13978–13980. doi: 10.1021/ja105296a.
- Yan J., Fan Z., Wei T., Qian W., Zhang M., Wei F. Fast and reversible surface redox reaction of graphene– MnO_2 composites as supercapacitor electrodes. *Carbon*, 2010, vol. 48, pp. 3825–3833. doi: 10.1016/j.carbon.2010.06.047.
- Zaaba N. I., Foo K. L., Hashim U., Tan S. J., Liu W.-W., Voon C. H. Synthesis of Graphene Oxide using Modified Hummers Method: Solvent Influence. *Procedia Engineering*, 2017, vol. 184, pp. 469–477. doi: 10.1016/j.proeng.2017.04.118.
- Shin J.-H., Hong S.-H. Fabrication and Properties of Reduced Graphene Oxide Reinforced Yttria-Stabilized Zirconia Composite Ceramics. *J. Eur. Ceram. Soc.*, 2014, vol. 34, no. 5, pp. 1297–1302. doi: 10.1016/j.jeurceramsoc.2013.11.034.
- Fernández-García L., Suárez M., Menéndez J., Pecharromán C., Menéndez R., Santamaría R. Dielectric behavior of ceramic–graphene composites around the percolation threshold. *Nanoscale Res. Lett.* 2015, vol. 10, no. 216. doi: 10.1186/s11671-015-0921-4.
- Liu F.C., Dong P., Lu W., Sun K. On formation of Al–O–C bonds at aluminum/polyamide joint interface. *Appl. Surf. Sci.*, 2019, vol. 466, pp. 202–209. doi: 10.1016/j.apsusc.2018.10.024.
- Perevalov T. V., Shaposhnikov A. V., Gritsenko V. A., Wong H., Han J. H., Kim C. W. Electronic Structure of a- Al_2O_3 : Ab Initio Simulations and Comparison with Experiment. *JETP Letters*. 2007, vol. 85, pp. 165–168. doi: 10.1134/S0021364007030071.