IOCN 2025 Conference
The 5th International Online Conference on Nanomaterials
22–24 September 2025 | Online
IMET RAS
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Nanostructured composite powders based on oxygen-free graphene and Zr/Ce oxides for advanced ceramics

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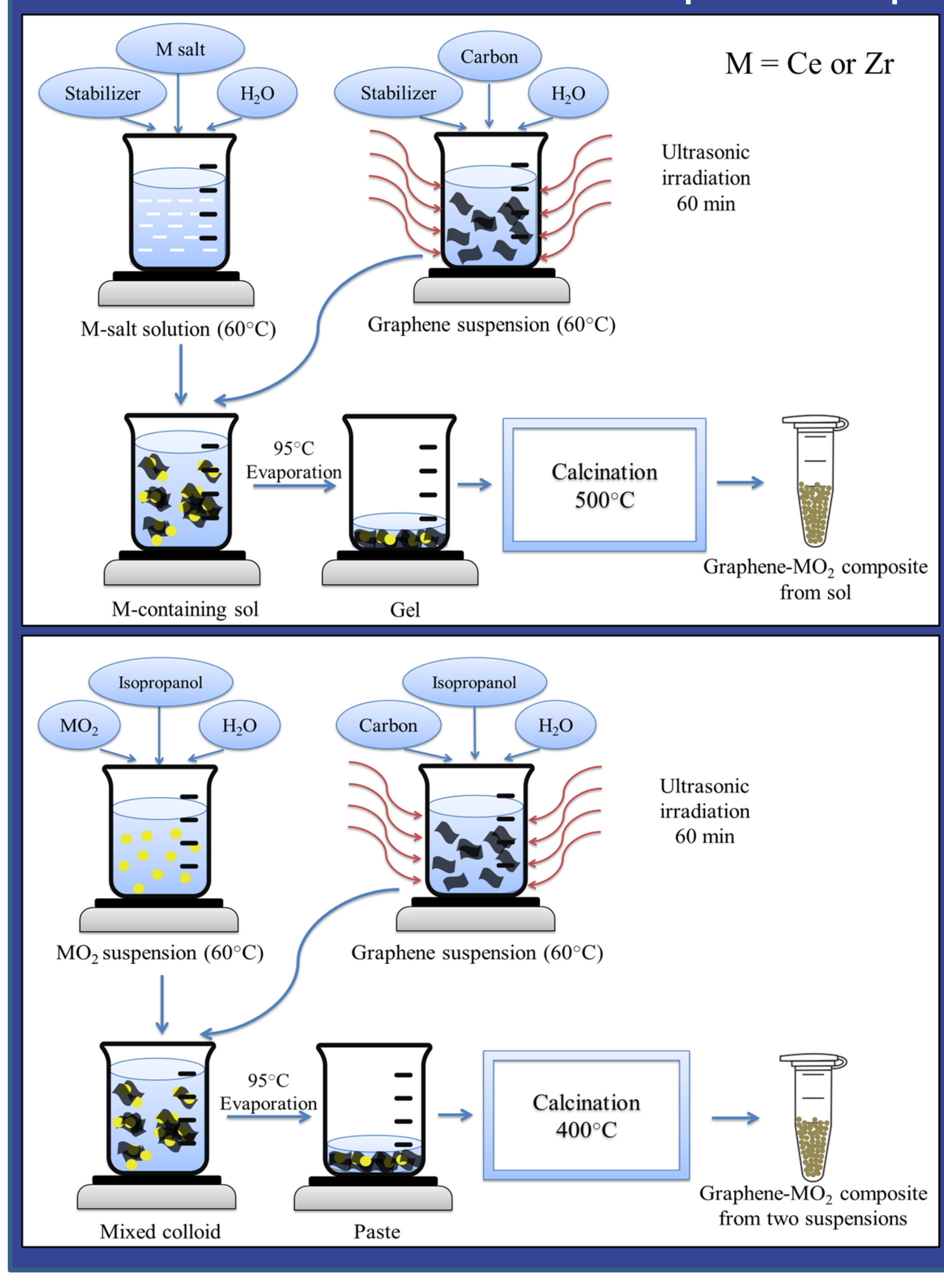
This study focuses on the development of novel nanostructured composites based on cerium or zirconium oxides and oxygen-free graphene, which are in high demand for applications in electronics, energy, and catalysis. The main objective is to propose an efficient synthesis method for hybrid powders combining sol-gel and sonochemical techniques, ensuring uniform nanoscale distribution of components and optimal properties of the resulting ceramics. The formation mechanisms of graphene suspensions and hybrid structures are theoretically substantiated, and the influence of graphene on mass transfer and sintering processes is elucidated. The results obtained form the basis of a technology that enables the production of high-density and structurally homogeneous fine-grained ceramics for a wide range of modern applications.

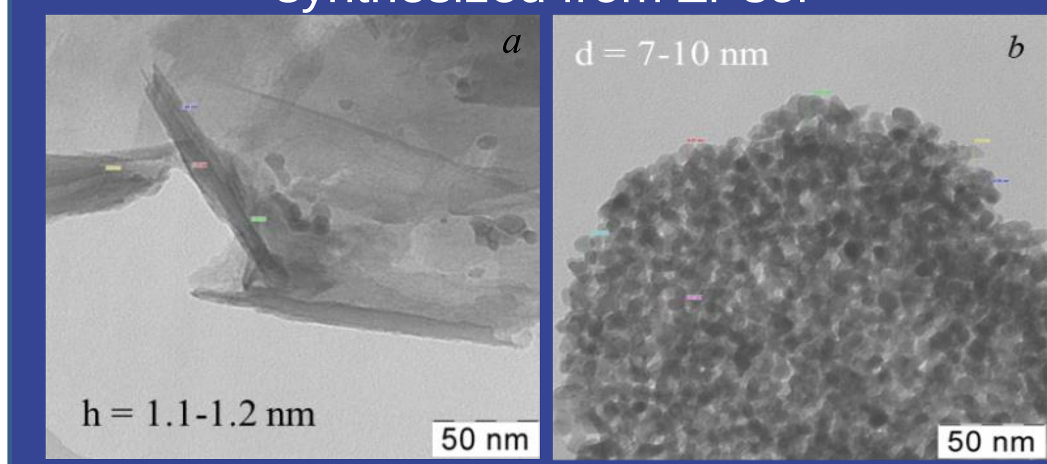
Schemes of developed composite syntheses



For the synthesis of composites based on oxygen-free graphene and metal oxides, a method based on a combination of sol-gel and sonochemical techniques has been developed in two modifications.

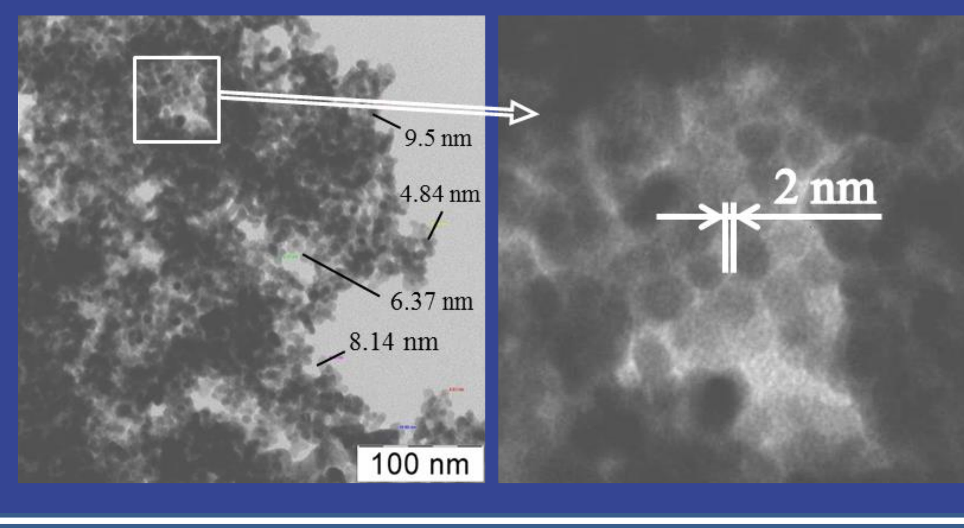
The synthesis included:
1) sonochemical preparation of oxygen-free graphene suspension;
2) connection of graphene suspension with M-containing sol or with MO_2 nanopowders suspensions in aqua-alcohol mixture;
3) evaporation of the mixed colloid to form gel or paste;
4) heat treatment of gel or paste in an air furnace to produce graphene-MO_2 composite powder.

TEM images for a grapbene shetts and graphene-zirconia powdery composite synthesized from Zr-sol



Multilayer graphene sheet with a thickness not exceeding 2 nm in suspension (a) and graphene-ZrO_2 composite obtained from it (b). In composite, the ZrO_2 crystallites with sizes of 7-10 nm are discretely incorporated into graphene sheets. Zirconia nanocrystals are discretely incorporated into graphene sheets at distances of 1–2 nm from each other.

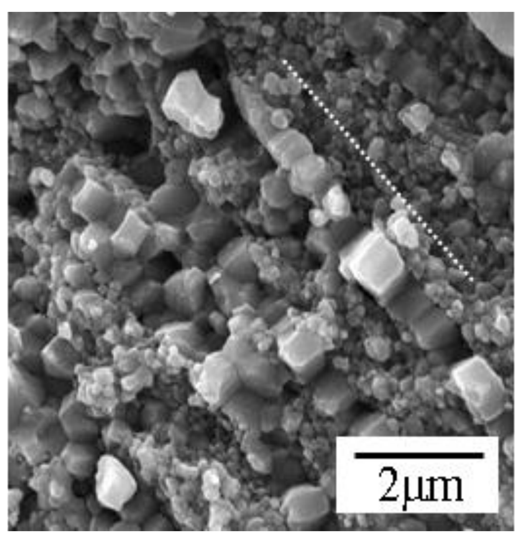
TEM images for a graphene-ceria powdery composite synthesized from Ce-sol



The composite consisted of thin agglomerates formed by crystallites with predominant sizes of 4-10 nm, which practically form a "lace". At the same time, the nanocrystals are not densely packed, but form a single whole, being separated by 1-2 nm gaps. More precisely, these semitransparent graphene layers in the composite contribute to the formation of CeO_2 nanocrystals associates, while at the same time preventing their enlargement.

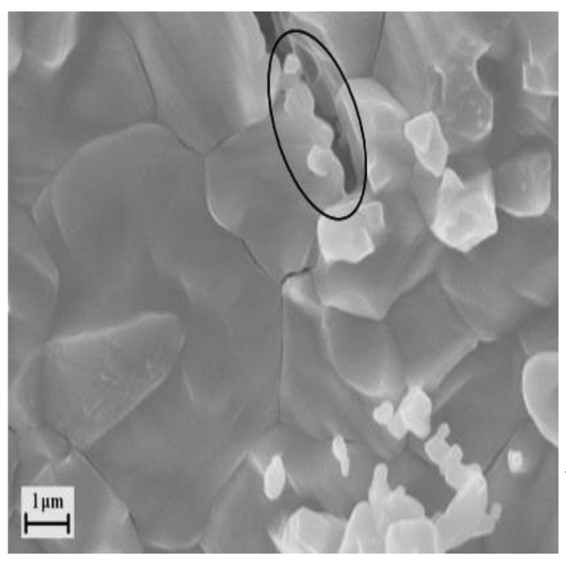
SEM

Hot pressing



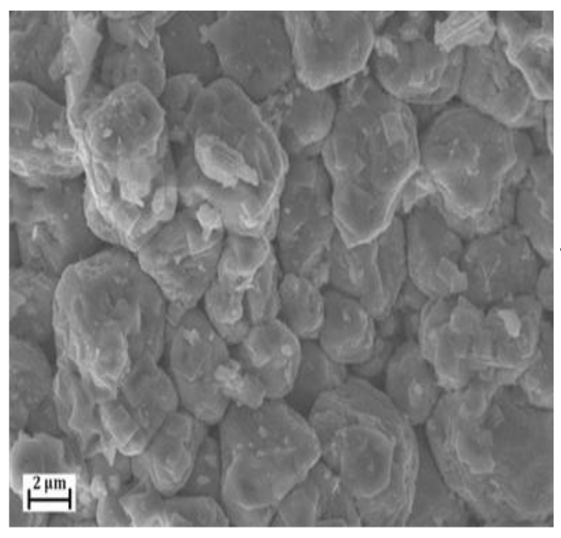
Fine-grained ceramics with a grain size of less than 1 micron were obtained, most of the grains were rounded and had a diameter of 100-300 nm. On the chip, the material looks uniform, individual grains with sizes of 400-500 nm are observed only sporadically.

Vacuum sintering



The ceramics exhibit fine equiaxed and layered grains with a layer thickness of about 30 nm, as well as a combination of well- and poorly sintered areas containing granules of 0.1–0.4 μm in size. The relative density of such a sample is 80.4%. An atypical pore of 5×0.5 μm in size was revealed, formed due to the non-uniform distribution of the powder and limited by 1–2 grains, while no signs of grain destruction or intergranular spaces were detected.

Spark plasma sintering

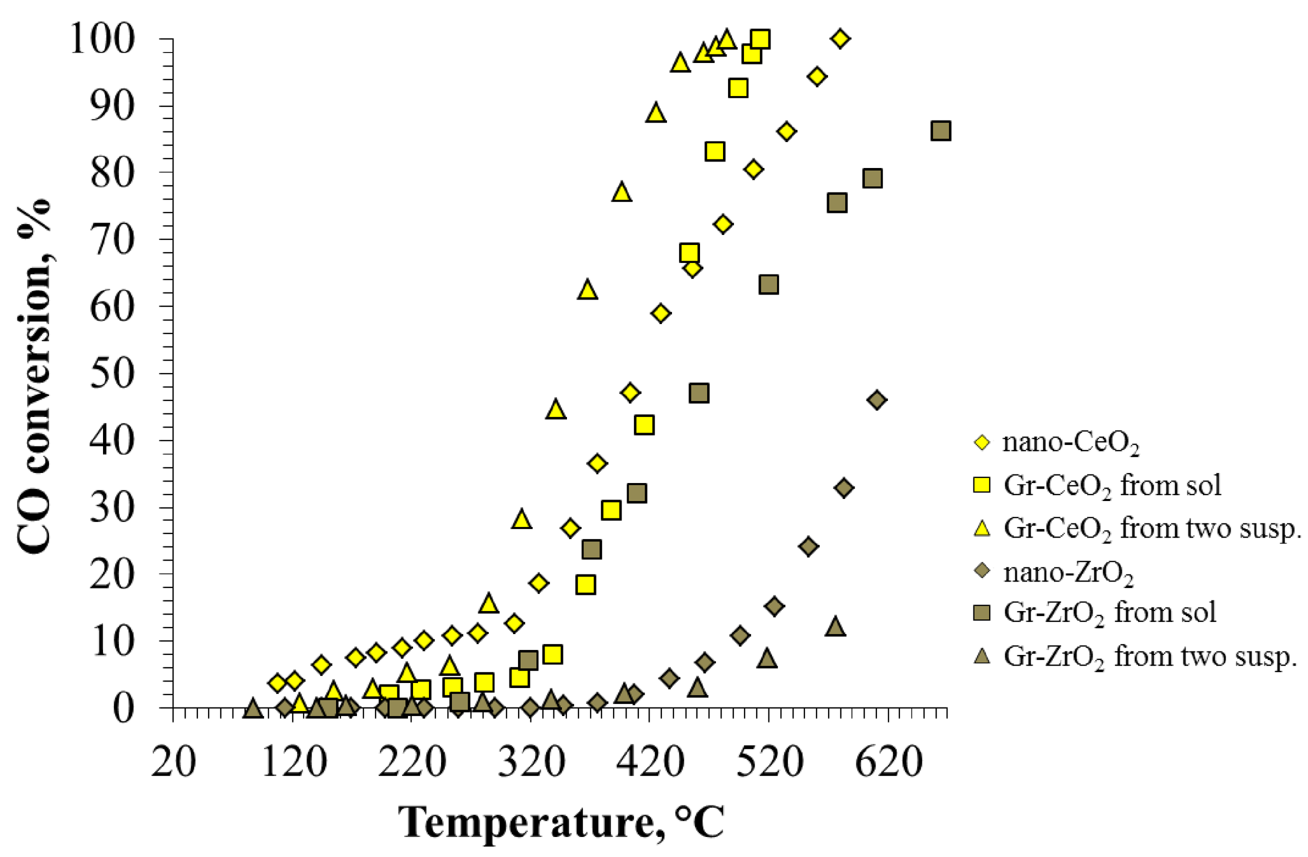


The examined sample exhibits a plate-like grain structure with predominantly grain 3–5 μm, combined with high material homogeneity and a relative density of 97.6–98.0%. The microstructure is characterized by pronounced intergranular boundaries with weak sintering, as well as the presence of fine granules and cubic ZrO_2 crystallites on the surfaces of rounded grains. The preferential grain orientation is attributed to the presence of graphene sheets, on which the ZrO_2 crystallites were originally anchored.

Catalytic Activity of Synthesized Composites in CO Oxidation

The CO oxidation on the synthesized composite powders was carried out in the temperature range of 70-700°C in a flow-through setup with gas chromatographic analysis. It was determined that the composite catalyst synthesized from Zr-containing sol and graphene exhibits a marked increase in catalytic activity for CO oxidation. At 580 °C, this sol-derived composite achieves more than double the CO conversion compared to single nano-zirconia, due to the formation of a more defective zirconia structure and a higher density of active surface sites. This performance surpasses that of catalysts produced by simply mixing graphene with zirconia nanoparticles.

In the case of graphene-ceria composites it was found that at temperatures below 290°C, the conversion of CO on the composite samples was lower than on pure nano-CeO_2. In the range of 280-290°C, the conversion of CO on the composite obtained from two suspensions increases sharply and a change in the reaction mechanism occurs. Complete conversion of CO is achieved at 485°C, which is 95°C lower than on pure nano-CeO_2. On the composite obtained from the sol and suspension, a change in the mechanism of CO oxidation occurs in the range of 350-360°C, and complete conversion of CO is achieved at 510°C, which is 70°C lower than on pure nano-CeO_2.



The CO conversion curves on nanostructured MO_2 and composite powders

The values of apparent activation energy of CO oxidation on synthesized powders

Catalyst	Apparent activation energy, kJ·mol^{-1}
Nano-ZrO_2	86.1
Gr-ZrO_2 from Zr-sol	41.4
Gr-ZrO_2 from two susp.	31.7
Nano-CeO_2	11.8
Gr-CeO_2 from Ce-sol	18.1
Gr-CeO_2 from two susp.	29.1

Conclusions

1. A positive effect of graphene on the ceramic microstructure has been demonstrated, enabling the production of dense (98%) and fine-grained material with high structural homogeneity via the SPS method.
2. Oxygen-free graphene on the surface of MO_2 crystallites accelerates surface oxygen exchange processes, making these composites promising for electrical engineering and catalysis.
3. The incorporation of graphene sheets and the method of their integration into the structure significantly affect the activation energy of sintering and the mechanism of mass transfer.
4. The obtained results can be used to develop an efficient technology for sintered ceramics production at all stages, starting from precursor solutions and colloids.

The study was carried out in Baikov Institute of Metallurgy and Materials Science, RAS, in accordance with the State Assignment 075-00319-25-00