Synthesis of a Graphene-Containing Composite by Deposition of Oxygen-Free Graphene on Nanocrystallite CeO_2

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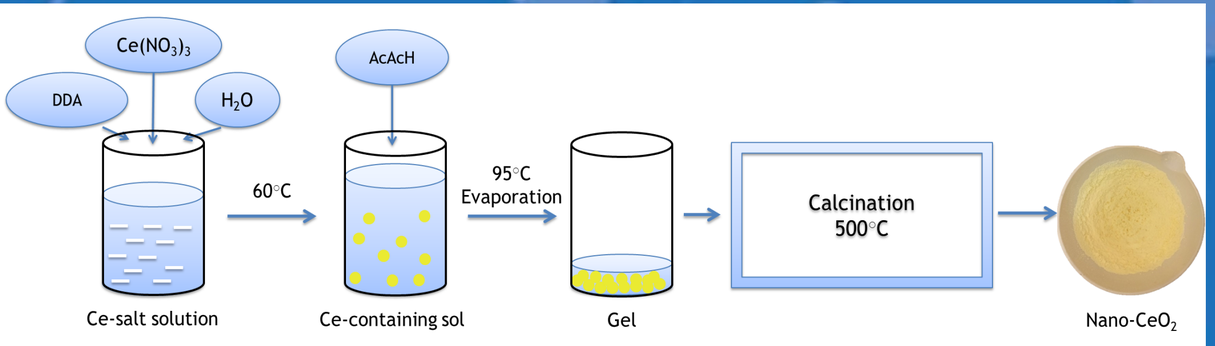
Currently, researchers and developers are interested in materials for supercapacitors, which are in demand for the development of small-sized electronic devices. Graphene-containing materials based on CeO_2 are promising for these proposes. The content of graphene in the composite should not exceed 2 wt.% for the effective use of the material. Wherein the graphene sheets should contain a minimum amount of oxygen and be uniformly distributed in the material bulk. The fulfillment of these requirements is the most difficult problem to solve.

The aim of this work is to develop a method for the synthesis of hybrid structures based on nano-CeO_2 and oxygen-free graphene, which consists in depositing the latter onto metal oxide powder.

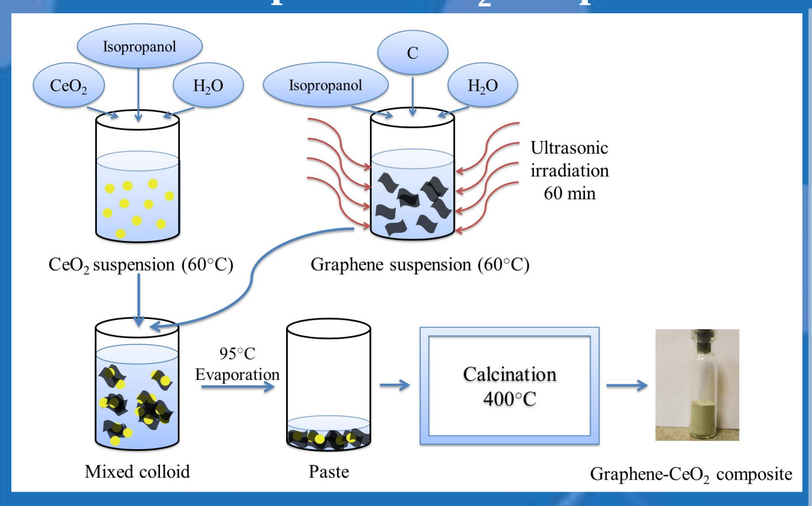
Nano-CeO_2: scheme of synthesis*



Nano-CeO_2 was synthesized by sol-gel method: 1) mixing of $Ce(NO_3)_3$ aqueous solution and dodecylamine (DDA) alcohol solution; 2) addition of acetylacetone (AcAcH) as complexing agent; 3) evaporation of the resulting sol to form a gel; 4) heat treatment at 500°C in oven for 1h.

*Ponomarev I V, Trusova E A, Afzal A M. Synthesis of graphene-CeO_2 nanocomposite using dodecylamine, Inorganic Materials: Applied Research, 2023, 14, 3, 868-875

Graphene-CeO_2 composite: scheme of synthesis*

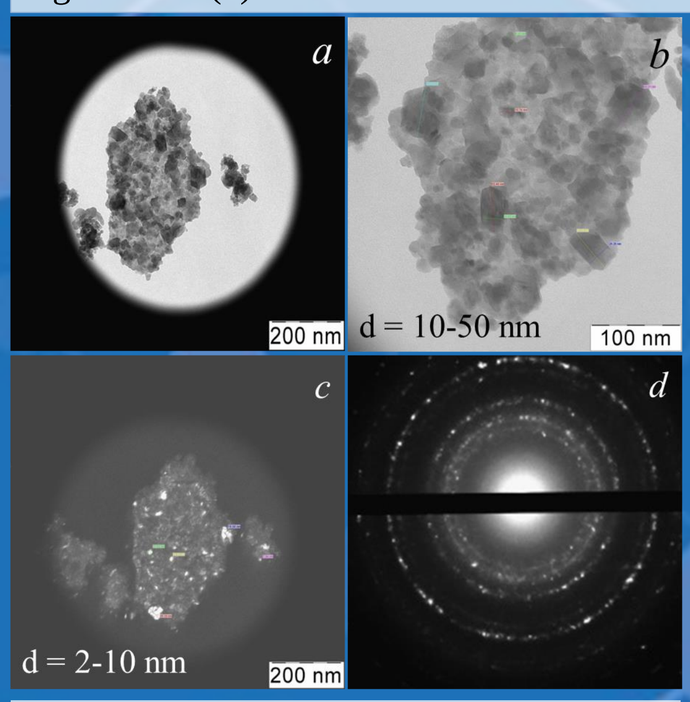


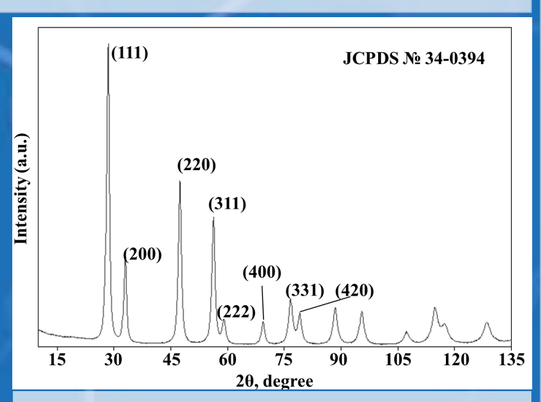
Stages of synthesis:
1. obtaining an oxygen-free graphene suspension by ultrasonic exfoliation;
2. synthesis of CeO_2 nanopowder by sol-gel method;
3. mixing the aqua-alcohol suspension of synthesized nano-CeO_2 with the decanted graphene suspension;
4. evaporation of the mixed colloid to the paste state;
5. heat treatment at 400°C in oven for 1h.

*RU 2790846 C1 (2023). Trusova E A, Ponomarev I V, Afzal A M. A method of obtaining nanostructured composites based on oxygen-free graphene and aluminum or cerium oxides

Nano-CeO_2: morphology and composition

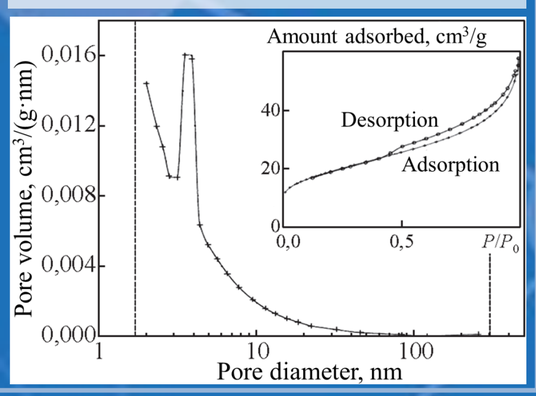
TEM data for the crystalline CeO_2 nanopowder: light-field (*a* and *b*) and dark-field (*c*) images and electron diffraction pattern for the sample area shown in Figs *a* and *c* (*d*).





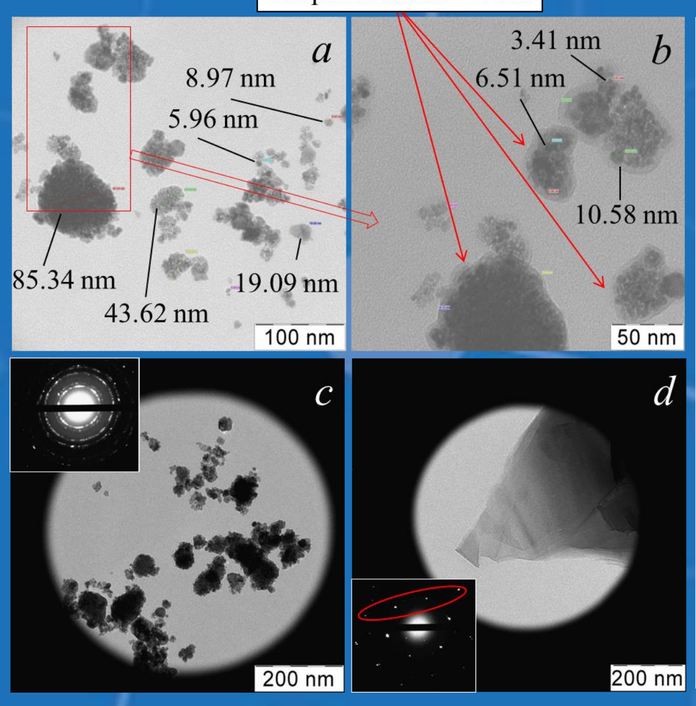
The XDR pattern corresponds to fluorite type face-centered cubic lattice (JCPDS card № 34-0394). The average crystallite size of CeO_2 is 13.1 nm.

According to N_2 adsorption-desorption data, the specific surface area of pure nano-CeO_2, calculated by the BET-method, was 68 m^2/g. The average pore diameter was 4.5 nm which corresponds to a mesoporous system, while micropores provided less than 4% of volume and about 13% of the powder surface.



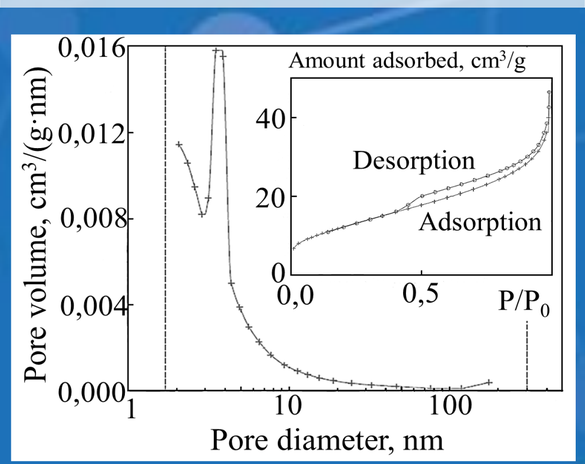
Morphology study of graphene-CeO_2 composite

Graphene shells – 4 nm

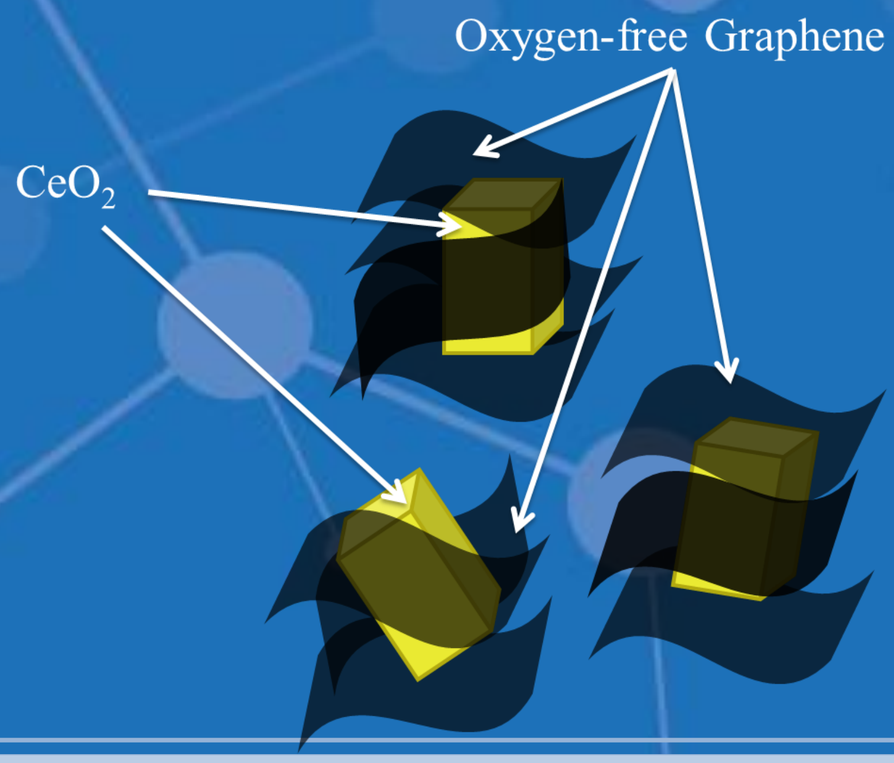


Graphene-CeO_2 composite powder consisted of agglomerates with sizes not exceeding 100 (20-60) nm, which had graphene shells 3-6 nm thick (*a*,*b*). CeO_2 crystallites inside the agglomerates had sizes 3-11 nm, were randomly and not tightly packed and wrapped with graphene sheets (*c*, inset). The electron diffraction pattern of peripheral part of agglomerate, where graphene sheets mainly appear (*d*, inset) corresponds to multilayer graphene, and the ratio of the characteristic reflection intensities indicates that the graphene sheets had variable layering: multilayer sections were adjacent to single-layer ones.

According to N_2 adsorption-desorption data, the specific surface area of graphene-CeO_2 composite was 45 m^2/g. The average pore diameter was 4.7 nm which corresponds to a mesoporous system, while micropores provided less than 3% of volume.



Mechanism of graphene-CeO_2 composites formation from two suspensions



Conclusion:

Thus, a method has been developed for the synthesis of hybrid structures based on nanocrystalline CeO_2 and oxygen-free graphene with a content of the latter of no more than 1 wt.%. The developed method makes it possible to obtain the thinnest sheets of oxygen-free graphene and uniformly distribute them among the CeO_2 nanocrystallites. The proposed method for the synthesis of composite nanostructured powders based on graphene and CeO_2 can be used as the basis for an economical and environmentally friendly technology for the nanopowders production, which are in demand in the development of materials for small-sized electronic devices.

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