Hydrothermal Synthesis of Nanohybrid Gr-CeO₂

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Nanohybrids (NHs) materials are a conjugation of metal oxides with a carbonaceous coating or doping. These combinations have been pursued to enhance the original oxide performance and/or incorporate multifunctional properties. NHs have emerged as a new class of compounds that are interesting in diverse areas such as: chemistry, physics, material sciences, biology and medicine [1]. When CeO₂ and Graphite are conjugated, the resulting properties are expected to be different, for cases when one or more of the components properties will become dominant. This can be a function of the conjugation or the synthesis procedure. Such changes may be manifested in their resultant size, shape, crystalline structure, surface chemistry, etc.

Natural graphite flakes (-10 mesh, 99.9% purity from Alfa Aesar Co.) was used in this work as raw material. Graphite was processed in a high-energy SPEX 8000M mill. The balls to powder ratio was kept 5 to 1 (in weight). Milling was accomplished after a period of 8h under an inert argon atmosphere. Ceria synthesis was performed mixing 2.0 mg of chelating agent (citric acid, C₆H₉O₇) and 2.0 g of Ce(NO₃)₃·6H₂O in 75 mL ethanol/water solution 9:1 (in volume). The Nanohybrid Gr-CeO₂ (NH Gr-CeO₂) was prepared by mixing the above solution with the milled graphite following this route: 1.0 mg of graphite was added in the solution; the mixture was sonicated for 0.5h and heated at 160°C for 24 h. After cooling, the solid sample was filtered, washed, dried and calcined at 500°C for 2h, under a protective argon atmosphere to avoid graphite oxidation. The microstructural characterization was carried out through two electron microscopes: a Hitachi TEM model 7700 and a Jeol SEM model JSM-7201F. XRD studies were performed using a Bruker diffractometer model D8 Advance.

Fig. 1 presents two SEM images of CeO₂ and NH Gr-CeO₂, where one can notice a coral-like structure in both cases, the observed particles exhibiting a low agglomeration after graphite addition. Fig. 2 (a-b) displays SEM micrographs and EDS elemental analyses of products. There is an important concentration of carbon in the NH Gr-CeO₂ sample. Based on XRD studies, the mean crystallite size was calculated using the Scherrer equation, the determined values for CeO₂ and NH Gr-CeO₂ were 14 nm and 11 nm, respectively. In Fig. 2c we observe nanoparticles of CeO₂ with sizes lower than 20 nm, which agrees with the XRD results. As was described, the citric acid was used as a chelating agent to inhibit growth and to reduce agglomeration of the particles [2,3]. Fig. 2d shows graphite sheets decorated with CeO₂ nanoparticles on their surface. These particles were homogeneously distributed. Fig. 2e presents a STEM/EDS elemental mapping, which confirms the presence of carbon as a main component of the prepared NH Gr-CeO₂.

References:
Figure 1. SEM micrographs: a) CeO$_2$ and b) NH Gr-CeO$_2$.

Figure 2. SEM micrographs and EDS elemental analysis: a) CeO$_2$, b) NH Gr-CeO$_2$. TEM micrographs: c) CeO$_2$, d) NH Gr-CeO$_2$, and e) TEM micrograph and corresponding EDS maps of NH Gr-CeO$_2$ particle.