Design of organic, inorganic and hybrid materials via solgel processing for technological applications

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OBJECTIVES AND NOVELTY

Materials with a wide variety of shapes and chemical, porous, and structural properties can be easily obtained by the sol-gel process, prompting a strong interest due to the versatility of this methodology and the application of these materials in many different technologies. Based on this fact, the search for even more efficient processes on an industrial scale includes continuous innovation in the applicability of the sol-gel synthesis, through the optimization of raw materials and energy consumption. In this regard, the use of microwave heating (MW) stands out as a successful technology for the reduction of operating times and costs in the sol-gel synthesis of organic and carbon gels with controlled porous properties. However, further knowledge to extend its use to other gels and/or other specific applications is still needed.

The aim of this work is **to develop organic, inorganic and hybrid materials using the sol-gel process assisted by microwave heating for technological applications,** exploring the possibility of extending the use of MW technology to the synthesis of monolithic materials, as well as its applicability in syntheses of gels with different chemical composition (such as silica gels and RF/ or C/Si hybrid gels). The established methodologies will be applied to obtain materials with specific properties to fulfil the requirements of technologies of growing interest including the demand for sustainable and clean energy and environmental protection. Specifically, and based on the nature of the gels, the objective for the application of carbon gel derivatives is **to achieve competitive performance in the extraction of micropollutants** and **to evaluate their role as catalysts/catalyst supports in the revalorization of glycerol**. While, for the hybrid materials, the objective is **to develop strategies to take advantage of the presence of hybrid bonds to improve their thermal insulation properties** and **to produce crystalline species of interest (Si, SiC) in the development of anodes for lithium-ion batteries (LIBs)**.

RESULTS

Studies on the use of MW heating for the synthesis of sol-gel materials showed a considerable reduction of the synthesis time of about 90%. The work on the synthesis of monoliths revealed the need for a different configuration of the MW device control system, since the dimensions of the containers limit the precise control of the temperature, thus affecting the reproducibility of the synthesis. Despite these limitations, it was possible to obtain monolithic RF gels with high porosity and controlled macropore size. Further characterization of such monoliths proved their good mechanical properties, and the possibility to modulate the tortuosity of the polymeric network by tuning the variables of the sol-gel process. Futhermore, a possibility to synthesize monoliths incorporating fiber arrays in their structure was found by simply reducing the temperature prior to gelation. On its part, the good response of organic orthosilicates to MW radiation improved the synthesis of silica and hybrid gels. In the case of RF/Si gels, keeping the homogeneity of the sol along the process was an important issue, which was successfully managed by fixing appropriated rates of ethanol in the precursor mixtures and by the addition of an aminosilane, which favoured the interaction between RF and silica species.

The MW-assisted sol-gel methods were used to synthesise materials with properties adjusted to the needs of different technologies. On one hand, macroporous carbon monoliths with good permeability were obtained, but only the addition of graphene oxide to promote highly ordered domains favoured their interaction with aromatic compounds. The resultant graphene aerogels (GA) were competitive to graphene sponges (GS) in the extraction of micropollutants, since recoveries of about 80% and no matrix effects were found (Figure 1a). On the other hand, mesoporous carbons with developed surface area and different concentration of oxygen functionalities showed good catalytic activity and selectivity in the oxidation of glycerol (Figure 1b).

In the case of hybrids, the method developed allowed the synthesis of gels with silica contents of 10-90%, porosity higher than 70% and controlled pore size in the entire range. It was found that, in comparison with RF or silica gels, RF/Si materials with low silica content (ca. 10%) showed a slightly higher thermal insulating capacity due to their hybrid microstructure (Figure 2a). In addition, by adjusting the porous properties, their thermal conductivity can be further reduced reaching values of 25 mW/mK (superinsulators). However, C/Si hybrid gels with high silica content (> 50%) proved to be potential precursors of crystalline silicon species (Si and SiC). In comparison with composites (i.e., physical mixtures of the involved species), the materials obtained from C/Si hybrids showed higher development of SiC and better stability (Figure 2b), favouring the electrochemical performance of LIBs anodes based on those materials.

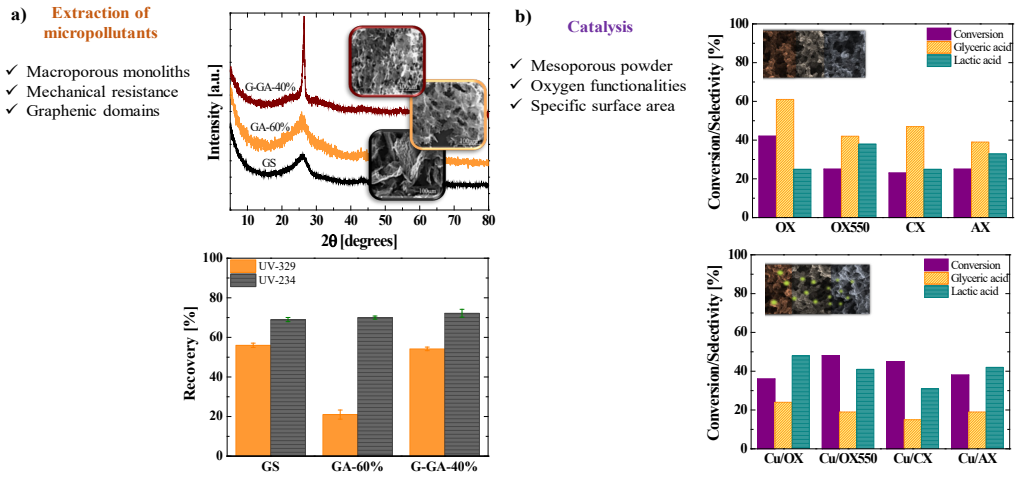

Figure 1. Carbon gel designed properties and their performances as a) extracting material in SPE of micropollutants (benzotriazoles UV-329 and UV-234) and b) catalyst in the oxidation of glycerol.

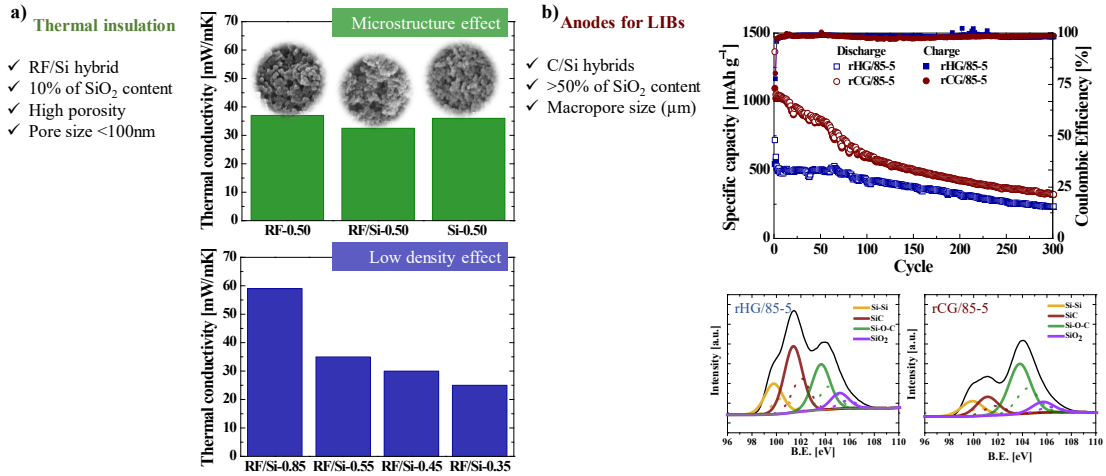

Figure 2. Hybrid gel designed properties and their performances as a) insulation materials and b) precursor for anode materials in LIBs.

CONCLUSIONS

The microwave-assisted sol-gel process is an efficient alternative for the synthesis of materials with different chemical nature and tailored properties. However, for their scale-up application, it is important to take into account the configuration and specific design of the microwave device, in order to have an optimised and effective production. Nevertheless, through this method it was possible to obtain RF gels (powders and monoliths), their carbon derivatives, silica gels and hybrid gels with properties (such as high porosity, controlled pore size, good mechanical properties, and in the case of RF monoliths, also modulating their tortuosity through the sol-gel variables), all designed to fulfil the requirements of specific applications.

The tailored sol-gel materials exhibited varied chemical and textural properties suitable for surface interaction, diffusion and electrochemical processes, which added value to the proposed synthesis methods. An excellent performance for the extraction of aromatic micropollutants from water was reached with the introduction of graphenic domains in the RF gels, being a competitive alternative to graphene sponges. Thanks to their suitable surface chemisty, RF-derived gels showed a great catalytic potential in the oxidation of glycerol. On the other hand, superinsulator materials were developed from RF/Si hybrids, which were able to combine accurately microstructure, high porosity and pore size. Finally, the C-Si species derived from hybrid gels facilitated the development of materials with crystalline Si and SiC for use in LIBs, performing more stable cycling.

RELATED PUBLICATIONS

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