

# PREPARATION OF NANOPOROUS ZIRCONIA-EMBEDDED CARBON COMPOSITES: NOVEL APPROACH FOR DIRECT MODIFICATION OF SUPPORT SUBSTRATES

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## Introduction

Porous and high-surface-area carbons are of great interest because of their high surface areas, large pore volume, chemical inertness, and excellent mechanical stability [1]. Many nanoporous carbons are produced through templating approaches because the templating methods are the most promising and the simplest way to prepare two- or three-dimensional porous carbon materials with well-defined structural, textural, and morphological properties. These nanostructured carbons are used extensively as electrode materials for batteries, fuel cells, and supercapacitors [1,2].

Carbon materials are considered chemically inert under various reaction conditions. However, the surface of a porous carbon material often needs to be modified to create surface functional groups which facilitate the fine-tune interactions with guest molecules. Many researchers have tried to develop chemistries for functionalizing the porous carbon surfaces in order to have the full benefits of porous carbons which can be used as electrode materials [3].

We demonstrate here one way of the point-to-point attachment of guest molecules onto carbon composite surfaces via chemically covalent bonding between zirconia ( $ZrO_2$ ) embedded in the carbon framework and a phosphonic acid ( $R-PO_3H_2$ ). Modification of nanometer-sized  $ZrO_2$  particles with various phosphonic acids can be found elsewhere [4]. Our approach provides more flexibility for designing mesoporous electrode materials that have structures and bulk surface properties quite easily tuned by using different organic guest molecules and different inorganic functional components.

## Experimental

Nanoporous  $ZrO_2$ -carbon composites were prepared using a silica-templated sol-gel procedure by polycondensation reaction of resorcinol (R) and formaldehyde (F) in the presence of silica and zirconia sols. Resorcinol (99%, ACS reagent) and formaldehyde (37 wt% aqueous solution, ACS reagent) were used as a carbon precursor, and aqueous colloidal silica ( $SiO_2$ ) sol solution (Ludox HS-40 silica sol solution, particle size, 9-12 nm) was employed as templates [5]. The designed amounts of  $ZrO_2$  sol (which had been prepared using zirconium n-propoxide) and  $SiO_2$  sol were

mixed with the RF sol solution. The polycondensation (at 85 °C for 1 week) of R and F in the presence of  $SiO_2$  and  $ZrO_2$  sols generated  $ZrO_2$ - $SiO_2$ -RF gel composites. Carbonization (at 1000 °C for 5 h) followed by 5 M NaOH etching (at 80 °C for 20 h) of the  $SiO_2$  templates produced nanoporous  $ZrO_2$ -carbon composites. The composites with different  $ZrO_2$  loadings were prepared using the identical procedure. Fig. 1 depicts the overall procedure for the composite preparation.

As-prepared  $ZrO_2$ -carbon composites were then modified with meta-sulphophenyl phosphonic acid (m-SPPA), which was obtained following a reaction procedure described in the literature [6]. The grafting was performed by stirring 0.1 g of  $ZrO_2$ -carbon composite powders in 10 mL of m-SPPA (0.1 M) at 100 °C for 20 h. The resulting surface-modified composites were separated by filtration on a 0.2  $\mu m$  nylon membrane, washed with large amount of mQ water, and dried in the oven at 80 °C for 24 h [4,7]. The dried composites were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), X-ray diffraction analysis (XRD), thermal gravimetric analysis (TGA), gas porosimetry, and titration.

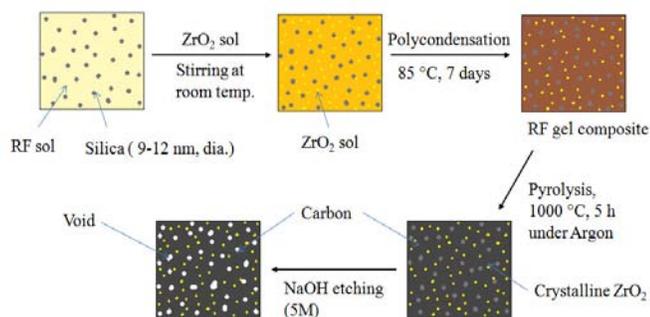
## Results and Discussion

After pyrolyzing  $SiO_2$ - $ZrO_2$ -RF composites,  $SiO_2$  particles were selectively removed by NaOH etching, and high surface area ( $\sim 800$  m<sup>2</sup>/g) nanoporous  $ZrO_2$ -carbon composites with high mesopores volume ( $\sim 4$  cm<sup>3</sup>/g) were obtained. The  $N_2$  adsorption-desorption isotherms exhibited the existence of mesopores, which was indicated by the hysteresis between adsorption and desorption isotherms. The pore size distribution calculated by the BJH method revealed that the carbon composites had a mean pore dimension of 12 nm.

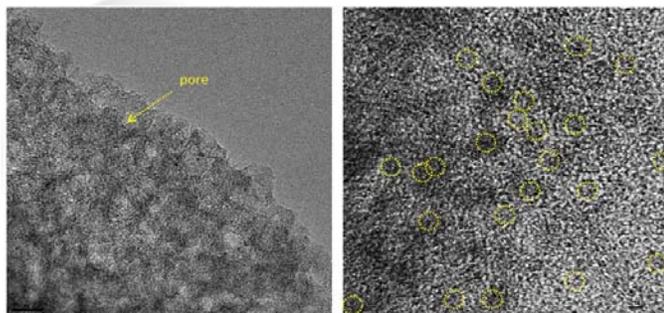
In support of these considerations, SEM and TEM observations were carried out. SEM images of the  $ZrO_2$ -carbon composites showed that pores were evenly distributed in the entire surface with pore diameters ranging roughly from 4 nm to 15 nm, but most pores were in the range of 10-15 nm. These results were consistent with prior nitrogen porosimetry analyses of similar samples (BJH analysis of nitrogen adsorption isotherm data) which revealed pores in this size regime. The direct evidence of the formation of  $ZrO_2$  nanoparticles embedded in the carbon framework was given by TEM micrographs (Fig. 2), which showed that nano-scale  $ZrO_2$  particles were distributed in the carbon framework.

The nature and crystallinity of the  $ZrO_2$  particles were confirmed by XRD (Fig. 3). The peaks in the XRD spectra were relatively broad, which was indicative of small crystalline size. The XRD patterns of the composites with different  $ZrO_2$  loadings exhibited the typical diffraction peaks corresponding to crystalline  $ZrO_2$ . They exhibited identical patterns, which revealed that the  $ZrO_2$  crystallites were about the same size in all the samples. The average size of the  $ZrO_2$  particles was calculated for each sample by applying the Scherrer equation. The calculated average particle sizes were in close agreement with the TEM data.

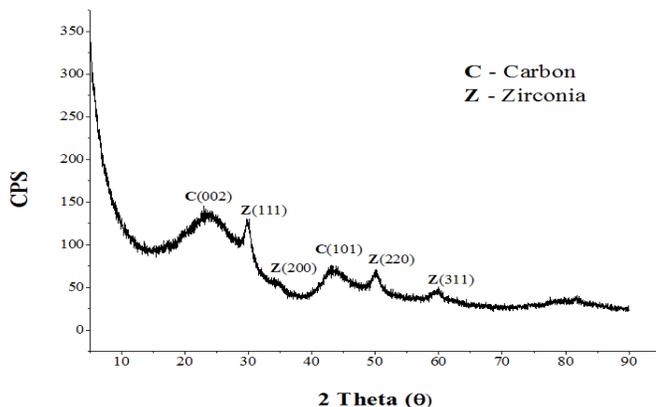
The  $\text{ZrO}_2$ -carbon composites were modified with m-SPPA (0.1 M) by applying heat (100 °C) for 20 h. The amount of m-SPPA covalently attached onto  $\text{ZrO}_2$  during the modification was determined by neutralization titration. The composite powders were stirred in 2 M NaCl for three days, and then the mixture was centrifuged, and the filtrate was used for titration. The results showed that the protons of the acidic groups  $-\text{SO}_3\text{H}$  were exchanged by sodium ions, and the ion exchange capacity computed on the basis of the composite weight was 0.1 - 0.15 meq/g.



**Fig. 1** Preparation of nanoporous  $\text{ZrO}_2$ -carbon composites



**Fig. 2** Selected transmission electron micrographs of  $\text{ZrO}_2$ -carbon composite after etching (left) and the identical composite at higher magnification (right).  $\text{ZrO}_2$  particles are circled.



**Fig. 3** Selected XRD patterns of  $\text{ZrO}_2$ -carbon composite

## Conclusions

The  $\text{SiO}_2$ -templating method was suitable to achieve a high level of control over pore size, volume, and interior surface area in the carbon framework. Nanoporous  $\text{ZrO}_2$ -carbon composites with a high surface area and a large pore volume could be prepared by using the templating method. The  $\text{ZrO}_2$  functionality present in the carbon framework was used for the point-to-point modification with m-SPPA. Modification of the composite with m-SPPA introduced  $-\text{SO}_3\text{H}$  groups to the composite surface. This approach will be one way to control both the amount and the distribution of robust reacting sites for future surface modification of carbon electrode materials.

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