

# NANOPOROUS CARBONS DERIVED FROM BINARY CARBIDES AND THEIR OPTIMIZATION FOR HYDROGEN STORAGE

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## Introduction and Objective

The transition from an energy economy currently dominated by fossil fuels to more environmentally friendly hydrogen requires a material that can store hydrogen effectively. Many types of materials have been tried, including carbon nanotubes, activated carbons, metal-organic framework compounds, metal hydrides, and clathrates, but none of these meets the target. Physisorption route of hydrogen storage relies on weak van der Waals bonding, and as the minimum potential energy between the surface of the storage material and hydrogen is at a distance of approximately one molecular size of hydrogen (~0.41 nm), extremely small pores are necessary for maximizing physisorption of hydrogen. Thus, the challenge for higher hydrogen storage using physisorption technique lies on synthesizing highly porous materials with narrowly distributed small pores. As most synthesis routes for porous carbon result in larger pores with wider pore size distributions (PSD), the challenge lies in the development of a synthesis route leading to narrowly distributed nanoporous carbons with controlled pore size. Carbide derived carbon (CDC) provides the possibility of producing small pores. The primary objective of this work is to synthesize tunable nanoporous carbons from binary metal carbides and establish a relation between the structure of the initial metal carbide and the properties of the resultant carbon. As there is lack of understanding of the effect of porosity, the other main objective of this work is to determine its effect on hydrogen sorption and optimize CDC for achieving the maximum hydrogen uptake. Unlike synthesis of most porous carbons which involves thermal decomposition of organic materials, CDC production is based on selective thermo-chemical etching of the metal(s) or metalloid from a rigid metal carbide lattice. The general reaction involved in synthesis of carbon from metal carbides can be written as:  $M_aC_{b(s)} + (c/2)Cl_{2(g)} \rightarrow aMCl_{c(g)} + bC_{(s)}$ , (1), where M represents a metal or metalloid.

## Results and Discussion

### 1. Synthesis of high specific surface area tunable nanoporous carbon and study of structure-property relation between initial metal carbide and resultant nanoporous carbon:

CDCs were synthesized from four metal carbides, three that have a uniform carbon-to-carbon distance in the lattice structure (ZrC, TiC and  $\beta$ -SiC) and one that has a non-uniform carbon-to-carbon distance in its lattice structure ( $B_4C$ ) [1-7]. With results from CDC produced from ZrC, TiC, SiC and  $B_4C$ , it was showed that carbides having a uniform carbon-to-carbon distance like ZrC, TiC and SiC are important for obtaining a narrow PSD, whereas non-uniform carbon to carbon distance in the initial carbide like  $B_4C$  is required for a broad pore size distribution (Fig. 1). In addition to controllable pore size within sub-Ångstrom accuracy in the range 5-14 Å, CDCs also offer a high specific surface area (SSA) of up to 2000 m<sup>2</sup>/g (Fig. 1d). This parametric study proves that the structure and porosity of CDCs depend on the initial metal carbide and the synthesis temperature. It explains how to tune and optimize the pore size for hydrogen storage.

### 2. Hydrogen Storage on CDCs:

(a) *Effect of Specific Surface Area on Hydrogen Storage:* Investigations of hydrogen storage in carbons as a function of specific surface area have been reported over the last three decades. In contrast to the conventional belief of direct dependence of hydrogen storage on specific surface area, we found that hydrogen storage is not directly proportional to SSA. This was shown by comparing two different CDC samples, one with a high SSA ( $B_4C$ -CDC), which yielded a lower hydrogen sorption and the other with a low SSA (TiC-CDC), which yielded a higher hydrogen sorption. Hydrogen sorption plotted as a function of SSA for a variety of CDCs and other porous carbons shows an increase with SSA, but a very large scatter suggests that parameters other than the total SSA may play an important role in hydrogen storage.

(b) *Effect of Pore Size and Pore Volume on Hydrogen Storage:* Storage capacity normalized to SSA plotted as a function of pore size (Fig. 2a) showed a clear dependence of hydrogen storage on pore size. Furthermore, materials with smaller pores should have a higher SSA for a given pore volume. We therefore suggested that the hydrogen uptake is dominated by small pores and thus not directly related to the total SSA. Thus, the contribution of subnanometer pores should be considered. Calculation of the SSA required for the 7 wt. % gravimetric uptake from this plot yields a value of ~3000 m<sup>2</sup>/g, which is practically attainable and has been shown in activated carbons, albeit for larger pore sizes. Plotting the hydrogen storage capacity of carbon surfaces as a function of the average pore size clearly defines the trend of increasing storage with decreasing pore size (Fig. 2a) but the data are scattered as contributions from both small and large pores are not separated. A good correlation was established for pores less than 1 nm (Fig. 2b) and no relation was established for pores greater than 1 nm (Fig. 2c), which clearly proves that subnanometer pores are required for achieving a high hydrogen uptake at ambient pressure and cryogenic temperatures. No dependency of total hydrogen uptake on the volume and SSA of larger pores could

be found (Fig. 2c). In addition, CDCs have demonstrated a higher storage capacity compared to single and multi-walled carbon nanotubes, the best activated carbons, and low-temperature metal hydrides. CDCs can store over 50% more H<sub>2</sub> than MOF-5 and several times that of carbon nanotubes. The heat of H<sub>2</sub> adsorption on CDC noticeably exceeded that on metal organic frameworks and carbon nanotubes with selected sorption sites having a heat of adsorption in excess of 10 kJ/mole.

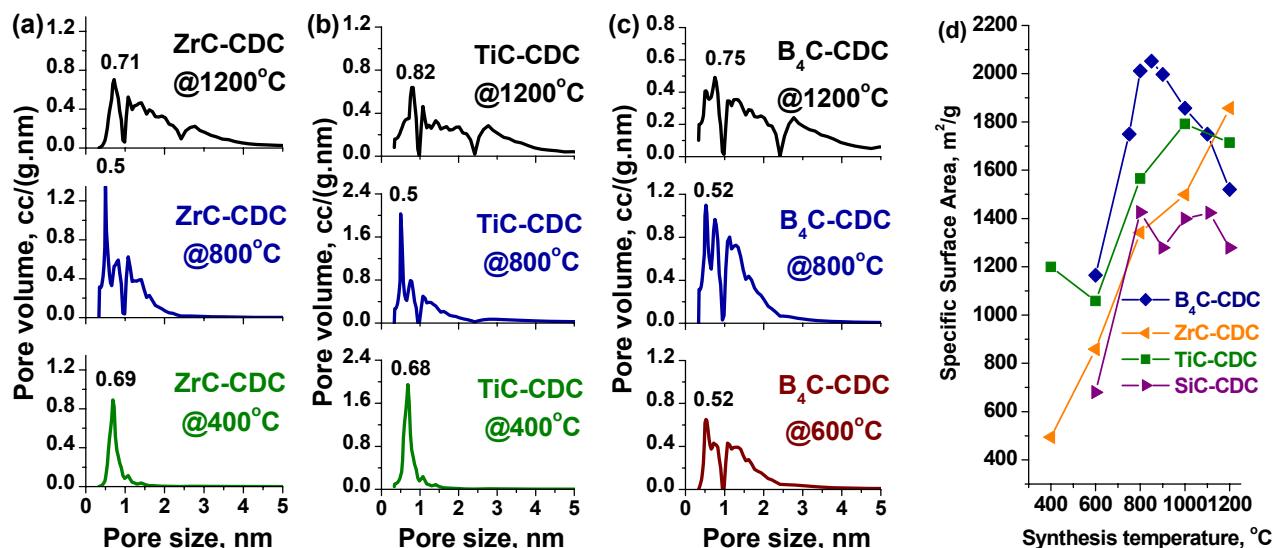


Figure 1. Pore size distributions (PSD) of nanoporous carbon synthesized from (a) ZrC, (b) TiC and (c) B<sub>4</sub>C at different chlorination temperatures. Carbides having uniform carbon-to-carbon distance such as ZrC, TiC and SiC, yield a narrow pore size distribution; whereas non-uniform carbon to carbon distance in the initial carbide material such as in B<sub>4</sub>C produces broad pore size distribution even at the lowest synthesis temperature. (d) SSA of CDC from ZrC, TiC, SiC and B<sub>4</sub>C as a function of synthesis temperature.

**Conclusions:** This work provides experimental evidence that a subnanometer pore size is needed for achieving a higher hydrogen storage capacity. It shows that a large volume of small open pores with a narrow PSD is the key for high hydrogen uptake. It has paved a way to designing porous carbons by optimizing subnanometer pores. Further research in this direction is expected to increase the hydrogen uptake well above 3 wt.% at 77 K and 1 atm reported here. Nano-sized pores are not only important for H<sub>2</sub> storage, but also for other gas storage like methane, chlorine, etc. Subnanometer pores in CDC electrodes in supercapacitor have led to an anomalous increase in capacitance [3]. In addition to providing new insights, this work has demonstrated a novel approach to manufacturing low-cost, high SSA nanoporous carbons with a tunable pore size. These remarkable and unique properties of CDCs may find numerous potential applications in gas storage, molecular sieves, catalysts, absorbents, battery electrodes, supercapacitors, water/air filters and medical devices.

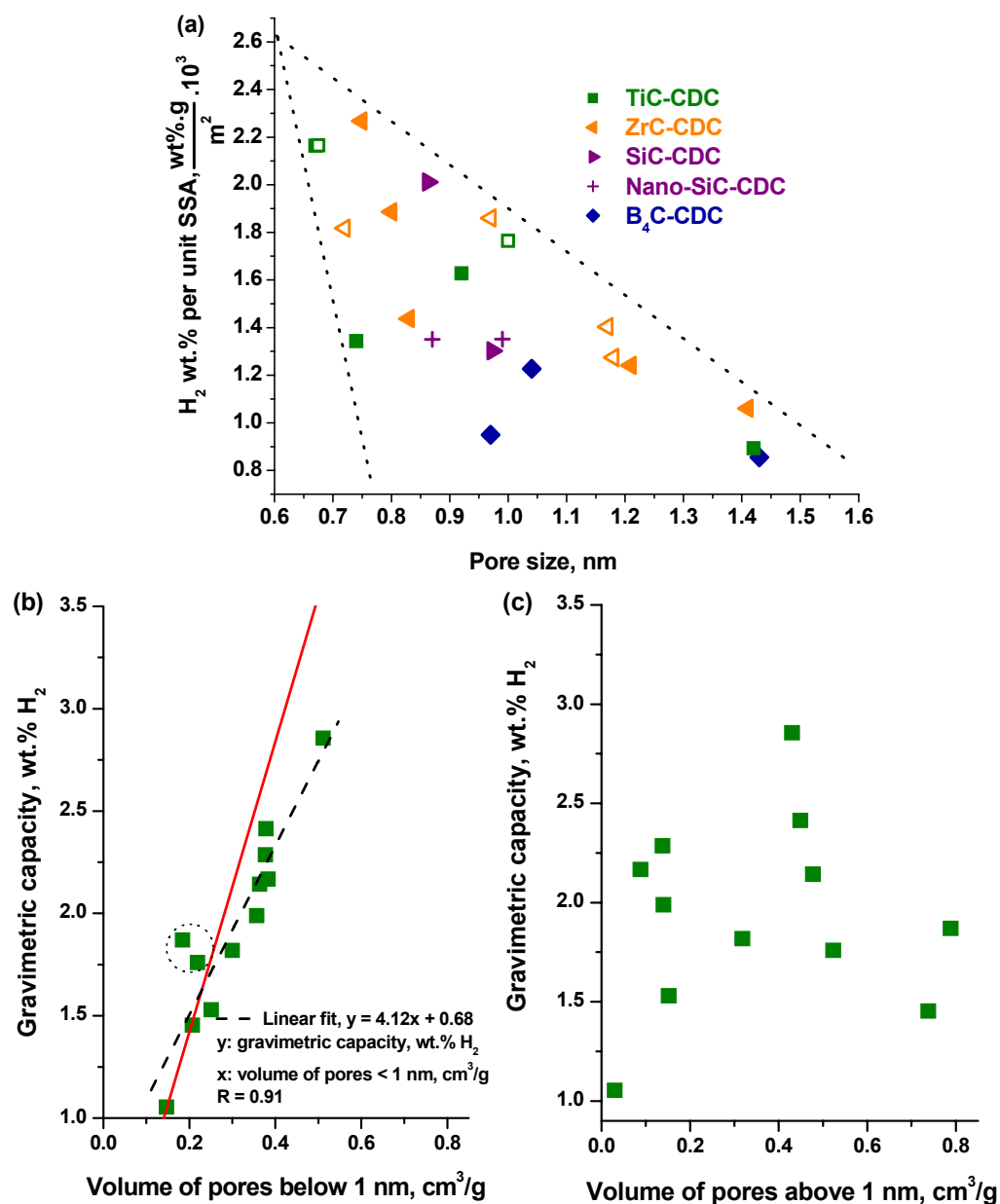


Figure 2. Effect of pore size on hydrogen storage. (a) Hydrogen storage normalized to surface area plotted as a function of pore size for several CDCs. The general trend defined by the dashed line envelopes indicates that the small pores are more efficient than the large ones for a given specific surface area. Extrapolation of data implies that for CDC with average pore size less than 0.7 nm a practically attainable SSA of  $\sim 3000 \text{ m}^2/\text{g}$  is required for 7 wt% storage at 77 K and 1 atm. Solid symbols stand for as-produced and hollow for hydrogen-annealed CDC. Hydrogen uptake at 1 atm and 77 K versus volume of pores (b) below and (c) above 1 nm. While hydrogen uptake was seen to increase linearly with pore volume for smaller pores, no correlations was found between the hydrogen uptake and pore volume for larger pores. The solid red line in (b) corresponds to the amount of liquid hydrogen that can be stored in pores as a function of pore volume.

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