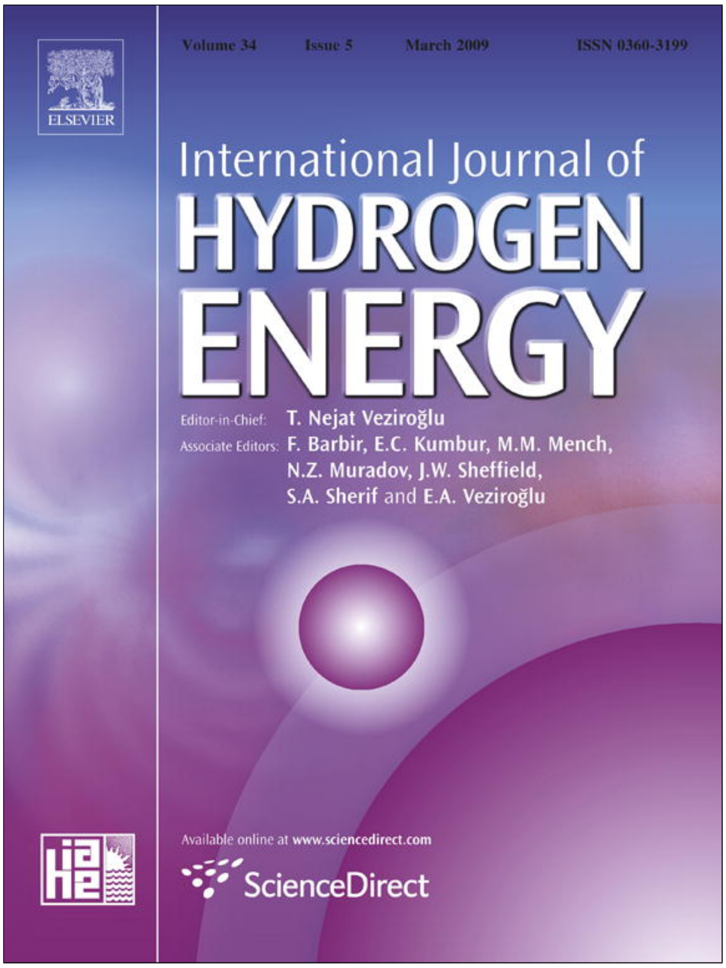

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Technical Communication

Hydrogen adsorption behavior of graphene above critical temperature

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ABSTRACT

We evaluate the hydrogen adsorption behavior of the pristine single-layer graphene sheets in a powder form, which was performed at cryogenic and room temperatures. Only 0.4 wt.% and <0.2 wt.% hydrogen uptake was obtained at 77 K under 100 kPa and room temperature under 6 MPa, respectively, for the pristine graphene sample with a BET specific surface area of 156 $m^2\,g^{-1}$. Structure/property investigations suggest that the low specific surface area and weak binding to hydrogen should be responsible for the small gravimetric uptake of pristine graphene sample.

1. Introduction

Nanostructured or porous carbon materials have received continuous interest as potential hydrogen storage media by physisorption, primarily due to its low atomic mass, relatively high chemical stability and tunable pore structure [1–3]. At present, however, the quantity of hydrogen adsorbed by any type of carbon materials falls short of the DOE 2015 system target [1]. Hence, it is highly desirable to explore materials that can be tailored to provide structure and composition meeting the specific demands of a practical hydrogen storage system. Quite recently, graphene, the first two-dimensional atomic crystal, emerges as a conceptually new class of carbon material. Its unique planar nanostructure and a wide range of unusual properties promise potential applications in a large number of areas such as electronics, sensors, composites and energy storage [4,5]. In the context of hydrogen storage, the calculation results suggest that graphene with a high specific surface area may serve as an attractive host for hydrogen adsorption if the stable dispersion of graphene sheets is available [6–8]. Of particular interest is the potential to develop the graphene-based hybrid systems in various forms, which may open up possibilities towards realizing high hydrogen loading through combining large surface area and tunable surface interaction [9]. In this regard, it is therefore of importance to experimentally evaluate the hydrogen adsorption behavior of well-defined graphene sheets, which may provide a fundamental reference for the further development of graphene-based systems. With this in mind, we herein present a study of hydrogen adsorption on pristine graphene sheets above critical temperature.

2. Experimental

The graphene sheets were prepared from artificial graphite using a chemical exfoliation method, which has been previously described in detail [10], and the morphology and layer-

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numbers of the as-prepared graphene samples were well characterized by atomic force microscopy (AFM, Veeco MultiMode/NanoScope IIIa), scanning electron microscopy (SEM, LEO, Supra 35, 15 kV) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010, 200 kV). The surface composition of the graphene samples was analyzed using X-ray photoelectron spectroscopy (XPS, VG ESCALAB 250, Al Kα). Pore structure of the pristine graphene sample was investigated using nitrogen cryosorption (Micromeritics, ASAP 2010M) and corresponding specific surface area was calculated from the adsorption data on the basis of Brunauer–Emmett–Teller (BET) theory.

Hydrogen adsorption measurements were performed on pristine graphene samples in a powder form using two volumetric systems. Cryogenic hydrogen sorption measurements were performed using a cryogenic-temperature swing-pressure apparatus at 77 K and 87 K up to 100 kPa [11]. The sample cell was placed inside a cryogenic thermostat, in which the operating temperature was controlled with a precision of ±0.1 K. Room temperature hydrogen sorption measurements were performed using a Sieverts' type apparatus at 290 K up to 6 MPa [12]. For both systems, the reference cell with a fixed volume was maintained under room temperature. The slight variation in temperature was recorded to correct the pressure value of the system. Leak tests were performed by verifying the stability of hydrogen pressure before each measurement. The ideal gas equation corrected with precise compressibility factors was used to calculate the amount of adsorbed hydrogen from the pressure drop.

At least 150 mg of graphene sample was used for each hydrogen sorption measurement. The hydrogen supply (purity: 99.999%) was further purified by using a hydrogen storage alloy system to minimize the H_2O/O_2 contamination. Prior to measurements, the samples were degassed and heated at 350 °C under dynamic vacuum for 2 h. The measuring process involved stepwise gas expansions from the reference cell to the sample cell. Corresponding pressure value was recorded upon reaching equilibration. To ensure reproducibility, three independent measurements were performed at desired temperatures for each sample.

3. Results and discussion

Hydrogen sorption properties of carbon materials correlate closely to the structural parameters and surface composition [1]. In this work, single-layer graphene sheets were prepared from artificial graphite by chemical exfoliation, and combined analyses of AFM/SEM/HRTEM results indicated that ~80% of the generated graphene sheets were single-layer, most of which showed a relative smooth planar structure [10]. XPS analysis revealed a high C/O ratio (10.8–14.9) without significant signals corresponding to the C–O species [10]. Here, the well-defined graphene sample allows reliable determination of its representative hydrogen sorption behavior.

Fig. 1 presents the nitrogen cryosorption isotherm of the pristine graphene sample in a powder form. The adsorption isotherm shows a slight adsorption in the low pressure region (<0.1 P/P_0) and a steep adsorption step at pressures higher than 0.9 P/P_0, with a hysteresis loop in the desorption branch.

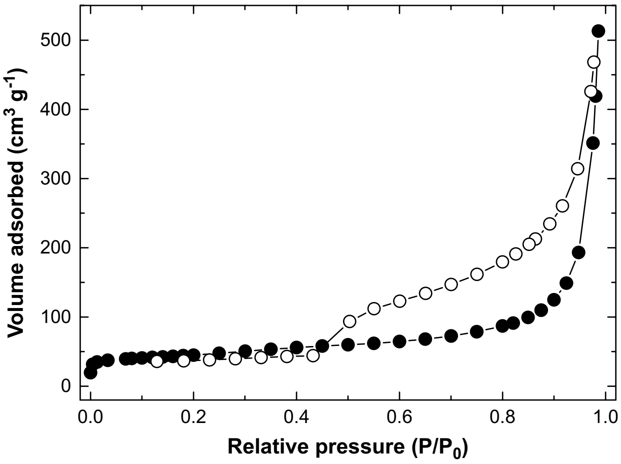

Fig. 1 – Nitrogen adsorption (solid symbols) and desorption (open symbols) isotherms of the pristine graphene sample in the powder form.

The characteristic planar structure of graphene suggests that the predominant nitrogen adsorption at $P/P_0 > 0.9$ occurs on its external surface and the internal surface of macropores formed by the re-stacking of graphene sheets. The hysteresis loop and low pressure adsorption also indicate the formation of mesopores and a small amount of micropores, respectively. BET analysis yields a relatively low specific surface area of 156 $m^2\,g^{-1}$. We note that the specific surface area of single-layer graphene was significantly decreased upon separated from its homogeneous suspension [10]. The significant loss of accessible surface area is probably due to the severe aggregation of graphene sheets in the absence of stabilizing effect from solution, which may be driven by the attractive interaction between the graphene planes. Clearly, aggregated graphenes are undesirable to hydrogen adsorption because both sides of single-layer graphene sheet in compact agglomerates are mostly inaccessible to hydrogen molecules, as evidenced by its hydrogen adsorption behavior below.

Fig. 2 shows the hydrogen adsorption isotherms of the pristine graphene sample up to 100 kPa at 77 K and 87 K. At both operating temperatures, the isotherms show a linear progression over the investigated pressure range. A low gravimetric uptake (ca. 0.4 wt.%) is observed at 77 K under 100 kPa, which is decreased to 0.35 wt.% upon increasing temperature to 87 K. Lower values are observed while increasing the temperature to room temperature. Even though a high pressure of 6 MPa hydrogen is applied, the hydrogen uptake is below 0.2 wt.% at 290 K. These values are significantly lower than the reported values of microporous carbon materials, only comparable to that obtained from multiwalled carbon nanotubes [1,13]. It has been proposed that gravimetric adsorption by physisorption is predominantly determined by the surface binding energy at low pressure and by the specific surface area at high pressure [1]. Therefore, the low gravimetric adsorption at cryogenic and room temperatures may be primarily attributed to the weak binding to hydrogen and low surface area, respectively.

To quantitatively evaluate the interaction of pristine graphene samples with hydrogen molecules, we calculated the

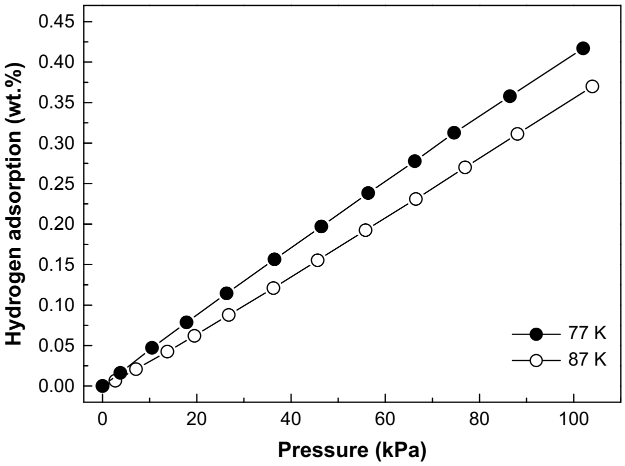

Fig. 2 – Hydrogen adsorption isotherms of the pristine graphene samples over the pressure range of 0–100 kPa at 77 K (solid symbols) and 87 K (open symbols).

isosteric heat (Q_{st}) of hydrogen adsorption by fitting 77 K and 87 K isotherms to the Clausius–Clapeyron equation [14]. As shown in Fig. 3, the Q_{st} value at the limit of zero coverage is determined to be ca. 3 kJ/mol, which corresponds to the low bound of physisorption of hydrogen on carbon materials [1]. Moreover, the Q_{st} value shows a significant drop with increasing hydrogen coverage and down to 0.85 kJ/mol at ~0.4 wt.% hydrogen, which indicates the presence of multiple sorption sites with different binding energies on the sample surface. Presumably, at low hydrogen coverage, the micropores observed serve as relatively high binding energy sites associated with confined geometry effects [15]. With the increase of hydrogen coverage, however, the predominant planar surfaces only display a weak binding to hydrogen molecule, suggesting that the aggregation of graphene sheets actually produces agglomerates with hydrogen binding comparable to graphite platelets. The above results suggest that, to increase the hydrogen uptake of graphene, structural and compositional modifications are required to retain its intrinsic high surface area and enhance the binding to hydrogen. For example, its characteristic two-dimensional nanostructure may be available for developing graphene-based hybrid structures, in which structural manipulation could be achieved following the "bottom-up" strategy by the choice of appropriate linking agents. Additionally, this method allows concurrent application of metal-doping to help optimize the surface binding energy [9]. With many synthetic and processing aspects to explore, we believe that the development of graphene-based systems presents additional opportunities towards achieving high performance hydrogen storage.

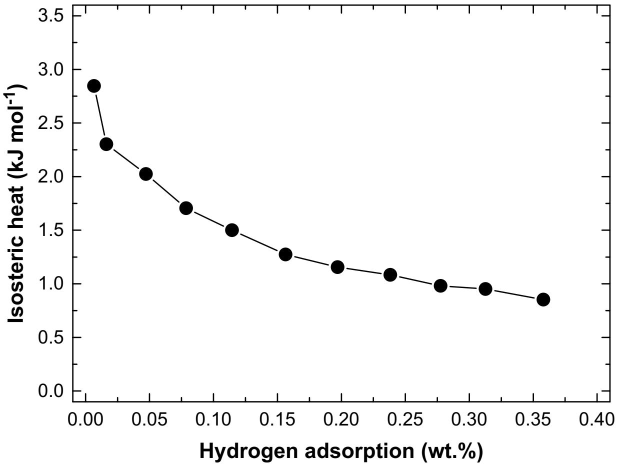

Fig. 3 – Isosteric heat of hydrogen adsorption on the pristine graphene sample as a function of the hydrogen amount adsorbed.

4. Conclusions

A small hydrogen uptake is obtained for the pristine single-layer graphene sheets in a powder form at cryogenic and room temperature, respectively. Unlike other nanostructured carbon materials, the attractive interaction between graphene planes drives them into compact agglomerates comparable to graphite platelets. Therefore, the resulting low surface area and weak binding to hydrogen greatly restrict the direct use of pristine single-layer graphene sheets for physisorption-based hydrogen storage. To increase the hydrogen storage capacity of graphene, structural and compositional modifications are required to retain its intrinsic high surface area and enhance the binding to hydrogen.

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