



The influence of potassium doping on hydrogen adsorption on carbon nanocone material studied by thermal desorption and photoemission

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ABSTRACT

Hydrogen adsorption/desorption on potassium doped carbon nanocones was studied by temperature programmed desorption (TPD), X-ray photoelectron spectroscopy, and ultraviolet photoelectron spectroscopy. TPD shows that the hydrogen storage was enhanced by up to 40% after potassium doping. Hydrogen adsorption on K-modified carbon nanocone material seems more stable than that on the undoped material. The XPS results indicate that there is charge transfer from potassium to carbon. The C 1s binding energy increases with increased potassium doping and the peak becomes wider. These binding energy shifts may be explained by work function changes related to potassium doping. The K 2p spectra indicate that there are two different local environments for potassium on the carbon cone material.

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1. Introduction

Hydrogen has been considered to be a promising alternative energy carrier since it could dramatically decrease the local pollution caused by traditional fossil energy. Therefore, it is of importance to find materials that can store hydrogen economically and which can be operated under ambient conditions. Since the report of hydrogen adsorption on carbon nanotube by Dillon et al. [1], many different carbon based nanostructured materials, e.g. multi walled and single walled nanotubes have been paid considerable attention. Recently, a new form of carbon material, namely carbon nanocones, was suggested to be a possible material for hydrogen storage [2]. It was shown that carbon cones consist of curved graphite sheets and could be regarded as cone-shaped fullerenes [3,4]. The open-ended carbon cone can be established by cutting 1–5 sectors of angle 60° from a graphene sheet and joining the edges made by the cut, with 1–5 pentagons at the apex [5,6]. Therefore, the surface curvatures of carbon nanocones are determined by the number of pentagons at the tip. Moreover, carbon nanocones have non-periodic structures, i.e. not only the curvature but also the surface electronic properties are changing when approaching the cone tip [7,8].

Because of these special properties it was suggested that carbon nanocones may be used for hydrogen storage. It was previously found that on the curved graphene the physisorption energies of molecular hydrogen can be enhanced significantly compared with those on planar graphene [9]. The curved graphene can be obtained by introducing five atom carbon rings (pentagons). The hydrogen storage results of experiments and simulations show that at the cone tip area there is a strong interaction between hydrogen molecules and the graphene sheet. This interaction increases dramatically when moving from the cone base to the cone tip [10]. Furthermore, the enhancement of the interaction seems to increase with increasing number of pentagons in the cone. Simulations of hydrogen adsorption isotherms have shown that hydrogen inside the conical part is more densely packed than that in the free liquid and approaches the solid hydrogen density [11]. This can be attributed to strong quantum effects [12,13]. For both interaction and hydrogen adsorption density it was found that the enhanced adsorption at the conical part is much stronger than the tube part in carbon nanotubes [10,14,15]. Therefore, it was speculated that the carbon nanocones may have better performance on hydrogen storage as compared to carbon nanotubes.

In a previous work the hydrogen adsorption/desorption on carbon nanocones was studied by thermal desorption and photoemission [16]. It was found that the adsorbed hydrogen is released at temperatures in the range from 230 to 290 K. Furthermore, it was found that the hydrogen desorption peak on carbon nanocones is

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much stronger (about five times) than that on graphite powder. Preliminary hydrogen desorption experiments have indicated that the carbon nanotube material has a similar adsorption ability as the carbon nanocone containing material. This may be explained by the composition of the carbon nanocones material; as mentioned previously, only 20% of the raw sample material consists of carbon cones with different opening angles while the remaining 70% is carbon nanodisks and 10% soot [16,17]. The carbon nanodisks may be considered to be the limiting case of a cone, with the apex angle 180° . The transmission electron microscope and electron diffraction study show that the carbon nanodisks have multi-layered structure of stacked graphite sheets; and most nanodisks have radii between 0.4 and 1.5 μm and the rim thickness ranges from 10 to 30 nm [17]. The average distance between the graphene layers in carbon nanodisks (0.376 nm) is much higher than the typical value for graphite (0.336 nm). This is most likely caused by relatively mechanical weaknesses between the different carbon layers [17]. The role of the nanodisks in adsorption of hydrogen remains undetermined. Compared with graphite the carbon nano disks consist of small-sized graphite sheets and have greater interlayer distance. It may be speculated that carbon nano disks may have higher hydrogen adsorption ability than graphite.

Carbon nanotubes have been considered to be an interesting material for hydrogen storage. However, since the interaction between hydrogen molecules and carbon nanotubes is due to weak van der Waals interaction carbon nanotubes do not have sufficiently large hydrogen storage capacity as hoped for. To improve the hydrogen storage ability on carbon nanotubes efforts have been made by using various dopants [18–20]. Doping of nanotubes by both electron-donor and electron-acceptor dopants has shown clear evidence for electronic charge transfer between the dopants and carbon. Charge transfer plays an important role in hydrogen adsorption on doped carbon nanotubes [20,21]. Experiments and simulations indicate that the charged carbon nanotubes have enhanced hydrogen storage ability as compared to pure nanotubes. In general negatively charged nanotubes are expected to have higher hydrogen adsorption. Typical electron-donor dopants like alkali metals are expected to transfer their valence electrons to the carbon π^* states in carbon nanotubes. This charge transfer may induce an increase in electron density on the nanotube surface near the alkali atom. The interaction between the hydrogen molecule and the nanotube surface may thus be enhanced [22]. On the other hand the positively charged alkali atoms polarize the hydrogen molecules. This means that the alkali atoms actually act as a bridge in the hydrogen uptake and interact with hydrogen molecules and the carbon nanotubes simultaneously. The charged-induced polarization results in stronger interaction between H_2 and alkali atoms compared with the interaction between H_2 and pure nanotubes [22–24]. Both these two effects enhance the physisorption binding energy of hydrogen molecules on alkali-doped nanotubes and therefore more hydrogen molecules are adsorbed on the carbon nanotubes. The concavity of graphite may have an effect on the hydrogen physisorption energy. Density functional calculations show for alkali-metal-doped graphite that the hydrogen physisorption energy on curved graphene can be improved about three times compared with that on clean flat graphene surface [25]. Therefore carbon nanocones might be a promising system for improved hydrogen storage by alkali metal doping.

In this paper we study effects of doping of potassium on a carbon nanocone containing material. We find that doping of potassium can change the hydrogen adsorption properties on the carbon nanocone containing material as well as improving the hydrogen storage. To investigate the mechanics of hydrogen adsorption on potassium-modified-carbon nanocones surface science techniques were used.

2. Experimental

The carbon nanocone containing material was obtained from n-TEC AS at Kjeller, Norway. In the carbon powder nearly 20% of the material consists of carbon cones with different apex angles; while the remaining 80% is mainly discs (ca. 70%) and soot (ca. 10%) [26]. A scanning electron microscopy (SEM) image of the material is shown in Ref. [16]. The powder sample was pressed to a thin pellet in a stainless steel holder of size of 11 mm \times 12 mm \times 3 mm. A thermocouple was spot welded on the back side of the sample holder. The sample holder was heated by passing current through supporting tungsten wires. The temperature of the carbon cone pellet was assumed to be close to the temperature of the sample holder which was measured using a K type thermocouple. The carbon cone pellet was cleaned by annealing to 1150 K while the pressure in the vacuum chamber remained below 1×10^{-9} Torr.

Temperature programmed desorption (TPD) spectra were recorded using a Transpector H100M quadrupole mass spectrometer from Leybold-Inficon. The tip of the mass spectrometer was shielded to minimize contributions from the edges and back side of the sample as well as the sample support. The temperature was varied by means of a Eurotherm temperature controller. The TPD measurements were performed in the range 110–1000 K with a heating rate of 2 K/s. The sample was cooled by liquid nitrogen in order to enable measurements below ambient temperature. Hydrogen was dosed at a pressure of about 1×10^{-5} Torr. The TPD measurements were initiated when the pressure in the vacuum chamber was reduced to 2×10^{-10} Torr. It was assumed that the pumping speed of the vacuum chamber was sufficiently large so that the signal from the mass spectrometer could be assumed to be proportional to the desorption rate.

The potassium deposition was achieved using a dispenser source from the SAES Getter Company (Milano, Italy). The potassium dispenser was positioned about 2 cm from the sample surface and was resistively heated by a current of 6 A to give a quite stable beam flux. During potassium deposition the sample holder was cooled by liquid nitrogen at a temperature of 110 K. The potassium source was thoroughly degassed prior to use. The deposited potassium was removed from the sample surface by heating the sample to 900 K after each experiment. The background pressure was below 2.5×10^{-10} Torr during the evaporations.

The photoemission measurements were performed by using a hemispherical SES 2002 electron analyzer (GammaData-Scientia). A monochromatized Al K α source (GammaData-Scientia) provided the exciting radiation for the X-ray photoelectron spectroscopy (XPS). A He discharge lamp with a toroidal grating monochromator (SPECS) was used for ultraviolet photoelectron spectroscopy (UPS). The energy resolution for XPS and UPS was estimated to be 0.4 eV and 0.1 eV, respectively. All spectra were measured in angle integrated mode around normal emission. The working pressure in the chamber was below 2×10^{-10} Torr. The measurements of the work function of the sample were made from UPS He I (21.2 eV) spectra with a sample bias of -5 eV and observing the low kinetic energy cut-off of the secondary electron energy distribution curves.

3. Results and discussion

Hydrogen desorption properties of a carbon nanocone containing material were investigated by TPD after doping by potassium. Subsequent to K deposition the samples were exposed to hydrogen at different doses from 300 to 3000 L (1 L [Langmuir] = 10^{-6} Torr s). Fig. 1 shows the thermal desorption spectra after an exposure of 900 L hydrogen in the temperature range 130–900 K for a carbon cone sample which was doped by various amount of potassium. Fig. 2 shows the XPS core level intensity ratio $I_{\text{K}2p}/I_{\text{C}1s}$ as a function

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