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Atomic Resolution Investigation of metal-Assisted Hydrogen Storage Mechanisms in Activated Carbon Fibers

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Hydrogen attracts an interest as alternative future energy carrier to overcome the foreseeable energy crisis. Solid state storage media, however, are not yet providing sufficient cyclic gas uptake capabilities. Promising candidates for hydrogen storage media are Pd-modified activated carbon nanofibers (ACF). During synthesis, thermal activation processes introduce micro- and nanoporosity into the ACF microstructure. It has been shown that modification of carbon structures with Pd nanoparticles enhances the hydrogen storage capabilities [1]. However, it was found that the hydrogen gas uptake exceeds the expected storage capabilities based alone on PdH_2 formation and physisorption on unsaturated carbons (Figure 1).

High-resolution TEM and aberration-corrected STEM was used to identify local storage sites and mechanisms in the ACF microstructure. HRTEM imaging is very sensitive to the atomic structure of the carbon fibers. Recorded micrographs show some degree of ordering in the ACFs with a large number of quasi-parallel grapheme sheets (Figure 1c). The termination of graphene layers creates small open volumes in the microstructure with diameters of the order of 6-8 Å [2]. Such nanoprosity was found to be highly efficient for the physisorption of hydrogen atoms. We have used HRTEM to quantitatively identify such re-occurring structures. In addition, selected area diffraction is used to determine the crystal structure and lattice constants of Pd particles embedded in the ACF microstructure.

The simultaneous acquisition of bright field (BF) and high-angle annular dark field (HAADF) images using aberration-corrected STEM enables the correlation of the carbon microstructure (as recorded in the BF image, Figure 2b) with the location and atomic structure of Pd nanoparticles as identified in the HAADF image (cf. Figure 2a). Especially the atomic and electronic structure of the Pd/ACF interface is critical for hydrogen storage mechanisms with respect to H_2 dissociation by the Pd particle and subsequent storage in the ACF microstructure close by (the so-called spill-over effect) [3].

Sub-Ångström imaging conditions enabled the detection of highly dispersed single Pd atoms in the volume of the carbon fibers. The presence of single Pd atoms stabilized by the ACF template might enable the formation of Kubas-like complexes [4] and hence reversible storage of up to six hydrogen atoms per Pd atom.

We are currently planning to use in-situ HRTEM to image potential changes in the carbon microstructure and the Pd particles due to exposure to hydrogen gas, which will offer more detailed information about the hydrogen storage mechanisms.

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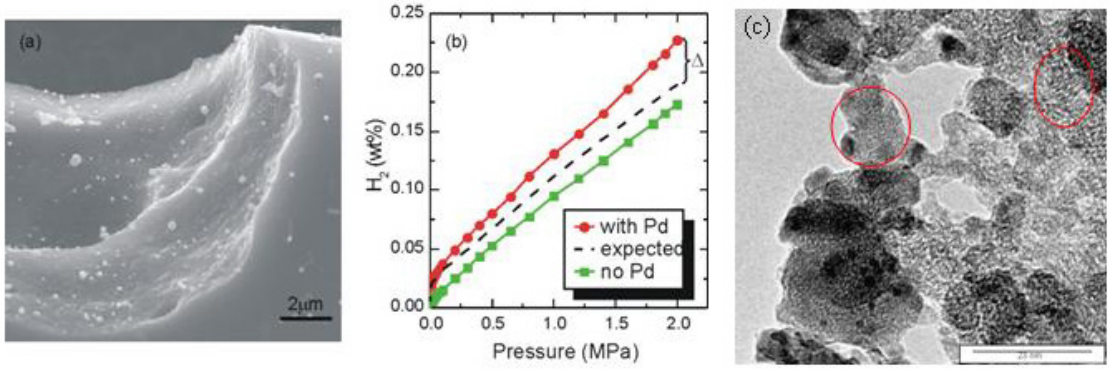

Figure 1: SEM micrograph (a) of activated carbon fibers with added Pd catalyst particles (bright contrasts). (b) Hydrogen adsorption isotherms for Pd-free and Pd-modified ACF (2.55 wt% Pd). The dashed line represents the amount of hydrogen required to convert the entire Pd content to palladium hydride (β-$PdH_{0.66}$). (c) HRTEM micrograph of Pd-modified activated carbon fibers. Some degree of ordering is observable within the carbon microstructure.

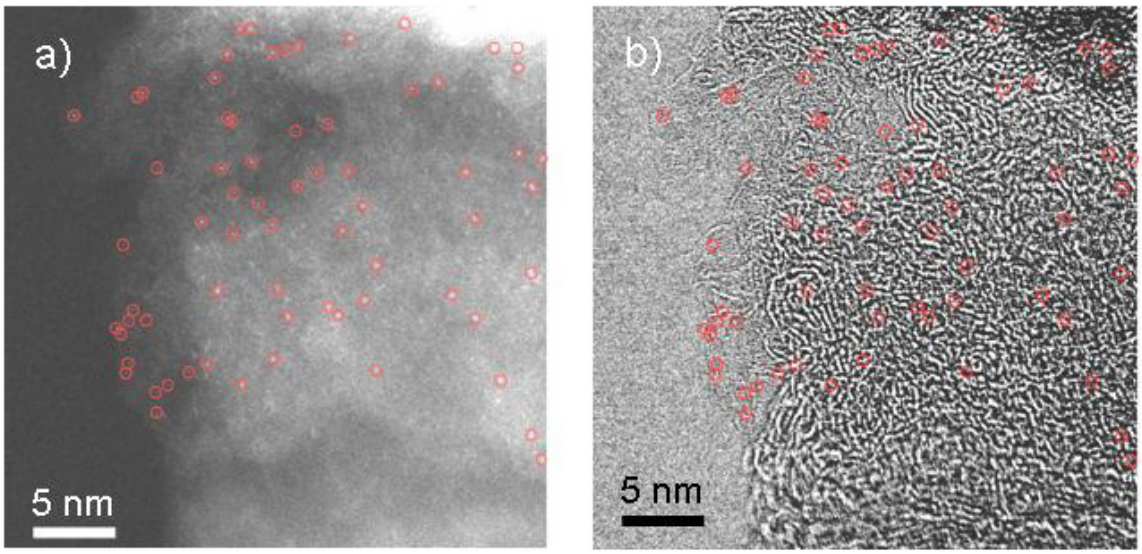

Figure 2: ADF (a) and BF (b) images recorded from an activated carbon fiber with highly dispersed single Pd atoms, which are encircled in red. Their location was also marked in the BF image (b)

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