Physical sorption of aluminum in carbon honeycomb structures: models and experiment

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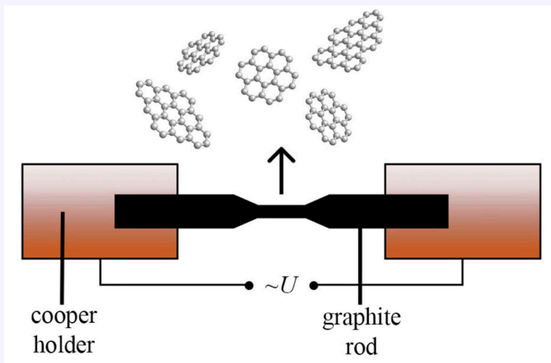
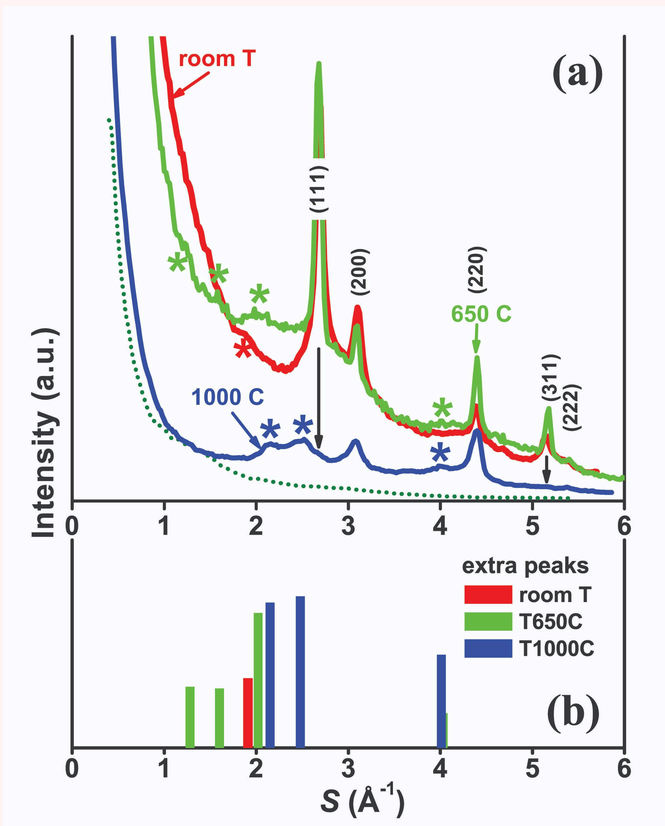
The **carbon honeycomb (CH)** structures have demonstrated previously their high storage capacity with respect to inert and molecular gases (Kr, Xe, CO_2) due to physical absorption in their unique 3D cellular architecture [1-3] as well as their structural stability and diversity owing to different chiralities (armchair, zigzag) and wall widths [3,4]. However it has been unclear how metal atoms will behave within the CH nanochannels.

The preliminary DFT theory showed that the single Al atom put on defect-free graphene planes, which are constituents of the CH walls, can be successfully adsorbed with the bonding energies ~0.6 eV without any noticeable deformation of a graphene layer. These results imply that the rather (pseudo)physical than chemical bonding is realized if to take into account the undisturbed supporting graphene planes. The bonding energy ~0.6 eV is relatively small as for chemical bonds but simultaneously this energy is certainly much higher as compared with typical interactions in van der Waals adsorption.

We used these calculations in order to build the proper models for Al filling the CH channels of different chiralities to be compared with the electron diffraction experiments made on the CH films filled with aluminum at the room and elevated temperatures.



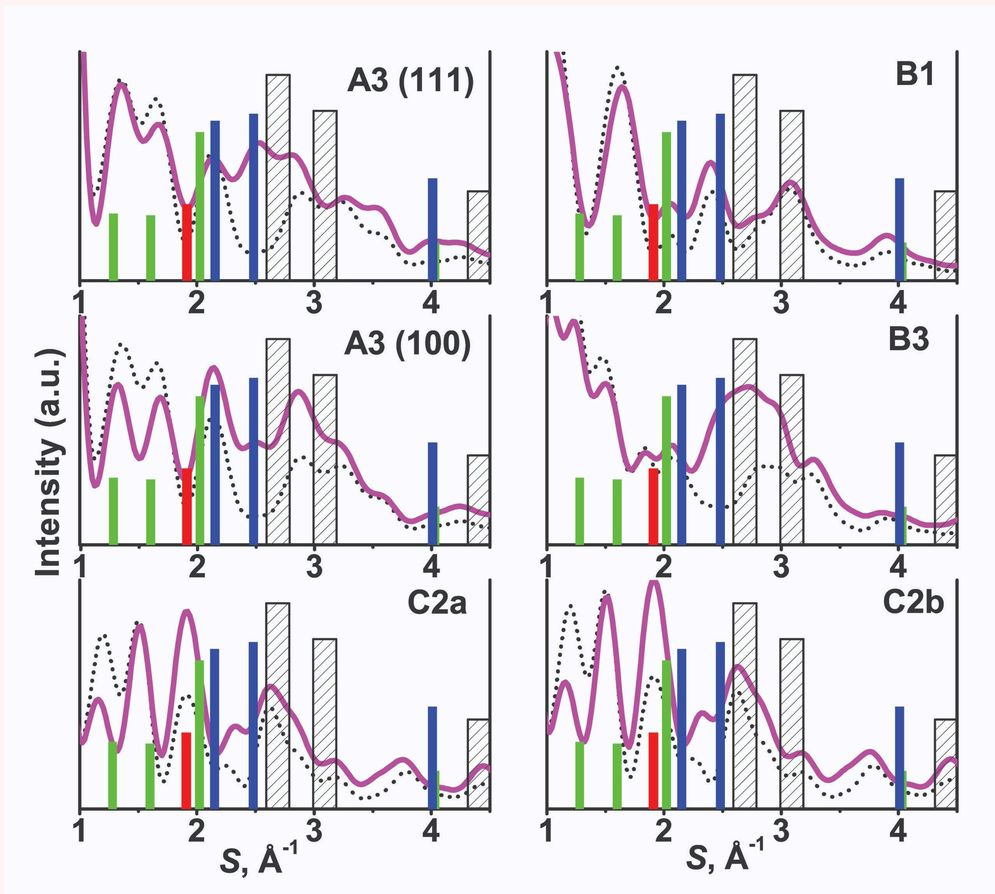
The CH structures are produced by sublimation of graphene patches from graphite, which further fly and either collide in vacuum and/or are deposited on the prepared substrates as upright standing formations producing CHs.



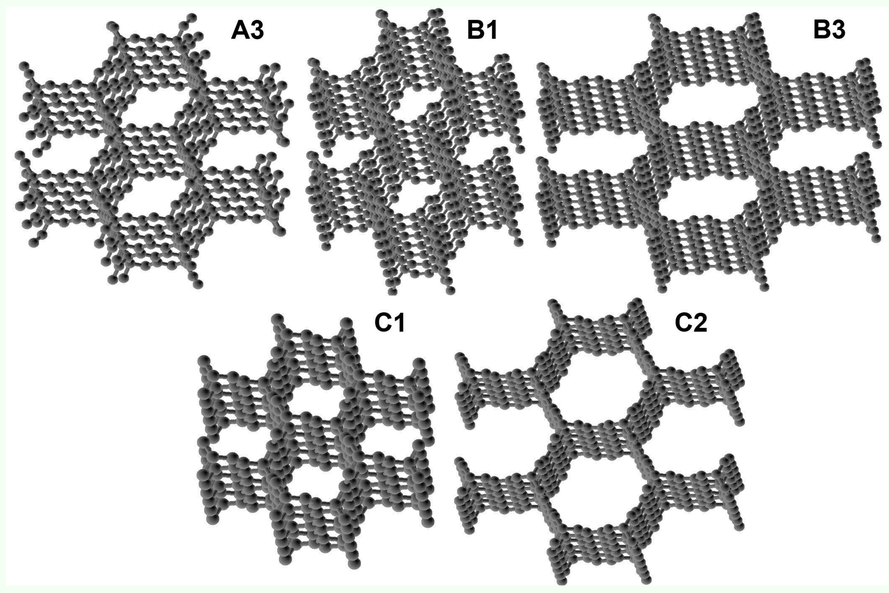
(a) The electron diffraction intensity I for aluminum deposited on the CH film at room T vs the wave scattering vector S (the red curve); the electron diffraction curve from the sample heated in vacuum up to T~650 C vs S (the green curve); the same for the sample heated up to T~1000 C vs S (the blue curve); the dot line – the CH film. The asterisks – the features ascribed to the filling with aluminum.

(b) The specific peaks corresponding to the asterisks in (a).

All diffraction curves are recorded at room T.



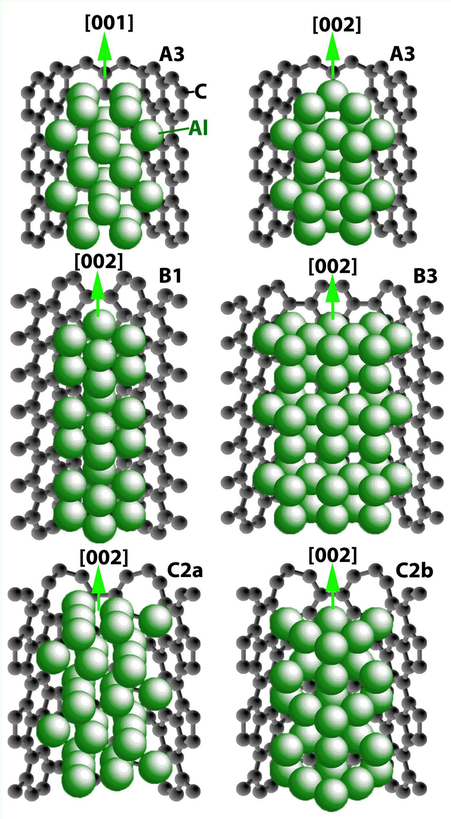
The calculated diffractograms for pure CH matrices (dotted black curves) and the CH matrices filled with Al (solid curves) compared with the experimental data above (b) presented by columns of the same colors as (red – room T, green – 650 C and blue – 1000 C) show good coincidence in peak positions. The wider pattern columns show the positions of the bulk Al peaks, the comparison in these positions should be excluded.



The CH structures of three types A, B and C with two chiralities (armchair for A and Zigzag for B and C) and various wall widths indicated by the numbers as proposed in [4].

The structural models of the CHs filled with Al, built to be compared with the experimental diffraction results. For the A3 structure we show two different orientations of Al clusters inside the channels, one with the FCC axis [001] oriented along the CH channel and the other with the hexagonal [002] axis along the channel. For the C2 structure we considered two hexagonal clusters filled with Al rotated with respect to each other by 30 deg. The CH structures of the type B show the essentially different filling levels in B1 and B3 depending on the channel sizes.

These models showed the best coincidence in peak positions between experimental and calculated diffractograms (from the total 15 models tested).



Summary

We studied the Al uptake in the CH matrices following the general rules as we have found earlier for gases. The Al pieces were evaporated from the heated tungsten crucible, and the Al vapors were deposited on the CH films. Such samples were studied as prepared after the Al deposition and after heating in vacuum up to ~650 C, then up to ~1000 C by means of high-energy electron diffraction in the setup EMR-100.

The calculated diffractograms are based on the set of the structural models built in accordance with the preliminary theoretical prediction. The comparison of the model diffractograms with the extra peaks on the experimental diffraction curves enabled us to confirm that experimental diffractograms can be successfully described by the structural models of the Al uptake in the CH structures assuming (pseudo) physical sorption of aluminum in the CH channels.

At room temperatures such a sorption occurs due to the direct Al vapor deposition in the wider CH channels. When the samples were heated up to ~650 C the diffusive mechanism of sorption from the initially deposited Al island films was found to be operative. And finally at the highest in our experiments T~1000 C the Al films melt and in a liquid form penetrated inside the CH channels.

The obtained results open up a unique opportunity for creating a new class of materials based on the CH structures with nanosized channels, which can be filled by the nanosized metallic rods with the expected one-dimensional metal-based conductivity along the rods and a variety of the other intriguing properties. It is interesting to note that the CH structures were already predicted to possess the high capacitance for the other metals Li and Na and can be applied in the relevant types of batteries demonstrating the reversible metal filling.

References

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