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Modulation of chemical interactions across graphene layers and metastable domains in carbon materials

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Attachment of palladium clusters to carbon surface was investigated by SEM and STEM methods that have suggested plausible modification of chemical interactions across graphene layers; the fact can explain mismatches between domain structures and alignment patterns of palladium nanoparticles observed experimentally by the electron microscopy.

Carbon materials have been used in chemistry and catalysis for more than a century and made substantial impact on various fields of science. At the present time, a huge number of catalysts and reagents based on carbon materials was developed for research and industry.[1,2] However, only in the recent years, after tremendous interest in graphene, detailed investigations of carbon materials at molecular level and estimations of effect of carbon structure on metal-containing catalysts were emerged to a new level.[3]

Recently we have shown that Pd_2dba_3 complex possesses intrinsic dynamics and easily decomposes with formation of Pd nanoparticles even under ambient conditions.[4] In the present study we have utilized this fascinating feature of Pd_2dba_3 for covering carbon surface with Pd nanoparticles. We have prepared Pd nanoparticles supported on graphite and investigated the morphology of Pd/C system using field-emission scanning electron microscopy (SEM) and scanning transmission electron microscopy (STEM).[†] We have found that Pd nanoparticles did not settle on the graphite surface uniformly (neither chaotically), but formed certain patterns on carbon surface. At the first sight we concluded that nanoparticles lined up along visible graphite edges and grain boundaries, which is expected and was discussed in the literature.[5,6] However, the further analysis evidenced more complex patterns with non-obvious surface distribution of attached particles.

Figure 1(*a*) shows studied graphite surface coated with palladium nanoparticles. We used a low accelerating voltage of 30 kV for the microscopy observation, which allowed us to study the morphology of a thin layer of graphite on the edge of the carbon particle without a damage of the sample by electron beam. Carbon material, metal nanoparticles and several sets of dark/grey lines were clearly seen in the studied Pd/graphite sample.

Important to note that dark/grey lines, visible in the image, had different widths and directions. Variation of image recording parameters (such as angle of sample tilt, focal length, and accelerating voltage) did not affect detected patterns. It appears the observed combination of dark/grey lines originates from the moiré effect.[7] This effect is known to appear when one or few graphene layers in a stack of graphite rotate on a small angle around the axis perpendicular to the basal plane of graphite. Such arrangement results in overlapping of periodic lattice and, consequently, leads to interference of electron beam of the microscope. Observation of moiré effect in graphite by TEM was reported by Gillin *et al.* in 1968.[8] The moiré pattern in graphene was observed by Kuwabara *et al.* in 1990 by scanning tunnel microscope upon characterization of a freshly cleaved sample of highly oriented pyrolytic graphite.[9] Afterwards, numerous publications have focused on the moiré effect in graphene and graphite studied by STM methods.[10] From simple geometric considerations the constant of the superlattice can be calculated by the formula $d = p/[2\sin(\alpha/2)]$, where α is the angle of rotational misorientation, d is the distance between two pale lines (*i.e.* constant of superlattice), and p is the lattice constant.[7] With this simple relationship, the angle of shift of the two planes can be calculated according to the formula: $\alpha = 2\arcsin(p/2d)$. From the structural point of view, the wider the observed lines, the smaller the angle of graphene layer rotation.

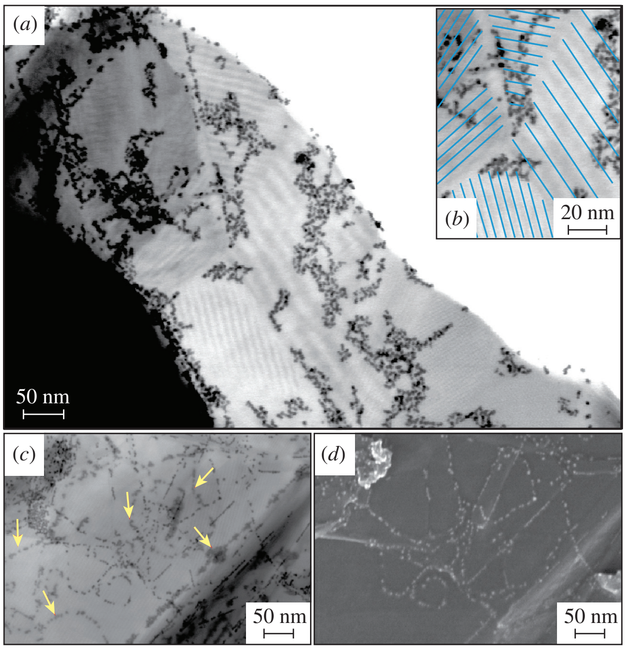

Figure 1 Pd nanoparticles supported on graphite studied by (*a*)–(*c*) STEM and (*d*) SEM methods. Directions of the dark/grey lines on graphite surface are highlighted by straight lines in the insert (*b*). Arrows on the STEM image (*c*) indicate Pd nanoparticles, which were not visible in the SEM image of the same region of the sample (*d*).

[†] *Experimental details.* STEM: powdered sample was attached on copper grid and fixed in aluminum specimen holder with copper cap. Images were acquired by transmitted electron detector (scintillator + photomultiplier system) in bright field image mode at 30 kV accelerating voltage and at working distance of 8 mm. SEM: the same sample was used and the image was recorded at the same region. Images were acquired in secondary electron mode at 30 kV accelerating voltage and at working distance of 8 mm. The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM).

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For the studied sample, the longest distance between the white lines on graphite surface was around 100 Å, and the smallest distance was around 35 Å. According to the above formula and considering that the lattice constant of graphene is 2.46 Å, the angle of graphene sheets rotation was estimated as 1° 24′ for the lines with 100 Å step and 4° 1′ for the lines with 35 Å step.

As shown in Figure 1(*a*), the areas with bounded Pd nanoparticles and chains do not always match those areas, where one type of direction and geometry of moiré patterns was observed. The finding suggests that domain structure does not always affect the interaction of metals with the surface of the carbon material.

Microscopy images of the same region of surface characterized by both SEM and STEM methods have further highlighted the observation [Figure 1(*c*),(*d*)]. Note that many additional Pd nanoparticles and nanoparticle chains became visible in the STEM mode. The nanoparticles and chains were only partially seen in the secondary electrons mode of SEM, which reflects morphology from the surface of the sample.

Presumably, additional particles, appeared in the STEM image, may be bound between the graphene layers, penetrated into the inner part of the carbon sample or located on the other side of the sheets. It is important to note that the distribution pattern in the curvature of lines and chains also retained for these palladium particles.

To summarize, two experimental findings deserve a special note: (i) binding of metal nanoparticles does not always correlate with simple domain structure of the carbon material, where defective and most reactive carbon centers are expected; (ii) appearance of more complex 3D carbon structures (metastable 3D carbon domains) could be proposed by joint analysis of SEM and STEM images.

These experimental observations gave us an idea that graphene layers modulate chemical interactions across their surface. This modulation (modification) of chemical reactivity can be sensed by reactive particles and active species. Such domains and patterns of carbon materials were not obviously visible upon surface characterization of native carbon material with standard analytic tools (prior to Pd nanoparticles attachment).

We anticipate more detailed studies in the nearest future dealing with the origins of chemical reactivity across graphene layers and the nature of carbon domains.

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