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Optical manifestations of the condensation of topological defects in continuous layer multishell carbon nanoparticles

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We report the observation and the explanation of the famous 220 nm spectral feature in UV absorption from continuous layer multishell carbon nanoparticles. Historically, attempts to find this feature in carbon allotropes led to the discovery of the C_{60} fullerene. We discerned the physical origin of this feature to be the well-defined pentagonal corner defects in polyhedral multilayer carbon nanoparticles. These new topological columnar defects should have large influence on the electronic properties of nanomaterials and are worthwhile further detail studying.

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It is known that the whole area of fullerene research was initiated to explain the origin of the ”universal” 217.5 nm peak in extinction from interstellar dust.[1] Special carbon soot (“camel hump smoke”) showing a similar feature in UV absorption was proved to contain C_{60} molecules.[2] After eliminating the intensive contribution from the background of carbon particles (carbon black) the strong 216, 264, and 339 nm peaks from C_{60} molecules were resolved. By virtue of the Hückel approach for π-electron systems mostly all the difficulties of classification and calculation of the C_{60} spectrum were reduced to pure topological and symmetry consideration.[1,3] Yet, C_{60} molecules cannot account for the origin of the 217.5 nm feature.[2] In addition, C_{60} molecules are too sensitive to the production conditions unlike the carbon black which includes aggregated multishell carbon onions, carbon polyhedral particles 5–50 nm and the so-called soot. The soot has a locally layered structure in form of basic structural units (BSU) while carbon onions and polyhedral particles have continuous carbon layers. Although the onions were claimed to be carriers for the 217.5 nm feature, the origin of the peak was mistaken for collective excitations from plasmons.[4] Considering a slight uncertainty in the determination of the peak position we will further on refer to this feature as the 220 nm one.

The carbon structures in question consist of multiple continuous graphene sheets. The inner hexagonal structure of a graphene sheet induces a network topology which tells on the geometry of the sheet: the introduction of one pentagon leads to a positive local curvature (a local cone) while one heptagon leads to a negative local curvature (a local saddle). For an arbitrary graphene sheet those defects may be scattered all over the sheet possibly in pentagon-heptagon pairs for a nearly flat or perfectly spherical sheet. Citing Ref. 5, “The intriguing revelation that 12 pentagonal “defects” convert a planar hexagonal array of any size into a quasi-icosahedral cage explains why some intrinsically planar materials form quasi-crystalline particles, as appears to occur in the case of soot.” What has been overlooked through all the years is that in order to keep the average distance 3.4 Å between the layers in a multilayer stack of continuous graphene sheets, those pentagons and heptagons should be inevitably condensed or grouped one over another in columnar structures to make multilayer cones and saddles. In the absence of heptagons exactly 12 such pentagon columns should exist for a multishell closed cage.[6] Interestingly, icosahedral quantum dots for tetravalent semiconductors were recently predicted to have radial channels of pentagonal rings which results in electron spectra not possible in the bulk.[7]

One may suggest that the topology of the π-electron systems will dominate and determine relevant electronic spectra even for mesoscopic (and, finally, macroscopic) bodies and that the topology-induced peculiarities in such systems can be distinguished in experiment with UV absorption, which is traditional for π-electron systems. Topological phases for electron wave functions in graphitic cones were studied theoretically in Ref. 8 where it was shown that the local density of states (LDOS) changes near the cone apex and can be finite at the Fermi level. The case considered in Ref. 8 does not distinguish any spectral features because it deals only with the change in the linear part of the graphene sheet spectrum in the vicinity of the Brillouin zone corners, i.e., with the contribution from delocalized electrons. It was even proposed in Ref. 8 to etch away the pentagonal apexes of the graphitic cone to obtain a pure mesoscopic normal metal ring. On the contrary, it is those apexes that are the main subject in our work. It is important for what follows that the tight binding calculations show that the pentagonal and heptagonal defects in a hexagonal graphene sheet have the LDOS formed by the levels of an isolated n-member ring only broadened by the coupling with the ligand hexagons.[9]

Here we show that condensed columnar stacks of pentagons—5 Member Ring Columns (5MRCs) in multilayer topology-induced corner structures in the so-called shell-shaped carbon nanoparticles (SCNP)[10] —produce an atomlike electronic spectrum of these continuous layer nanoparticles and are the origin of the famous 220 nm feature in UV absorption, which has been a long-standing problem. The sharp 220 nm feature in UV absorp-

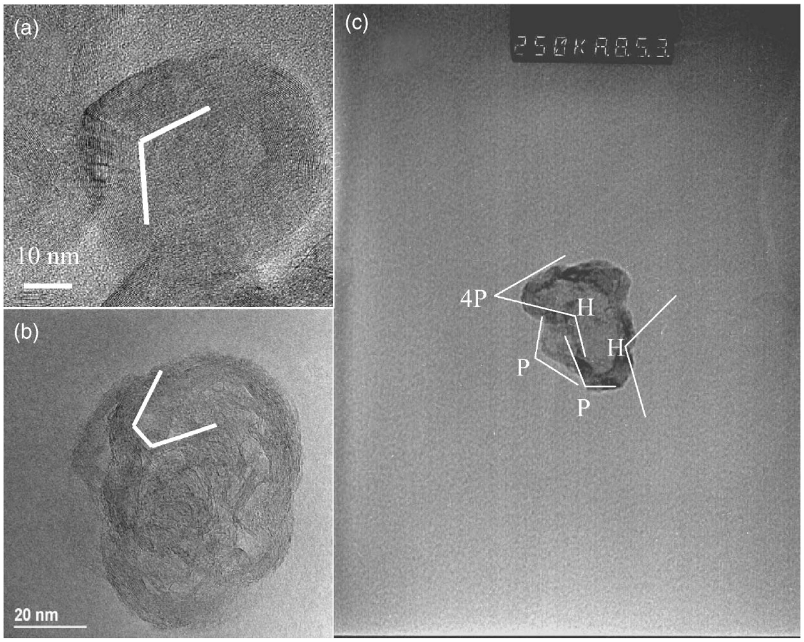

FIG. 1. The geometry of different type SCNPs seen from TEM images. (a),(b) The apex angle 112.88° for 5MRCs is marked with white lines; (c) the pentagon and heptagon induced angles are marked with letters P and H, respectively.

tion spectra appears due to 5MRCs on the background of the broad 260 nm Surface Plasmon Resonance (SPR) feature from delocalized electrons. We discover and enhance the 220 nm feature over the SPR by reducing the collective plasmon through breaking the SCNP agglomerates after heavily boiling the pristine SCNPs in nitric acid following the method described in Ref. 11 and using sodium dodecyl sulfate (SDS) for preventing further contacts between SCNPs. The chemical treatment does not break the continuity of the shells in individual SCNPs but makes them hydrophilic due to slight oxidation of the outer shell so that SCNPs repel each other in water. All the particles with discontinuous shells including soot are quickly dissolved in nitric acid. A suppression of the SPR can also be achieved by breaking the continuity of the graphene layers in flat parts of SCNPs by ballmilling. We speculate that 7MRCs made of heptagon

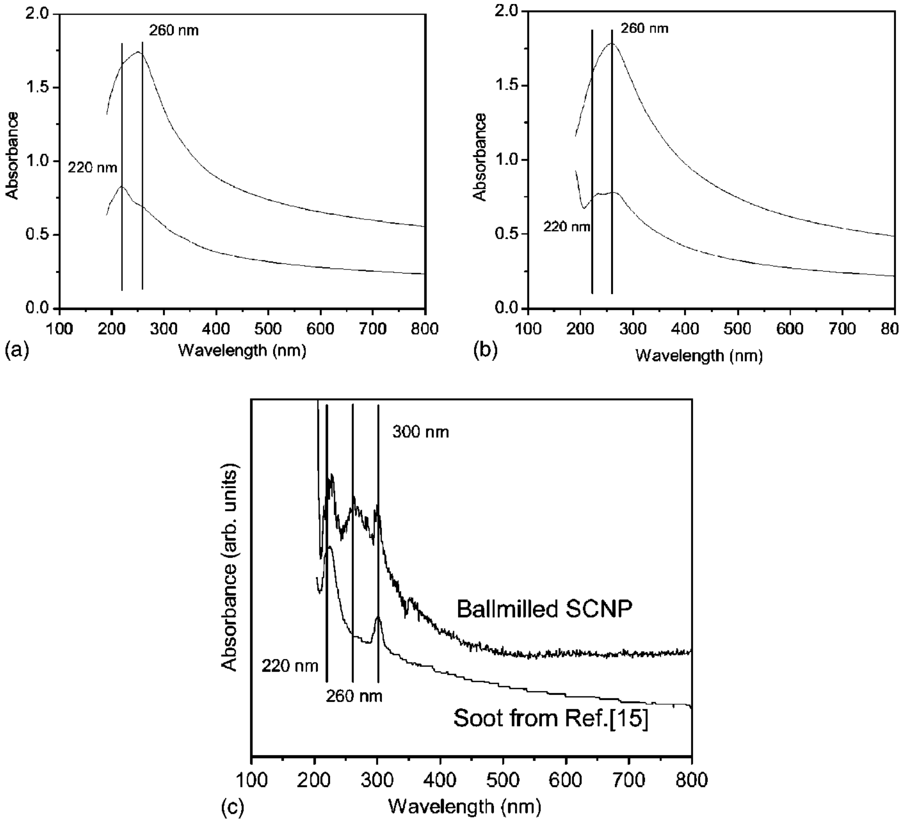

FIG. 2. UV absorption spectra for SCNPs: (a) on quartz plates; (b) in water solutions; (c) ballmilled for 2 hours. The vertical lines show the position of 220 nm, 260 nm, and 300 nm features. The upturns in absorbance seen in (b) and (c) for the wavelengths less than 200 nm indicate the presence of some amount of flat graphene sheets with around 6 eV graphite plasmon especially pronounced for ballmilled samples where such sheets inevitably appear in debris. We proved it by comparing the spectra with the ones from acetylene soot with numerous BSUs. The soot shows only the upturn with no other features.

saddles may bring an additional sharp feature to the spectrum at longer wavelengths.

Continuous graphene sheets if closed produce compact nanoparticles. SCNPs are of special interest because their closure demands existing pentagonal defects in overall hexagonal graphene sheets. The same is also true for capped nanotubes and in this respect the capped regions may have the properties of nanoparticles in the vicinity of the caps. From the Euler theorem there should be 12 pentagons for a closed shell. Usually defect pentagon-heptagon pairs can exist at any amount. For a spherical onion, this amount should be sufficiently large to keep the curvature smooth. If there are only 12 pentagons and all the others are hexagons, a large shell may attain a polyhedral (icosahedral) shape with extended flat regions—a giant fullerene of $N=60n^2$ atoms, where n is an integer.[5] For a multishell structure the corner region can be roughly seen as a round cone of one pentagon in the apex which gives the cone angle $\alpha_1=2\ \arcsin(5/6)=112.88°$. This angle is shown in Figs. 1(a) and 1(b) for two SCNPs of different type. It is important that pentagons from different shells of a SCNP are forced by the topology and geometry to be condensed in the apexes of distinct Russian-doll-type cones unlike the situation with round onions where the pentagons are randomly scattered all over the shell. The same is true for heptagons in a multishell SCNP. In Fig. 1(c) we marked the 7MRC with the letter H and showed the angle $\beta_1=2\ \arcsin[\sqrt{2}\ \sin(5\pi/24)]=118.84°$ for the lateral projection of the saddle with one heptagon. The cone with the mark 4P contains four pentagons in its apex with the angle $\alpha_4=2\ \arcsin(2/6)=38.94°$. Yet multipentagon apexes are rare and decompose into one-pentagon 5MRCs. Therefore multishell cones and saddles make spatially separated and well-defined 5(7)MRCs, and as far as heptagons are present, the number of condensed 5MRCs can be larger than 12 by the number of 7MRCs.

For the cone with the angle α_1, a π-orbital axis vector (POAV) defines the pyramidalization angle[1] which can be calculated to be 12.298° degrees against 11.6° degrees for C_{60}. This means even stronger π-σ hybridization for 5MRCs than for C_{60} and thus stronger electron affinity. Also the pentagon ring stands a little more isolated from the ligands in a 5MRC than in C_{60} and much more than in large round onions. This fact is crucial for understanding the origin of the spectral feature at 220 nm. The lack of the 5MRCs with nearly isolated pentagonal rings in perfect multishell carbon onions explains why they cannot show any UV feature except the 260 nm hump from the SPR. The same holds for single- and multi-walled carbon nanotubes.[12,13] Only after a heat treatment which converted the initially round onions into the polyhedral ones (it can be concluded from the dramatic enhancement and narrowing of the G-band in Raman spectra from post-annealed samples) with many 5MRCs to appear, did the samples start showing the 220 nm feature in the UV spectra.[4]

The consequences of the topological condensation of defects in SCNPs have not been discussed in literature before. In our simplified analysis we follow Ref. 3 where the initially separated 12 pentagons in a C_{60} fullerene were gradually connected and the icosahedral group split the initially degenerated spectrum of the 12 pentagonal rings into the full C_{60} spectrum. For the 5MRC as well as for a graphitic cone the situation is simpler because the local symmetry remains roughly the same as for an isolated pentagon ring. It means that only some broadening due to ligand hexagons and slight bandlike splitting due to extended states along the 5MRC may appear. Thus, the simplest approach, when in the first approximation the spectrum of one isolated pentagon(heptagon) ring is taken for the spectrum of 5(7)MRC, is possible.

The energy levels of an isolated pentagon ring can be calculated from the formula of the Hückel theory,[14]

$$E_m=-2\gamma_0\ \cos(2\pi m/5), \tag{1}$$

where m is an integer and γ_0 is the resonance energy. For an isolated heptagon the energy reads

$$E_m=-2\gamma_0\ \cos(2\pi m/7). \tag{2}$$

According to (1) the energy difference between HOMO and LUMO levels for an isolated pentagon is 5.59 eV [calculated with $\gamma_0=2.5$ eV (Ref. 1)]. The corresponding excitation energy for isolated heptagons is 4.23 eV. Both are close to 5.62 eV (220 nm) and 4.12 eV (300 nm) for humps in the UV spectra measured in KBr pellets[15] for soot pellets with highly curved polyhedralike structures but with many interruptions in graphene sheets which effectively suppress 260 nm SPR. Some doping from metal vapor present in the system may also play a role in the enhancement of 5(7)MRC spectrum features. If the plasmon is weakened as it should be for isolated SCNPs, those two humps coming from topologically condensed pentagons (and possibly heptagons) should be pronounced as well.

Now we show how 5MRCs are revealed in the UV absorption of our polyhedral SCNPs. We performed UV absorption measurements with a Cary 5G UV-vis spectrometer with the resolution 1 nm in the wavelength range from 190 nm to 800 nm for agglomerated and isolated SCNPs both on quartz plates and in water solution. The water solution is stable because of the hydrophilic nature of the treated SCNPs. Figure 2(a) shows the domination of the 220 nm feature for isolated SCNPs on a quartz plate. When SCNPs were agglomerated more, the 220 nm feature was buried under the 260 nm SPR. The similar behavior is seen in the water solution as well [Fig. 2(b)]. Results with ballmilled samples (in KBr pellets to prevent agglomeration and with taking care to avoid contamination during the ballmilling) with broken shells revealed further enhancement of the 220 nm feature due to the further reduction of SPR. Also the 300 nm feature started to be seen for ballmilled samples [Fig. 2(c), the upper curve].

As far as a 5MRC can be viewed as an extended tubelike structure embedded into a SCNP one may expect to observe electronic effects from extended electronic states in this topological defect. The photoluminescence from these states might be similar to the fluorescence from single-walled nanotubes (SWNT)[16] due to van Hove singularities in a one dimensional system of 5MRCs. It is important that the 5MRCs are locally charged so that Coulomb effects can be pronounced adding to the peculiarity of the system. The field emission measured from the pentagonal corner of a polyhedral nanoparticle showed a surprising maximum of the electron density in the center of the outer pentagon[17] which can be explained as a revelation of the extended states in 5MRCs. For agglomerated SCNPs the fluorescence should be quenched similar to the quenching in agglomerated SWNTs because of electrical conductivity. That is why the separation and isolation of SCNPs is as crucial for the photoluminescence as for the observation of the 220 nm UV feature.

Indeed, we have checked the micro Raman spectra from agglomerated and isolated SCNPs to find that the most individually isolated SCNPs showed the most pronounced fluorescence spectra [Fig. 3(a)] which (after recalculation for the Raman shift from 514.5 nm excitation of an Ar-ion laser) follow the electronic spectra found in both light absorption and emission from isolated SWNTs [Fig. 3(b)].[16]

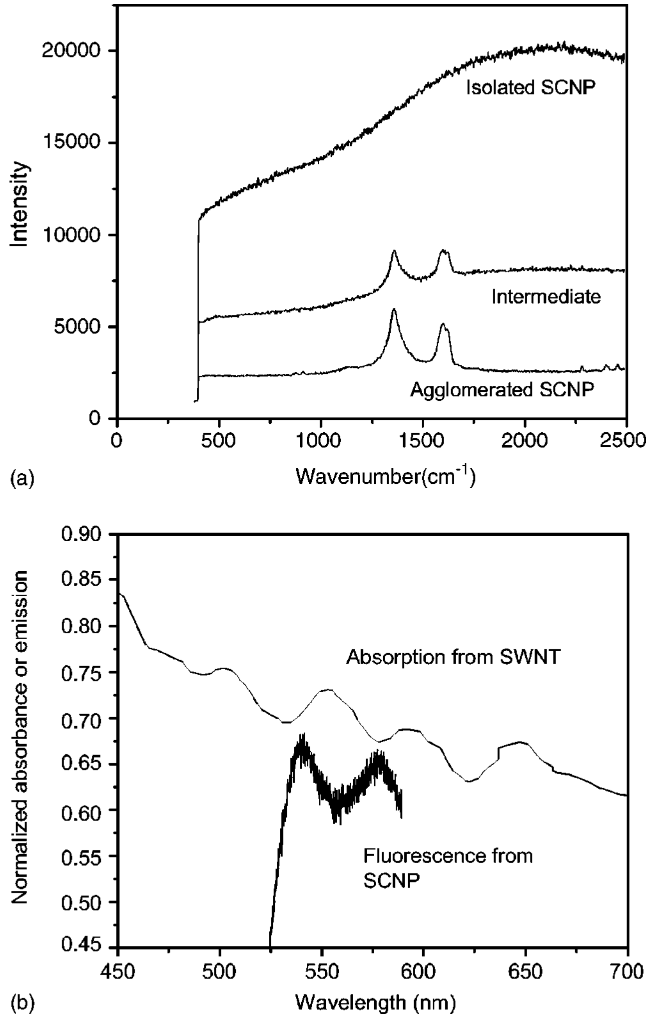

FIG. 3. Raman spectra from SCNPs. (a) a higher isolation of SCNPs with SDS brings a higher fluorescence intensity, which buries the characteristic Raman features at 1350 and 1590 cm^{-1}; (b) a recalculated fluorescence spectrum from the Raman spectrum obtained with 514.5 nm Ar-ion laser from isolated SCNP compared with a part of the light absorption spectrum for SDS isolated SWNTs from Ref. 16.

The existence of topology induced 5MRCs in SCNPs may control the cold electron field emission from SCNPs because it is possible for the emitting electrons to use the extended states along the column to escape from the corner of the particle. 5MRCs may be able to incorporate transition metals in a metallocenelike structure, where, say, an Fe ion is embedded between each two pentagons in the column. As far as the graphene sheet ligand for 5MRCs warrants the absence of CDW and Pierls instability in this one dimensional system, SCNPs may be interesting for high-temperature superconductivity when doped with alkali metals.

In conclusion, the carbon network topology of polyhedral continuous layer carbon nanoparticles induces new topological defects—columnar stacks of pentagon rings, which are responsible for the famous 220 nm feature in UV absorption.

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