Present research at Toyota Riken

"Field emission from nano-carbon and quest of its functional properties"

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Research Objects

Electronic states and atomic structures of nanocarbon surfaces and edges, and molecules adsorbed on nanocarbon field emitters are studied by using field emission microscopy (FEM). The obtained insights for nanocarbon field emitters will be exploited to develop a highly coherent, low energy projection resolution microscope. We also try to verify the theoretically predicted electron-spin ordering at the graphene edge by using field emission (FE) from an edge of graphene. Furthermore, exotic carbon substances called carbyne (sp-hybridized carbon), which is formed in CNT cathode films after FE experiment. We will clarify and explore the novel and functional properties of nanocarbon, which possesses a wide variety of structures and properties, aiming to develop nanoscience and technology related with nanocarbon materials.

Research Methods

1. Observation of electron orbitals and spin polarization at graphene edges by field emission

In the field emission from CNT and graphene, π-electron orbitals existing at their surface and edge prevail tunneling of electrons, being in contrast to conventional metal emitters where the tunneling are governed by free electrons. Depending the structure of carbon, spatial distribution and symmetry of the electron orbitals change greatly. For example, at the closed tip of CNT, the π-orbital spreads over the surface of a carbon hexagon net, whereas at the end of a broken CNT and/or the edge of graphene it extends perpendicular to the hexagon net surface. Therefore, it is expected that spatial distributions and natures of electron orbitals such as the symmetry can be obtained by observing FEM images (Fig. 1) from nanocarbon substances having different geometric structures. Furthermore, at the edge of graphene, it is theoretically predicted that electron spins are ferromagnetically ordered (Fig. 2). In this research, the spin state is studied by directly measuring the spin polarization of electrons field-emitted from the edge.

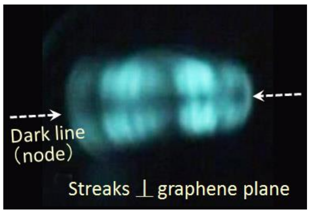

Fig. 1. FEM image of a graphene edge.

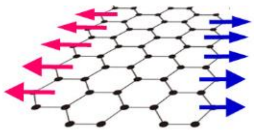

Fig. 2. Spin ordering at graphene edges.

2. Development of atomic resolution FEM and low-energy projection microscopy using CNT field emitters

It is well-known that FEM images of organic molecules such as copper-phthalocyanine adsorbed on a tungsten (W) needle show a four-leaf pattern, which was first observed by Müller who invented field ion microscopy. The FEM pattern has attracted much attention since then because it was considered to show directly the shape of the planar molecule with four-fold symmetry. However, even other organic molecules that do not have the four-fold symmetry give similar four-fold patterns, and phthalocyanine molecules sometimes show two-leaf and/or circular patterns. It has been argued that the FEM patterns from organic molecules do not necessarily reflect the shapes of molecules. The origin of the FEM image called the cloverleaf pattern and the relation with the molecular shape is still unclear and a mystery. We are trying to solve the mystery of the FEM image of the organic molecules by using advantages of the CNT emitter which is expected to have atomic resolution.

A highly coherent electron beam can be generated from the CNT tip because the electron emission originates from a coherently spreading electronic state. In fact, interference fringes are observed in the FEM images from 5-member rings located at the CNT tip. This indicates that electrons emitted from different emission sites (pentagons) interfere with each other. Such a highly coherent phenomenon does not occur in the traditional metallic field emitters like W needles.

Using this highly coherent CNT electron sources, a projection type electron microscope will be developed (Fig.3). Since the electron emission from the CNT tip occurs under low applied voltages, an electron beam with low energy on the order of 100 eV can be obtained. This low-energy electron projection microscopy has a possibility to obtain high magnification images of very thin samples comprised of light elements such as carbon, nitrogen and oxygen (e.g., organic and biomaterials).

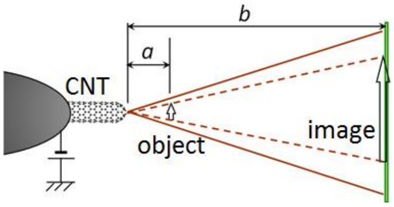

Fig. 3. Low energy projection electron microscope with a CNT field emitter.

3. Creation of a new substance of carbon

Carbon exists in a variety allotropes, e.g., diamond (sp^3 hybridization), graphite (sp^2), fullerene ($sp^{2+\alpha}$), and CNT ($sp^{2+\alpha}$). In addition to these well-known allotropes, sp hybridized one-dimensional carbon, carbyne, has been attracted much interest with significant controversy since the late 1960’s. Recently, linear carbon-chains (LCCs) confined inside CNTs have been reportedly found in high-temperature annealed double-wall CNTs (DWCNTs) and scarcely in multiwall CNTs produced by arc discharge. With a method different from these, we unexpectedly found the presence of bulk amount of LCCs in CNT films after an electric discharge of the films which were used as FE cathodes. LCCs were confined inside single-wall CNTs (Fig. 4) as well as DWCNTs. Our method is highlighted by the first formation of single-wall CNTs encapsulating long LCCs (> 9 nm in length), which could not be synthesized so far by the conventional thermal annealing of CNTs. Formation mechanism of LCCs encapsulated in CNT as well as their structural and electronic properties will be elucidated.

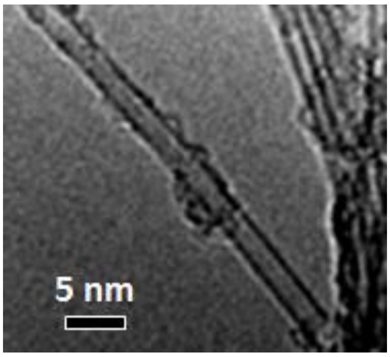

Fig. 4. TEM image of a LCC inside CNT.

Expected Effects

Nanocarbon electron emitters that possess unusual properties, e.g., generation of a highly coherent electron beam, manifestation of electron orbitals participating electron emission, unique edge states with polarized spins and so on, have potential abilities to provide new insights to the understanding of electronic properties of nanocarbon materials and to develop a novel electron microscope. In addition, FEM with nanocarbon emitters would enable to clarify the mysteries of FEM images of organic molecules that are unsolved 80 years since the Müller’s first report on four- and two-leaf patterns of organic molecules. Emergence of graphene based spintronics and creation of a new carbon allotrope, e.g., carbyne are also expected.