Recent advances in the development of low-dimensional materials for electrochemical applications: CECRI, Karaikudi

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Low-dimensional nanomaterials with exciting novel properties and magical performance is a rapidly growing research field that is truly multidisciplinary. A great deal of research efforts has been dedicated in the past two decades towards the preparation and characterization of these low-dimensional nanomaterials. The literature blossomed on nanomaterials already indicated about the origin of novel properties with size. However, it is equally important to know how the properties of materials and their function vary with their dimension without any size effects? To unravel this interesting question, researchers at CSIR-CECRI were working towards the development of low-dimensional materials such as 1-D and 2-D nanomaterials and study their interesting properties with special emphasis on electrochemical applications. Recent research findings from our institute suggest that the tunable properties of these low-dimensional materials are attractive for a variety of applications such as energy storage, sensing, catalysis and in optoelectronics.

Keywords: Electrochemical applications, graphene, low-dimensional materials, nanotechnology.

RAPID advancement in many contiguous areas of nanotechnology in the last decade has provided excellent opportunities to design appropriate functional materials with desired electronic, electrical, mechanical, optical/photonic and thermal properties customized for specific applications like solar cells, biosensors, rechargeable batteries and supercapacitors. For many of these functional materials, numerous research reports have shown that dimensionality plays a critical role in addition to the composition and arrangement of atoms in determining their fundamental properties. Low-dimensional materials (such as two-dimensional, one-dimensional and zero-dimensional) belong to one such group where unprecedented opportunities exist for the development of high-quality, large-area materials with controllable layer thickness. The emergence of such systems would not only expand our understanding of the underlying science, but essentially lead to the discovery of several unknown phenomena and applications. However, new insights of the low-dimensional materials have already contributed to the scientific frontiers such as topological insulators, spin- and valley-tronics[1,2]. Herein, the term spin-tronics represents a totally new area where the spin of the electron is considered as an additional degree of freedom other than electronic charge for information storage and processing. On the other hand, 'valley-tronics' refers to a new era where we essentially employ the wave quantum number of an electron in a crystalline material to store information. A plot between energy of electrons relative to their momentum will result in two deep valleys and thereby the name 'valley-tronics'. The ability to harness such unique properties and phenomena will provide exciting technological advances. CSIR–Central Electrochemcial Research Institute is working on the development of such novel, low-dimensional materials such as graphene, graphene nanoribbons, graphene quantum dots, molybdenum-di-sulphide (MoS_2) for applications in energy storage, biosensing and materials protection, which are considered to be the critical technologies of this millennium despite daunting challenges with respect to cost, scalability, durability and reproducibility for large-area electrodes.

Graphene is a two-dimensional monolayer of carbon atoms packed into a honey comb-like lattice. Since its discovery, graphene has shown to be an excellent candidate for the replacement of silicon-based electronic devices. Moreover, the observation of the integer quantum Hall effect at room temperature, breakdown of the adiabatic Born–Oppenheimer approximation, realization of the Klein paradox, possibility of high superconductivity, excellent transparency up to 98% over a broad wavelength range, metal-free magnetism, ultrahigh carrier mobility (>200,000 $cm^2\ v^{-1}\ s^{-1}$), extremely high modulus (~1 TPa), high tensile strength (~100 GPa), ballistic electronic propagation, etc. have made graphene as one of the 'most sought-after' materials for futuristic devices, including electrochemical devices. Electrochemists are excited mainly because many conventional technologies where they used graphite could now be re-engineered to be replaced by graphene layers designed (accurately used one, two or few layers) with more precise spatial control.

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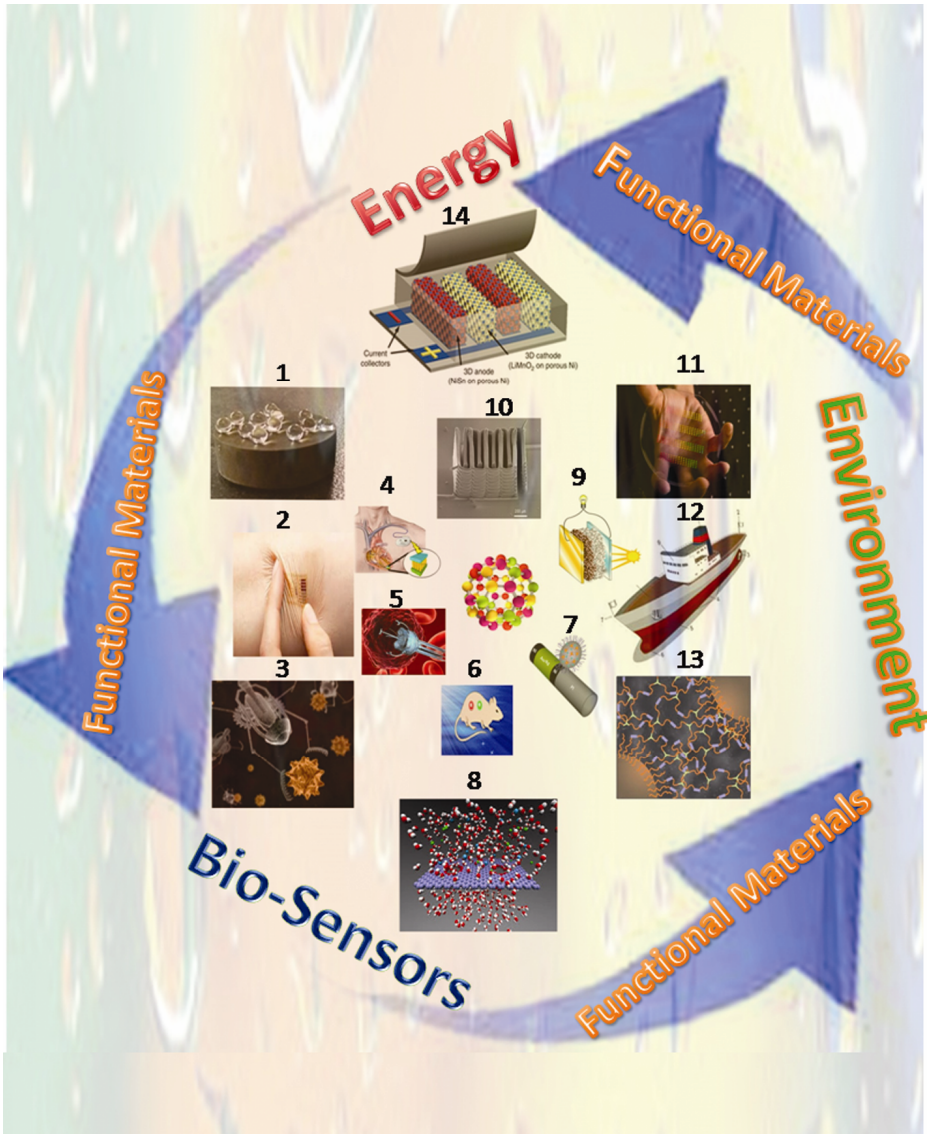

Research activities at CECRI. 1, Super hydrophobic surface; 2, Wearable skin; 3, Nanocapturing vehicle; 4, Wearable bioharvester; 5, Nanoshuttle, 6, Bio-imaging; 7, Drug delivery cargo; 8, Membrane for water purification; 9, Solar cell; 10, Nanofluric channel; 11, Next-generation chips; 12, Anti-corrosive paints; 13, Nanonetwork; 14, 3D printing.

Some of these could also be replaced by nanocomposites due to their enormous theoretical surface area and higher mechanical strength. Further, graphene could be coupled with flexible oligomers or polymers or even simple molecules for achieving higher capacity, enhanced energy density, rapid charge and discharge and more durability. Also, graphene is a suitable material for electrochemical capacitors, especially due to its flexibility and capability for surface manipulation to augment charge storage. In graphene, ion adsorption occurs at the surfaces and also on the edges of the sheets. As a consequence, the potential at which the process occurs varies continuously as a function of the surface charge coverage, which is a critical requirement for supercapacitive materials. Further, the unique combination of enormous surface area and excellent electrical conductivity enables graphene to be a unique platform for energy storage applications.

A team of researchers at CSIR–CECRI has employed graphene as an anode material for Li-ion batteries with several remarkable features. Alternatively, scientists at CSIR–CECRI are also working towards the development of Li-metal anodes for direct use by employing graphene as a coating material, which is expected to overcome dendrite growth that will cause thermal runaway (fire) and internal shortage associated with bare lithium. In addition, our scientists are also exploring the usefulness of graphene as a composite material for enhancing the electrical conductivity and mechanical properties. For example, few layers of graphene wrapped on sulphur can cause wonderful performance for Li-sulphur rechargeable

batteries and upon the addition of graphene to low-conductivity materials, it is expected to aid charge transfer and promote high-rate charge–discharge cycles. On the other hand, graphene-based field effect transistors (FETs) exhibit only a low on/off ratio as a result of zero bandgap and hinders the dream of graphene microelectronics. Numerous efforts have been made to open the bandgap in the density of states (DOS) of graphene. Among various techniques, cutting graphene into narrow nanoribbons to open the bandgap through the lateral quantum confinement effect is one of the most promising means of achieving this target. More specifically, if the width of the graphene nanoribbons (GNR) is less than 10 nm, the gap would be large enough to synthesize graphene FETs with on/off ratios of about 10^7 at room temperature. GNRs with various edge structures such as armchair- or zigzag-edged can be obtained depending on the orientation in which the 2D graphene sheets have been dissected.

Graphene quantum dots (GQDs) are zero-dimensional materials that possess the characteristics derived from both graphene and carbon dots; thereby it exhibits quantum confinement and edge effects[3]. Other beneficial features of the GQDs include relatively better photostability and biocompatibility compared to that of other quantum dots. In one of the recent works, our researchers synthesized monodispersed GQDs in 2–3 nm range, which could function as multivalent redox species so that they are useful for a wide range of applications from molecular switches to resonant tunnelling diodes and single-electron transistors due to the ability of these quantum dots to store attofarad charge. Present focus is largely aimed at working towards a novel and simple strategy to synthesize transparent and highly conducting graphene GNRs in bulk, so that these would suit specialized applications in solar energy devices due to their tunable bandgap. We are also exploring to capture subtle effects on the voltammograms of graphene as a function of layer number as one or two or few layers of graphene as a working electrode reveals interesting charge permeation effects based on the solvent and supporting electrolyte.

MoS_2 is another exciting two-dimensional material that has been widely studied by few of our researchers. Although it belongs to a class of compounds called transition metal dichalcogenides (TMDs), the structure of MoS_2 has A and B sub-lattices occupied by either 'Mo' or by a pair of 'S' atoms, thereby the entire MoS_2 monolayer resembles as a triple layer of atoms. The difference between the A and B sub-lattices lifts degeneracy in the electronic structure. Further, the enhanced Coulomb interaction observed in MoS_2 is due to the minimum dielectric screening present in this material. Unlike graphene, MoS_2 exhibits a direct bandgap with associated excitonic effects. The bandgap varies between 1.2 and 1.8 eV depending on the number of layers. The availability of such a wide bandgap is expected to dramatically minimize the current leakage and thereby maximize the abruptness of turn-on behaviour resulting in the increased sensitivity of the biosensor. Moreover, the ultrathin nature of MoS_2 is a great advantage for a more favourable electrostatic interaction. Moreover, its two-dimensional planar structure is a key for patternability, which is critical for many applications. Recently, a team of our researchers has unravelled the usefulness of MoS_2 as a potential platform for the selective and sensitive detection of an important neurotransmitter, dopamine[4]. Another exciting finding of this work is that MoS_2 can be easily surface-functionalized with biomolecules such as enzymes, proteins and nucleic acids for a more accurate and high throughput biosensing. In the same work, the researchers also highlighted the ease with which the nanomaterial can be synthesized and employed as an electrode platform during the construction of biosensors for rapid and non-invasive electroanalysis. In another ongoing work, our researchers are exploiting the variable bandgap associated with MoS_2 to harvest light over a wide range from ultraviolet to infrared for photochemical water splitting. The advantage of MoS_2 for such application is that its metallic edge effects will be useful for charge transfer, whereas the basal plane inactivity prevents electrocatalytic decomposition.

The above discussion provides a snapshot of ongoing research activities in our institution. However, in-depth analysis is essential to arrive at electrochemical strategies to synthesize these low-dimensional materials such as h-BN, MoS_2, WS_2, VS_2 and $MoSe_2$. Further, electrochemical synthesis of GQDs with size control is also essential and the subtle change in cyclic voltammograms as a function of layer number shows several intriguing features not clearly understood. The rich chemistry of the low-dimensional materials offers avenues to study fundamental phenomena and their practical utility as illustrated by single-electron transfer for sub-2 nm quantum dots. Moreover, the tunable and versatile properties of these low-dimensional materials are attractive for a variety of applications such as energy storage, sensing, catalysis and opto-electronics, and many new types of devices are expected in the future.

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