Supramolecular Assemblies of Carbon Nanomaterials with Photochromic Molecules for Sustainable Molecular Electronics

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By

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ABSTRACT

The growing field of electronics always inspired the scientists to go for new materials and technology. In the past, the electronic industry depended mainly on inorganic materials especially metals for the fabrication of devices. The complete dependence over the metals led to the increase in energy consumption for the construction of devices and their functioning. Most important drawback associated with the gadgets and devices based on metals is the difficulty in their disposal. The excessive accumulation of damaged devices became hazardous to the environment. This made the scientists to explore organic molecules for the electronic development. The organic electronic materials failed to perform at conditions of high temperature, heat etc. The invention of carbon nanomaterials made the electronic industry to rely on them as they can withstand drastic conditions. The concept of smart materials based on carbon nanomaterials which can respond to external stimuli like pH, light, heat, redox potential inspired the scientists to make such stimuli responsive electronic devices. The hybrid materials developed by coupling photochromic molecules, a class of organic molecules which respond to the stimulus light coupled with carbon nanomaterials became the centre of attraction in the optically responsive smart materials.

The increased environmental issues shifted the focus of material researchers across the globe to go for sustainable/green materials. This led to the rise of a new path in the electronic industry termed ‘sustainable molecular electronics. This area involves the use of bioresources for the production of materials which are eco-friendlier for the device fabrication and gadgets. This thesis focuses on the development of such materials for the construction of molecular electronic switches.

The photochromic azobenzene molecules are derived from cardanol a well-known bioresource material obtained from cashew nut shell liquid. The azobenzene molecules are then coupled with various carbon nanomaterials to develop molecular switches. The different carbon nanomaterials selected are zero-dimensional

graphene quantum dot, one-dimensional carbon nanotube, two-dimensional graphene oxide and three-dimensional single-walled carbon nanohorn.

The graphene quantum dots (GQDs) is derived from a bioresource material honey. The GQDs show a green fluorescence. The GQDs are then coupled with photochromic azobenzene system DOAZOC1 derived from cardanol. The two-component system then selectively screened the presence of a harmful carbamate pesticide carbofuran. The entire process resulted in a fluorescence switch GQD-DOAZOC1-Carbofuran. This fluorescence switch is then employed for developing three molecular devices: molecular fluorescent probe, molecular logic gate and molecular keypad lock.

The DOAZOC1 molecule is further coupled with acid-functionalized multi-walled carbon nanotube. Two different kinds of hybrids are prepared. The first one is the covalent hybrid, where the components are connected through anhydride linkage. The second one is the non-covalent hybrid formed through supramolecular interactions like hydrogen bonding and π-π stacking. Both the hybrids function as photo-tunable conductance switches.

Another azobenzene molecule AZOC2 is prepared from cardanol. This bulkier molecule is then coupled with reduced graphene oxide, a two-dimensional planar carbon nanomaterial to prepare both covalent and non-covalent hybrids. Here the hybrids exhibited photoswitching of conductance. The photomodulated conductance switches are again developed by coupling single-walled carbon nanohorn with DOAZOC1 molecule through covalent and non-covalent mode of functionalization. The mechanism of this conductance modulation in all the hybrids developed is investigated. The photo-isomersation ability of azobenzene molecules present in the hybrids are found to be responsible for the photoswitching of conductance in them. The non-covalent approach is observed as the better method of functionalization.

The present study therefore focuses on the development of fluorescence switch and conductance switch from bioresource based materials. We hope that the thesis will form a foundation to explore more ‘sustainable molecular electronic devices’.