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Review

Manipulating the electronic and chemical properties of graphene via molecular functionalization

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ABSTRACT

Graphene, a single atomic layer of sp^2-hybridized carbon atoms arranged in a hexagonal structure and the Nobel winning material in 2010, has attracted extensive research attention in the last few years due to its outstanding physical, chemical, electrical, optical and mechanical properties. To further extend its potential applications, intensive research efforts have been devoted to the functionalization of graphene. Examples include improving graphene solubility by attaching different chemical functional groups to its

Abbreviations: 2D, two-dimensional; ARPES, angle-resolved photoemission spectroscopy; An-CH_3, 9,10-dimethylanthracene; An-Br, 9,10-dibromoanthracene; AIE, aggregation induced emission; BSA, bovine serum albumin; CVD, chemical vapor deposition; CFG, chemical functionalized graphene; CCl_4, carbon tetrachloride; ClAlPc, chloroaluminium phthalocyanine; CRG, chemically reduced graphene; CVs, cyclic voltammograms; CCG, chemically converted graphene; DCD, differential charge density; EA, electron affinity; E_g, energy gap; EG, epitaxial graphene; F_{16}CuPc, cooper-hexadecafluoro-phthalocyanine; FETs, field effect transistors; F-SAMs, 1H,1H,2H,2H-perfluorooctyltriethoxysilane; FF, fill factor; FRET, fluorescence resonance energy transfer; GO, graphene oxide; GC, glassy carbon; GOD, glucose oxidase; HOMO, highest-occupied-molecular-orbital; H_2N-SAMs, 3-aminopropyltriethoxysilane; IP, ionization potential; ITO, indium tin oxide; IgE, human immunoglobulin E; I_{ds}, source drain current; J_{sc}, short circuit current; LUMO, lowest-unoccupied-molecular orbital; MG, methylene green; Na-NH_2, 1,5-naphthalenediamine; NEXAFS, near-edge x-ray absorption fine structure; ODA, octadecylamine; OPVs, organic photovoltaic cells; PVA, poly(vinyl alcohol); PES, photoemission spectroscopy; PCE, power conversion efficiency; PEDOT:PSS, poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate); P3HT, poly(3-hexylthiophene); PCBM, phenyl-C61butyric acid methyl ester; PyS, pyrene-1-sulfonic acid sodium salt; PDI, diasodium salt of 3,4,9,10-perylenetetracarboxylic diimide bisbenzenesulfonic; PBASE, pyrene buanoic acid succidymidyl ester; PCA, 1-pyrenecarboxylic acid; PBS, phosphate-buffered solution; QHE, quantum Hall effect; rGO, reduced graphene oxide; ReG, reduced graphene sheets; R_{ct}, charge transfer resistance; SLG, single-layer graphene; SAM, self-assembled monolayers; THF, tetrahydrofuran; TTF, tetrathiofulvalene; TPA, tetrasodium 1,3,6,8-pyrenetetrasulfonic acid; TCNQ, tetracyanoquinodimethane; TCCP, meso-tetra(4-carboxyphenyl)porphyrin; vdW, van der Waals; VL, vacuum level; V_{th}, threshold voltage.

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basal plane, modulating the charge carrier type and concentration via surface transfer doping by coating it with various metals films or organic molecules, improving the bio-selectivity by decorating it with different π-conjugated organic molecules, and so on. Different methods have been developed to functionalize graphene. Among them, non-covalent molecular functionalization represents one of the most effective and promising methods. The extended π-conjugation is largely preserved without creating extensive structural defects on the graphene sheet, thereby retaining the high charge carrier mobility. In this review, a brief summary about different functionalization methods of graphene and its derivatives by covalent and non-covalent interactions will be presented, with particular focus on the non-covalent molecular functionalization. A broad review of the applications of non-covalently functionalized graphene and its derivatives will be presented in detail, including field-effect-transistors, organic optoelectronics, and molecular sensing.

Contents

1. Introduction

Graphene is a single layer of carbon atoms packed into a two-dimensional (2D) honeycomb lattice. The sp^2 hybridized carbon bonds contain in-plane σ bonds and out-of-plane π bonds [1]. The π bonds contribute to the electron conduction of graphene and provide weak interaction between graphene layers or graphene and the substrate. Graphene has shown exceptional physical properties because of its peculiar structural characteristics, making it a promising candidate as a building block in next generation nanodevices.

The charge carriers in graphene behave like relativistic particles and can be described by the Dirac rather than the Schrödinger equation [2,3]. Due to the two equivalent carbon sublattices in its honeycomb lattice, cone-like valance and conduction bands intersect at the Fermi level at the K and K′ points of the Brillouin zone, giving rise to a linear dispersion of the energy spectrum described by $E = \hbar v_F K$.