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Semiempirical study on the absorption spectra of the coronene-like molecular models of graphene quantum dots

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Abstract

Polycyclic aromatic hydrocarbons of the general formula $C_{6n^2}H_{6n}$ (coronene family) were used as molecular models of graphene quantum dots (GQDs). Absorption spectra of the model compounds were calculated by ZINDO/S method. The $S_0 \rightarrow S_1$ transition energy (E_1) was found to decrease with n as $E_1 = 4.75\times n^{-0.633}$ eV. This transition is forbidden in symmetric compounds but 'switches on' upon symmetry breaking. The energy of the first bright optical peak (E_{br}) was found to decrease with n as $E_{br} = 6.31\times n^{-0.6}$ eV. The data obtained corroborate the earlier finding that the size-independent optical properties of GQDs are determined by relatively small isolated sp^2 clusters separated by sp^3 (oxygen-contained) 'defects' rather than the whole (corrupted) graphene sheets; such nanoparticles actually are not *quantum dots*. GQDs of pure (without defects) graphene sheets with fully π-conjugated sp^2 systems should exhibit size-dependent optical properties due to the quantum confinement effect.

Keywords: coronene; graphene quantum dot; cluster; absorption; ZINDO/S

1. Introduction

The fundamental building block of all graphene materials is a graphene layer, which, according to the recommended nomenclature, is defined as 'a single-atom-thick sheet of hexagonally arranged, sp^2-bonded carbon atoms occurring within a carbon material structure' [1].

Graphene quantum dot (GQD) consists of a single to several layers of graphene sheets several nanometers in lateral size. Graphene composed fully of the sp^2-hybridized carbon atoms exhibits no fluorescence due to a zero optical bandgap. Compared to 'infinite' graphene sheet, experimentally obtained GQDs are limited in size and always contain both the sp^2 and sp^3 carbon atoms (and heteroatoms); both these factors open the optical bandgap (splitting valence and conduction bands to discrete molecular orbitals) and result in fluorescence.

Apart from the ability to emit light (photo- and electroluminescence), GQDs are inexpensive, nontoxic, photostable, water-soluble, biocompatible, and environmentally friendly objects. Due to the combination of these remarkable properties, GQDs can find possible numerous applications as photodetectors, solar cells and light-emitting diodes [2,3],