Size-dependent Electronic Properties of Strongly Confined Graphene Quantum Dots

Milan Sýkora^{1,2}

Zhiqiang Ji,² Enkeleda Dervishi,² Stephen K. Doorn,² Lucia Demovičová,³ Michal Pitoňák⁴ ¹Laboratory for Advanced Materials, ³Dept. of Inorganic Chemistry, ⁴Dept. of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, 842 15 Bratislava, Slovakia ²Los Alamos National Laboratory, Los Alamos, NM 87544, USA Suboram@uniba.st

sykoram@uniba.sk

We developed a new method for preparation of uniform ensembles of small (<2 nm) Graphene Quantum Dots (GQDs), using a systematic bottom-up step-wise synthesis. The new approach facilitates quantitative investigation of the effect of quantum confinement on the electronic structure of the GQDs using readily accessible ensemble level techniques. Using these techniques, we experimentally show how the bandgap, valence and conduction band offsets and exciton binding energies systematically vary with the size of these strongly confined GQDs. The interpretation of the experimental results is supported by detailed DFT modelling. Experimental results indicate that the standard Dirac fermion model and tight-binding modelling approach do not adequately describe the electronic properties of GQDs in the strongly confined regime, which is attributed to stronger carrier-carrier interactions in the GQDs compared to the bulk graphene. Raman spectroscopy studies reveal that even these small GQDs show key D and G spectral features characteristic for periodic graphene structures and that the variation in the ratios of the corresponding band intensities (I_D/I_G) with the GQD size is in good agreement with the prior studies of highly defected large area graphenes,

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Figure 1: Examples of the strongly confined GQDs prepared by a new "bottom up" synthesis approach and the experimentally determined dependence of the electronic structure on their size.