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Won Kook Choi

ZnO–Nanocarbon Core–Shell Type Hybrid Quantum Dots

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Nanoscience and nanotechnology offer means to assemble and study superstructures, composed of nanocomponents such as nanocrystals and biomolecules, exhibiting interesting unique properties. Also, nanoscience and nanotechnology enable ways to make and explore design-based artificial structures that do not exist in nature such as metamaterials and metasurfaces. Furthermore, nanoscience and nanotechnology allow us to make and understand tightly confined quasi-zero-dimensional to two-dimensional quantum structures such as nanopalettes and graphene with unique electronic structures. For example, today by using a biomolecular linker, one can assemble crystalline nanoparticles and nanowires into complex surfaces or composite structures with new electronic and optical properties. The unique properties of these superstructures result from the chemical composition and physical arrangement of such nanocomponents (e.g., semiconductor nanocrystals, metal nanoparticles, and biomolecules). Interactions between these elements (donor and acceptor) may further enhance such properties of the resulting hybrid superstructures. One of the important mechanisms is excitonics (enabled through energy transfer of exciton-exciton coupling) and another one is plasmonics (enabled by plasmon-exciton coupling). Also, in such nanoengineered structures, the light-material interactions at the nanoscale can be modified and enhanced, giving rise to nanophotonic effects.

These emerging topics of energy transfer, plasmonics, metastructuring and the like have now reached a level of wide-scale use and popularity that they are no longer the topics of a specialist, but now span the interests of all "end-users" of the new findings in these topics including those parties in biology, medicine, materials science and engineerings. Many technical books and reports have been published on individual topics in the specialized fields, and the existing literature have been typically written in a specialized manner for those in the field of interest (e.g., for only the physicists, only the chemists, etc.). However, currently there is no brief series available, which covers these topics in a way uniting all fields of interest including physics, chemistry, material science, biology, medicine, engineering, and the others.

The proposed new series in "Nanoscience and Nanotechnology" uniquely supports this cross-sectional platform spanning all of these fields. The proposed briefs series is intended to target a diverse readership and to serve as an important reference for both the specialized and general audience. This is not possible to achieve under the series of an engineering field (for example, electrical engineering) or under the series of a technical field (for example, physics and applied physics), which would have been very intimidating for biologists, medical doctors, materials scientists, etc.

The Briefs in NANOSCIENCE AND NANOTECHNOLOGY thus offers a great potential by itself, which will be interesting both for the specialists and the non-specialists.

More information about this series at http://www.springer.com/series/11713

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Preface

Lower-cost and higher-performing metal oxides have emerged as alternatives to precious noble and rare materials due to abundance, stability, and electrical and chemical capacities. In particular, enormous interests have been paid on metal oxide/nanocarbons (CNT, C_{60}, graphene, carbon fiber, amorphous carbon, etc.) hybrid materials in the electrochemical reactions on energy conversion and storage and their electrocatalyst systems. It has been demonstrated that assembling metal or metal oxide nanomaterials (Au, Pt, TiO_2, ZnO, SnO_2, etc.) on graphene sheets can exhibit enhanced efficiencies in excitonic solar cells and photocatalytic reactions, due to graphene's excellent electron-conducting property. Also, various kinds of metal oxide with CNT have been used as electrocatalysts for water splitting, as supercapacitors, as anodes for Li ion secondary battery anode, as sensors detecting reducing gases, and as charge transfer layers for solar photovoltaic cells and light-emitting diodes. These hybrid materials showed prominently enhanced performance because nanocarbons have flexibility, easy functionalization, and high electrical and thermal conductivity.

Hybridization of metal oxide with nanocarbons was known to easily occur from chemical reaction between metal oxide and induced chemical groups on nanocarbon surfaces by facile acid treatment. And now the strongly coupled metal oxide/nanocarbon hybrid can be synthesized by controlling the optimum degree of oxidation, and thereby balancing inorganic carbon coupling showing high electrical performance. Despite many efforts to manipulate more uniform metal oxide–nanocarbon nanocomposite structures, the metal oxide nanoparticles were still randomly scattered and nonuniformly attached to the nanocarbon surfaces. Also, in most cases the hybrid materials still remain 2D planar structures. For higher and more effective performance of the hybrid structure, 3D conformal coating on metal oxides is highly demanded. To our knowledge, consolidated core–shell structure metal oxide NPs encircled by nanocarbons with high conformality have been rarely reported. Since consolidated ZnO–graphene core–shell type hybrid quantum dots were for the first time synthesized using chemical reaction between ZnO embryo nanoparticle and acid-treated graphene in 2012, this emissive hybrid quantum dots were used for the realization of white light-emitting ZnO–graphene quantum dots (ZGQDs) LED. In this book, ZnO–templated synthetic method to form conformal 3D nanocarbon hybrid materials is introduced.

In Chap. 1, as an introduction, the general physical and chemical properties of ZnO and nanocarbons (CNT, graphene, C_{60}) are briefly summarized. As one of the important applications of metal oxide nanoparticles, recent research on charge transport layer or charge injection layer of ZnO or TiO_2 or their composites with polymer is overall reviewed from the former studies in electronic devices of solar photovoltaic cells, electrochemical electrodes, and light-emitting diodes. In addition, previous researches on metal oxide–nanocarbon hybrid structures are also introduced in the fields of supercapacitors, Li ion secondary battery, electrocatalysts, photovoltaic cells, and light-emitting diodes.

In Chap. 2, synthetic processes of ZnO–graphene and ZnO–C_{60} hybrid quantum dots, and the formation of nanoring single-walled CNT using ZnO–SW (single-walled) CNT are described in detail. Nanostructure of these hybrid quantum dots are precisely analyzed by high-resolution TEM, HR-HAADF (high-resolution high-angle annular dark field) STEM (scanning transmission electron spectroscopy), and X-ray diffraction. Chemical functional group induced at the interface between ZnO nanoparticles and nanocarbon surface is confirmed by X-ray photoelectron spectroscopy. Optical properties of these hybrid quantum dots are investigated by Raman spectroscopy, which is specifically well known for analyzing nanocarbon materials. The charge transfer phenomenon from the conduction band of ZnO to graphene quantum dots is carefully examined by the fitting curves of the time-resolved photoluminescence (TRPL) decay (the biexponential function calculates the lifetime in the UV range). Based on density functional theory (DFT), two blue emissions in PL newly arising in ZnO–graphene QDs are well explained as electron transitions from the conduction band (CB) of ZnO, lowest unoccupied molecular orbital (LUMO), LUMO+2 levels induced by epoxy oxygen on graphene to the valence band (VB) of ZnO. The formation of nanoring SWCNT, with the diameter of 20–30 nm, is well described by the agglomeration of ZnO nanoparticles.

In Chap. 3, applications of these ZnO–graphene, ZnO–C_{60} hybrid quantum dots, and NR-SWCNT are introduced. In the cases of ZnO–graphene and ZnO–C_{60} hybrid quantum dots, four things are presented: UV photovoltaic solar cells, high-efficiency inverted ZnO–graphene QD-based white LED, flexible QD LED, and in a photoelectrochemical water splitting device, the high-performing photoanode of ZnO–C_{60}. Also, as an example of NR-SWCNT application, when P(VDF-TrFE) piezoelectric polymer is mixed with NR-SWCNT, an enormous increase of permittivity from $\varepsilon = 10\text{–}12$ to ca. 63 is observed during a small dielectric tangent loss (tan δ)—as much as merely 0.06 at 1 kHz.

I would like to appreciate all members of the Soft Nano Electronic Laboratory (SNEL)—Mr. Dong-Hee Park, Mr. Se-Hee Cho, Mr. Tae-Hee Yoo, Mr. Choong Hye Kim, Mr. Jung-Hyuk Kim, Mr. Ju-Won Lim, Mr. Chang-Gui Jin, Mr. Bum Hee Lee, Mr. Chang-Hwan Wie, Dr. Rina Pandey, and Dr. Young-Taek Lee—for their continuous and persistent collaboration; in particular, my colleague Dr. D.I. Son, for his vigorous research for a number of applications of ZnO–nanocarbon hybrid materials; Mr. Byong-Wook Kwon, for the first realization of synthesis of the ZnO–graphene hybrid quantum dot structure; Dr. Do-Kyung Hwang, Dr. Young-Soo No, Dr. Jeong-Do Yang, and Mr. Hong-Hee Kim, for fabricating the flexible ZnO–graphene QD LED; Dr. S. Bae, for his contribution to fabricate and analyze the solar PVs using modified ZnO–graphene QDs; Prof. J.H. Park of Yonsei University, for his contribution to developing photoelectrochemical cells using ZnO–graphene as well as ZnO–C_{60}; Mr. Yun-Jae Lee, Ms. So-Ra Ham, and Prof. S.R. Kim, for developing and synthesizing the nanoring single-walled CNT; both Dr. Won-Seon Seo of KICET—for the transmission electron microscope analysis and valuable comments—and Dr. Chang-Lyoul Lee of GIST—for TRPL measurement and interpretation of the spectra, respectively; Prof. Yeonjin Yi and his graduate students, for the DFT simulation and calculation of the ZnO–graphene hybrid material; Dr. B. Angadi, Bangalore University, for his valuable comments and advice in composition; and Mrs. Cindy Zitter of Springer SBM NL and Mr. Smith Chae of Springer Korea, for their advice and guidance in the publication of this book.

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