

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, C₆₀, 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, TiO₂, ZnO, SnO₂, 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, C₆₀) 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 TiO₂ 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–C₆₀ 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–C₆₀ hybrid quantum dots, and NR-SWCNT are introduced. In the cases of ZnO–graphene and ZnO–C₆₀ 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–C₆₀. 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 $\epsilon = 10\text{--}12$ to ca. 63 is observed during a small dielectric tangent loss ($\tan \delta$)—as much as merely 0.06 at 1 kHz.

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