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Highlights on advances in SnO₂ quantum dots: insights into synthesis strategies, modifications and applications

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ABSTRACT

The applications of SnO₂ are benefited from its nanostructure with different sizes and novel morphologies. When the size of nanoparticles reduces to 1–10 nm, the unique physical and chemical properties will make prominent. SnO₂ quantum dots (QDs), a type of zero-dimensional ultrasmall SnO₂ nanomaterials with a size in 1–10 nm, have displayed unique physical and chemical properties, which are different from those of their larger-sized ones. This review summarizes various synthesis strategies of SnO₂ QDs and the methods of their modifications, discusses their applications in lithium-ion batteries, photocatalysis, and gas sensors. These applications profit from the characteristic properties inherent in SnO₂ QDs.

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IMPACT STATEMENT

This paper provides a comprehensive understanding for fabricating SnO₂ quantum dots and their modifications via various methods for the applications in lithium-ion batteries, photocatalytic degradations, and solid-state gas sensors.

1. Introduction

Tin dioxide (SnO₂), a kind of *n*-type semiconductor with wide-band-gap ($E_g = 3.64$ eV at 300 K), has very wide applications in the fields of gas sensors [1–10], lithium-ion batteries (LIBs) [11,12], photocatalytic degradations [13,14] and dye-sensitized solar cells (DSSCs) [15–19], photodetectors [20] and heterojunction diode [21]. The wide applications of SnO₂ are greatly benefited from the synthesis methods in its nanostructured materials with different sizes and novel morphologies. Nanostructured SnO₂ with various morphologies, such as three-dimensional nanospheres [22–24], two-dimensional nanofilms [21,25–28] or nanosheets [29,30], and one-dimensional nanowires [20] or nanorods [29–32] has been successfully fabricated and played an important

role in their applications. When the size of the SnO₂ nanoparticles reduces to 1–10 nm, the unique physical and chemical properties will make prominent due to quantum size effect [33]. So, SnO₂ quantum dots (SnO₂ QDs), a type of zero-dimensional ultrasmall SnO₂ nanomaterials with size in the 1–10 nm range, have attracted considerable attention owing to their unique physical and chemical properties which are different from those of their larger-sized ones. In recent years, many efforts have been devoted to the investigations on the synthesis of SnO₂ QDs. The synthetic methods of SnO₂ QDs mainly include hydrothermal and solvothermal synthesis, pulsed laser ablation approach, microwave assistant synthesis, and electron-beam irradiation. Applicable performances of nanomaterials rely on not only their sizes and

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nanostructures but also their components. In addition to fabricating SnO₂ in the scale of 1–10 nm, enhanced and optimized performances can also be obtained by modifying the SnO₂ host materials. Recently, modifications of SnO₂ QDs have become one of the most important research fields. The modifications are commonly conducted in two ways: (1) doping SnO₂ QDs with other chemical elements; (2) or embedding SnO₂ QDs in suitable matrix. The most important applications of SnO₂ QDs and their modified ones are in the fields as follows: lithium-ion batteries, photocatalytic degradations, and gas sensors. In this paper, by focusing on the SnO₂ QDs, we manage to facilitate the readers' comprehensive understanding on the synthetic approaches, modification strategies and their potential applications of SnO₂ QDs.

2. Synthesis strategies of SnO₂ QDs

Various synthesis strategies have been employed to prepare SnO₂ QDs. These synthesis strategies include the bottom-up methods (such as hydrothermal synthesis, solvothermal synthesis, microwave-assisted synthesis and electron-beam irradiation synthesis) and top-down method (including pulsed laser ablation decomposition). The following subsections will discuss in details the synthesis strategies commonly employed to fabricate SnO₂ QDs.

2.1. Hydrothermal synthesis

Hydrothermal synthesis is a widely used way for the fabrication of nanoparticles, which is normally performed in Teflon-lined stainless steel autoclaves under a controlled temperature and certain pressure. The temperature can be raised above the boiling point of water, reaching the saturated vapor pressure. The interior pressure in autoclave is determined by the reaction temperature and the filling degree of solution in the autoclave. In the past few years, hydrothermal synthesis has been widely used for the fabrication of SnO₂ QDs [34–44]. The spherical SnO₂ QDs have been obtained by the hydrothermal treatment of a aqueous solution containing certain amount SnCl₄·5H₂O and aqueous ammonia [34]. For example, 2.8 g SnCl₄·5H₂O and suitable amount of aqueous ammonia were dissolved in deionized water, followed by ultrasonic vibration, and then transferred to a 120 ml Teflon-lined stainless steel autoclave. The stainless steel autoclave was heated at 200°C for 24 h. The obtained SnO₂ QDs were almost spherical shape with diameters in the range of 2.6–7.8 nm. Besides spherical shape SnO₂ QDs, cuboid SnO₂ QDs have also been fabricated by similar method [35,40]. For example, cuboid SnO₂ QDs were prepared by hydrothermal reaction of

SnCl₄·5H₂O and CO(NH₂)₂ in an aqueous solution [35]. 0.08 g SnCl₄·5H₂O, 0.8 g CO(NH₂)₂ and 1.6 mL HCl fume were dissolved in 32 mL deionized water. The above solution was then transferred into a stainless steel autoclave, followed by ultrasonic treatment and heating to 90°C for 15 h. The particles were cuboid shape with the widths of 4.0 nm and the lengths ranging from 6.0 to 13.5 nm.

During these hydrothermal processes, the sizes and morphologies of SnO₂ QDs depend on the reaction conditions, including reaction temperature, duration of time and pH of solution. Zhang et al. [36] have investigated the influences of reacting temperature and time on the size of spherical SnO₂ QDs. In order to find growth kinetics of SnO₂ QDs, the hydrothermal reactions were conducted in different temperatures (140–220°C) and varied times (2–200 h). As shown in Figure 1, the spherical SnO₂ QDs with different particle sizes, varying from 2.2 to 7.0 nm, have been obtained under different reaction conditions.

Besides reaction temperature and reaction time, the pH value of the solution also has a vital influence on the size and morphology of SnO₂ QDs. Several spherical and cuboid SnO₂ QDs with different size have been prepared by hydrothermal reaction of SnCl₄·5H₂O with OH[−] in aqueous solutions with different pH values [37]. To hydrothermally fabricate SnO₂ QDs with varied shapes and sizes, different volumes of 25% aqueous tetramethyl ammonium hydroxide [N(CH₃)₄OH; TMAH] solution were added into aqueous solutions of SnCl₄·5H₂O, and the pH values of the mixed solution were adjusted from 1.2 to 14. The volume of the mixed solutions was then scaled to 50 mL with pure water. After that, the mixed solutions were transferred to a Teflon-lined stainless steel autoclave, and then heated at 150°C for 24 h. It was found that the sizes and shapes of the resulted SnO₂ QDs are dependent on pH values (Figure 2). All the SnO₂ QDs achieved at pH values between 7.3 and 13.7 exhibit narrow size distribution of 3.2 ~ 3.6 nm. However, the SnO₂ QDs prepared at pH < 10.7 were spherical. When pH was changed to 12.6, the shape of SnO₂ QDs turned into cubes, while the similar size distribution was kept with those achieved from pH < 10.7. When pH value was increased further, only cubic SnO₂ QDs with increasing size were obtained.

2.2. Solvothermal synthesis

Solvothermal synthesis is considered to be identical to hydrothermal method except that the solvents used in the solvothermal process are organic solvents, such as methanol, ethanol, oleylamine, and so on. Many articles presented that the SnO₂ QDs can be successfully obtained by solvothermal synthesis [45–49]. For

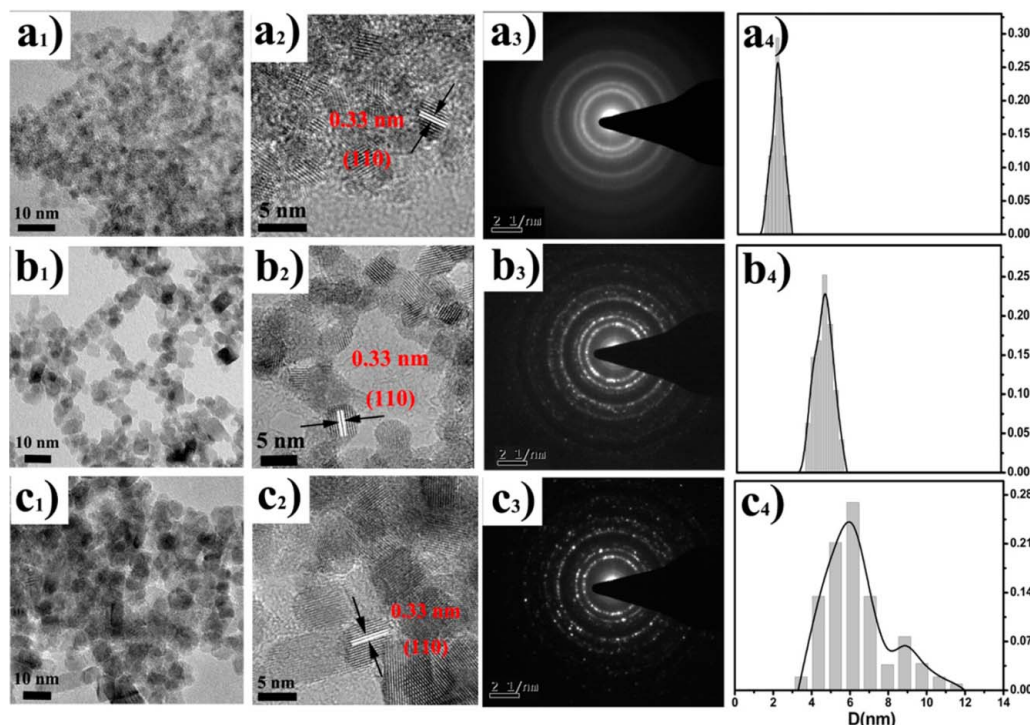


Figure 1. TEM, HRTEM, SAED images, and the corresponding size distributions of SnO₂ quantum dots prepared under different conditions: (a1—a4) 140°C, 2 h; (b1—b4) 200°C, 4 h; and (c1—c4) 200°C, 240 h. Reprinted with permission from Ref. [36]. Copyright 2015 American Chemical Society.

instances, Xu et al. [47] have prepared SnO₂ QDs through solvothermal treatment of SnCl₄·5H₂O in a mixed organic solvent. In a typical process, 1.7 mmol SnCl₄·5H₂O was added into a mixed solvent of 2.5 mL oleylamine, 20 mL oleic acid and 10 mL ethanol to form a mixed solution. Then, the mixed solution was transferred to a stainless steel autoclave, and heated at 180°C for 30 min. In this process, SnO₂ QDs with size of 0.5–2.5 nm were obtained. It was found that these SnO₂ QDs can be further assembled into SnO₂ nanowires by prolonging the reaction time.

Some organics, e.g. N-methylimidazole, oleylamine and oleic acid, can be used to inhibit the growth and aggregation of the nanoparticles because of their outstanding blocking effect. Monodispersed SnO₂ QDs can be prepared under solvothermal conditions using this type of organics as reaction solvent. Chen et al. [49] have developed a gram-scale fabrication of SnO₂ QDs by using an N-methylimidazole-based solvothermal method. The SnO₂ QDs are well-dispersed 4 nm nanoparticles. In the reaction process, N-methylimidazole not only facilitated the growth of the ultrasmall SnO₂ QDs by providing an alkaline environment, but also inhibited the growth and aggregation of SnO₂ QDs by capping the SnO₂ QDs through the hydrogen bonds.

2.3. Microwave-assisted synthesis

As a high-speed synthesis approach, microwave-assisted synthesis has grabbed more attention owing to its unique advantages compared with conventional heating: (1) fast heating rate, (2) uniform heating without thermal gradients, (3) and without superheating of the solvents. Microwave-assisted synthesis has become a useful and rapid approach for the fabrication of nanoparticles with shortening reaction time from hours to minutes.

Recently, microwave-assisted synthetic technique has been applied to prepare SnO₂ QDs [17,50–57]. For examples, Liu et al. [57] have synthesized SnO₂ QDs with diameters of 3–5 nm by microwave irradiating the solution of SnCl₄·5H₂O and alkaline. In this work, a dilute NaOH solution was dropped into 20 mL solution of 0.1 M SnCl₄·5H₂O until the pH value of the mixed solution reached 5. After the mixed solution was sonicated for 30 min, the solution was irradiated at 150°C for 10 min under a microwave irradiation power of 150 W. The synthesized SnO₂ QDs were well uniform and dispersive with size ranging from 3 to 5 nm. In these conventional microwave-assisted methods, strong alkaline solutions, such as NaOH, KOH, H₂NCH₂CH₂NH₂, are widely used. However, these strong alkaline solutions

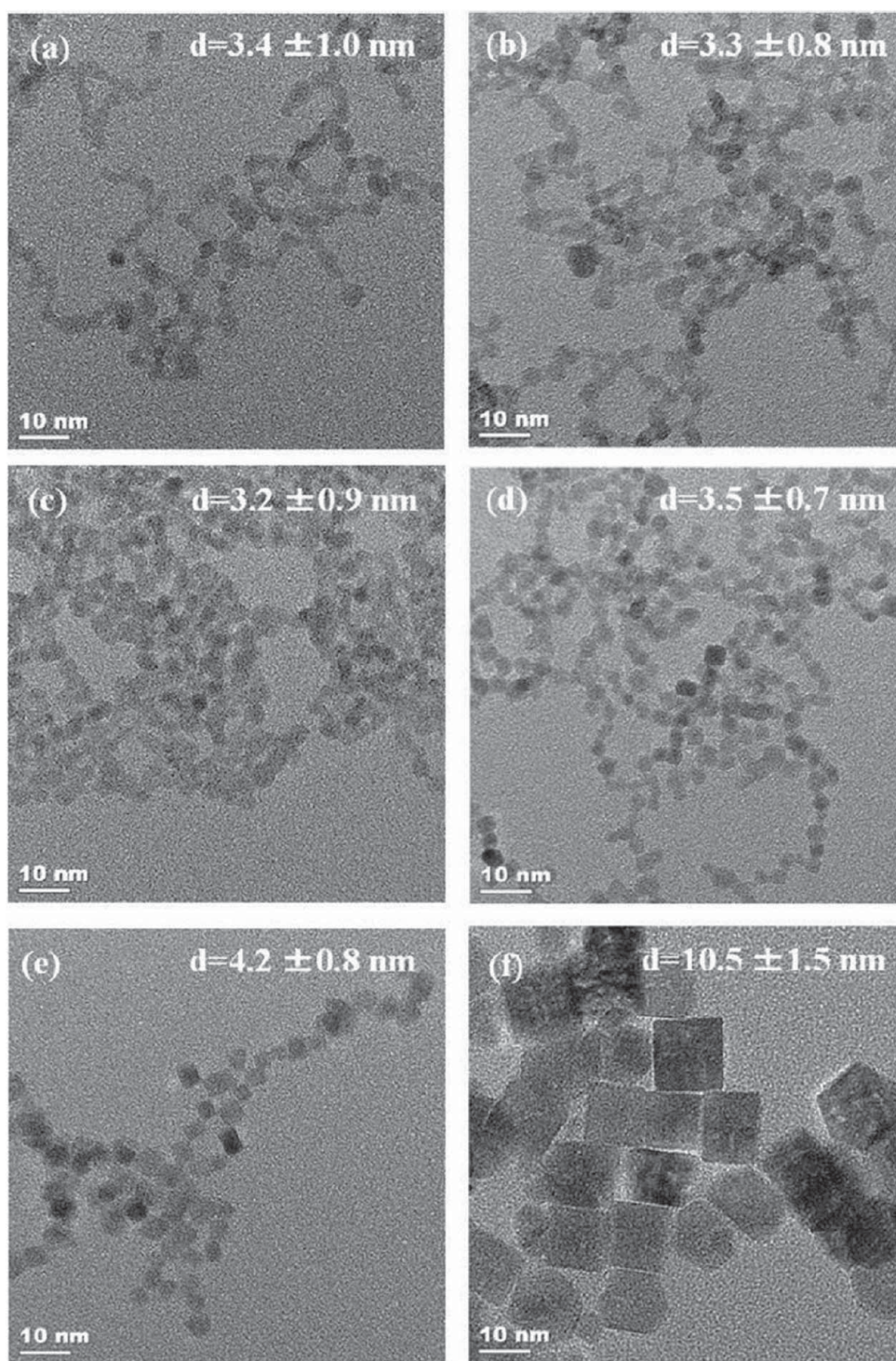


Figure 2. TEM images of the nanocrystals grown with TMAH at (a) pH 7.3, (b) pH 9.2, (c) pH 10.7, (d) pH 12.6, (e) pH 13.3, and (f) pH 13.7. Reprinted with permission from Ref. [37]. Copyright 2013 American Chemical Society.

are severely harmful to environment. Bhattacharjee et al. [50,54] have established a green, environment-friendly microwave-assisted synthesis of SnO_2 QDs. In their works, strong alkaline solutions were replaced by biological molecules, namely, serine [50] and sugar cane juice [54]. For example, for the biosynthesis of SnO_2 QDs,

0.01 M $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was treated with 10% sugar cane solution. The mixture was then placed into a microwave oven and irradiated for thirty 10 s shots. Figure 3(a,b) show the formation of highly uniform and well-aligned SnO_2 QDs. The size of SnO_2 QDs depicted in the Figure 3(a,b) is 3–4.5 nm, consistent with the crystalline

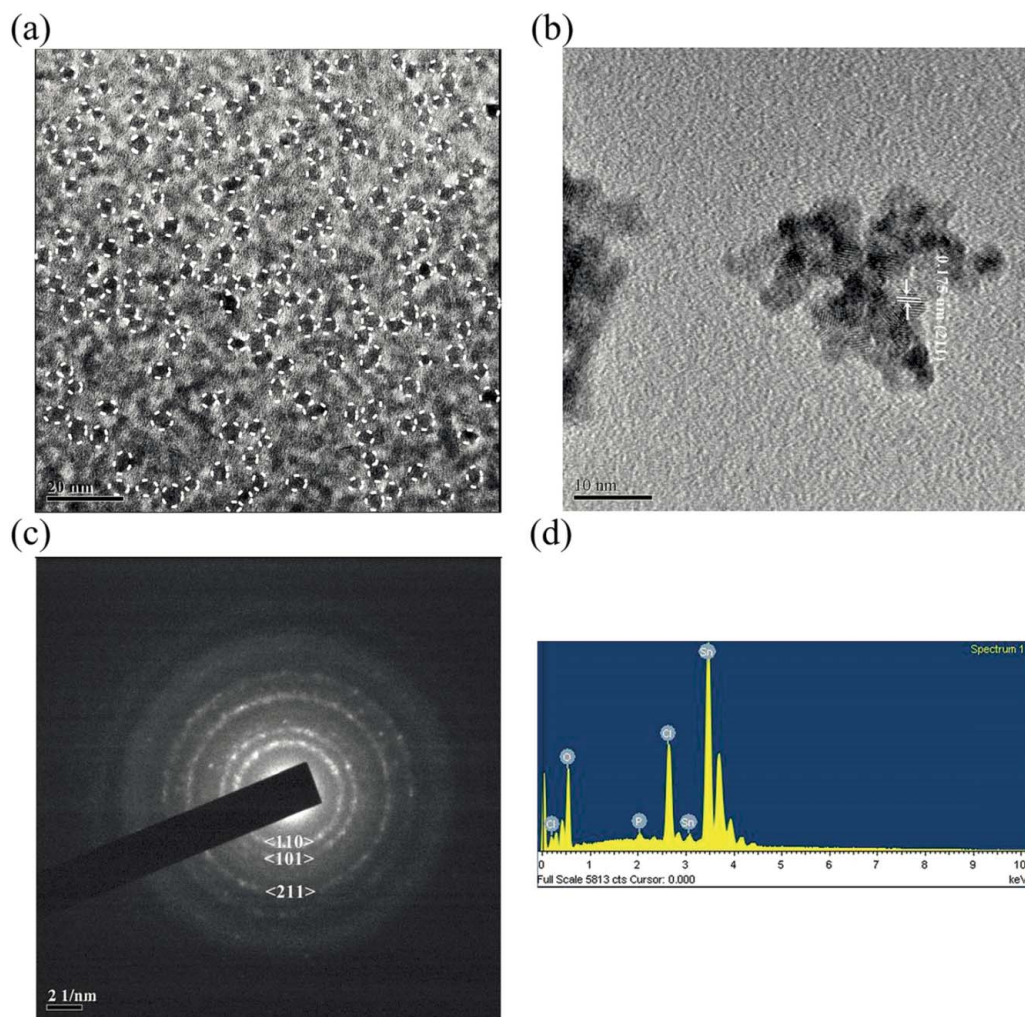


Figure 3. (a) TEM microphotograph of biosynthesized SnO_2 QDs, (b) HRTEM image of biosynthesized SnO_2 QDs, (c) SAED pattern of biosynthesized SnO_2 QDs, (d) EDS spectrum of biosynthesized SnO_2 QDs. Reprinted with permission from Ref. [54]. Copyright 2015 the Royal Society of Chemistry.

size calculated from their XRD data. The lattice planes depicted in Figure 3(c) is in good agreement with their XRD results of the SnO_2 QDs. Figure 3(d) demonstrated the presence of Sn and O.

The SnO_2 QDs with narrow size-distribution and better crystallinity can also be prepared via the reaction of tin precursors with nonaqueous solution. However, extreme operating conditions are often required, which makes it difficult for the large-scale synthesis of SnO_2 QDs with an economic way. Recently, ionic liquids, one of nonaqueous media, have been widely applied in nanosynthesis due to their special advantages including high polarizability, low toxicity, recyclability and high thermal stability. Ionic liquids are an excellent nonaqueous medium for the absorption of microwave due to their high polarizability. Xiao et al. [52] have integrated the advantages of ionic liquid and microwave irradiation to control nucleation of SnO_2 QDs. In their work,

highly crystalline and monodisperse SnO_2 QDs were prepared by dissolving $\text{Sn}(\text{OtBu})_4$ in dried [BMIM] BF_4 (1-butyl-3-methylimidazoliumtetrafluoroborate) under Ar atmosphere, followed by microwave decomposition of $\text{Sn}(\text{OtBu})_4$ for 1 min. For comparison, another sample was prepared by oil bath heating the same precursor for 1 h. Figure 4(a) shows that the SnO_2 QDs synthesized by the microwave decomposition of $\text{Sn}(\text{OtBu})_4$ in [BMIM] BF_4 have an obviously better crystallinity than that of the SnO_2 QDs synthesized by oil bath. Figure 4(b) exhibits the SnO_2 QDs synthesized by the microwave decomposition were nearly monodispersed with a narrow size distribution (4.27 ± 0.67 nm). It can be concluded that the microwave could initiate the reaction much faster than the oil bath method and might offer an additional energy for the crystal formation of SnO_2 QDs. Compared with the convenient hydrothermal and solvothermal method, the microwave-assisted method is more effective

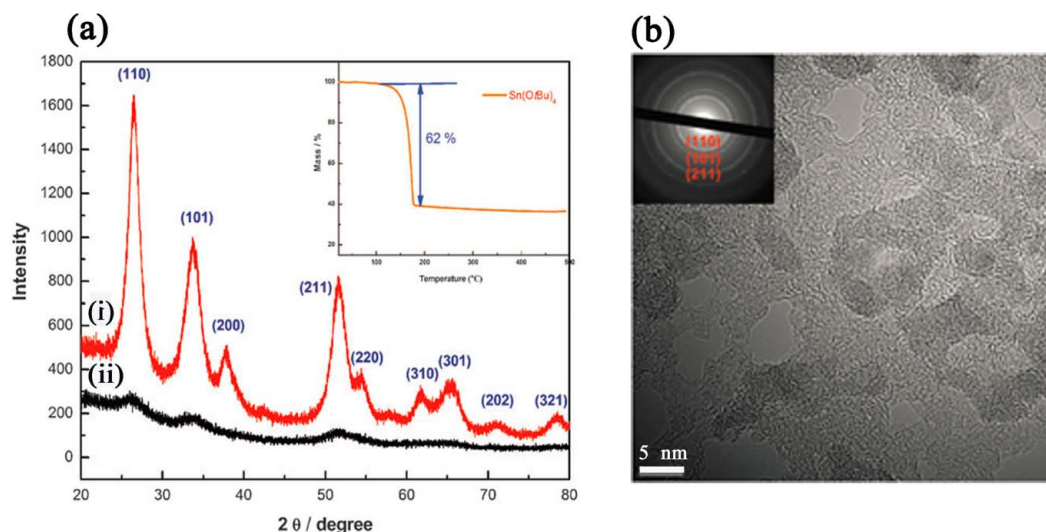


Figure 4. X-Ray powder diffraction patterns (a) of as-synthesized SnO₂ (i) by MW irradiation, (ii) by oil bath heating and TGA trace of the precursor (inset); HR-TEM image (b) of as-synthesized SnO₂ QDs and electron diffraction pattern (inset). Reprinted with permission from Ref. [52]. Copyright 2010 The Royal Society of Chemistry.

in time and energy saving, facile composition, size control.

2.4. Pulsed laser ablation decomposition

The above summarized hydrothermal, solvothermal and microwave-assisted approaches are ‘bottom-up’ method for the fabrication of SnO₂ QDs. Pulsed laser ablation of starting material, as a ‘top-down’ strategy, is a versatile method to produce nanoparticles. Using Sn or SnO as starting materials, some research groups have fabricated SnO₂ QDs by pulsed laser ablation of Sn or SnO [40, 58–62]. Singh et al. [58] have synthesized SnO₂ QDs with the average diameter of 2.5 nm by laser ablation of metal Sn in water. In detail, tin pellet was put into a glass vessel containing 20 mL of deionized water. The mixture of Sn and water was then irradiated for one hour by the 1064 nm wavelength Nd:YAG laser beam (35 mJ, 10 ns, 10 Hz). The fabricated SnO₂ QDs are ultrafine nanoparticles with a diameter from 1 to 5 nm.

The starting material with a low boiling-point is usually considered to be a better material to generate tiny nanoparticles in the pulsed laser ablation process. SnO is regarded as a better precursor for the formation of SnO₂ QDs, because of its lower boiling-point (1527°C) compared to that of Sn (2602°C). Some efforts for the fabrication of SnO₂ QDs by using SnO as precursor have been made [59,60,62]. The schematic illustration of the formation of the SnO₂ QDs is presented in Figure 5(a). SnO powders absorb the laser power and break down into tiny fragments of SnO, the SnO nanoparticles are then transformed into SnO₂ QDs via the reaction $\text{SnO} + \text{H}_2\text{O} \rightarrow \text{SnO}_2 + \text{H}_2$.

Pan et al. [59] have reported the synthesis of SnO₂ QDs by laser ablation method using SnO powder as material. First, 60 mg SnO was added into 20 mL deionized water. Second, the stirring mixture was irradiated by a pulsed laser beam (6 ns, 10 Hz, 1064 nm) for 30 min. Figure 5(b,c) show that the fabricated SnO₂ QDs have uniform diameter of 1.8 ± 0.3 nm. Figure 5(d) shows the lattice spacing of the SnO₂ QDs is 0.212 nm, which is related to the (210) crystal plane and consistent with the rutile SnO₂ phase data. Figure 5(e) described the transformation from SnO to SnO₂ QDs. It is found that using SnO powder as precursor can produce SnO₂ QDs with better size uniformity and smaller particle size compared to widely employed Sn powder. Pan et al. [60] have also investigated the influences of the laser irradiation time on preparation of SnO₂ QDs. With increasing laser irradiation time, the average size of the prepared SnO₂ QDs remarkably increases along with a wider size distribution.

2.5. Electron-beam irradiation synthesis

The electron-beam irradiation synthesis has many highly advantageous properties as follows: (i) this method is rapid, simple, and convenient, (ii) the method can be carried out at room temperature without catalysts, and (iii) this strategy is useful for mass production of nanomaterials. Our group has performed systematic investigations on the fabrication of SnO₂ QDs by electron-beam irradiation strategy [63,64]. For example, we have prepared a series of SnO₂ QDs by using electron-beam irradiation and evaluated their microstructure evolution. The primal SnO₂ QDs samples were prepared by adding dropwise 2 mol/L aqueous ammonia into a 0.2 mol/L SnCl₄

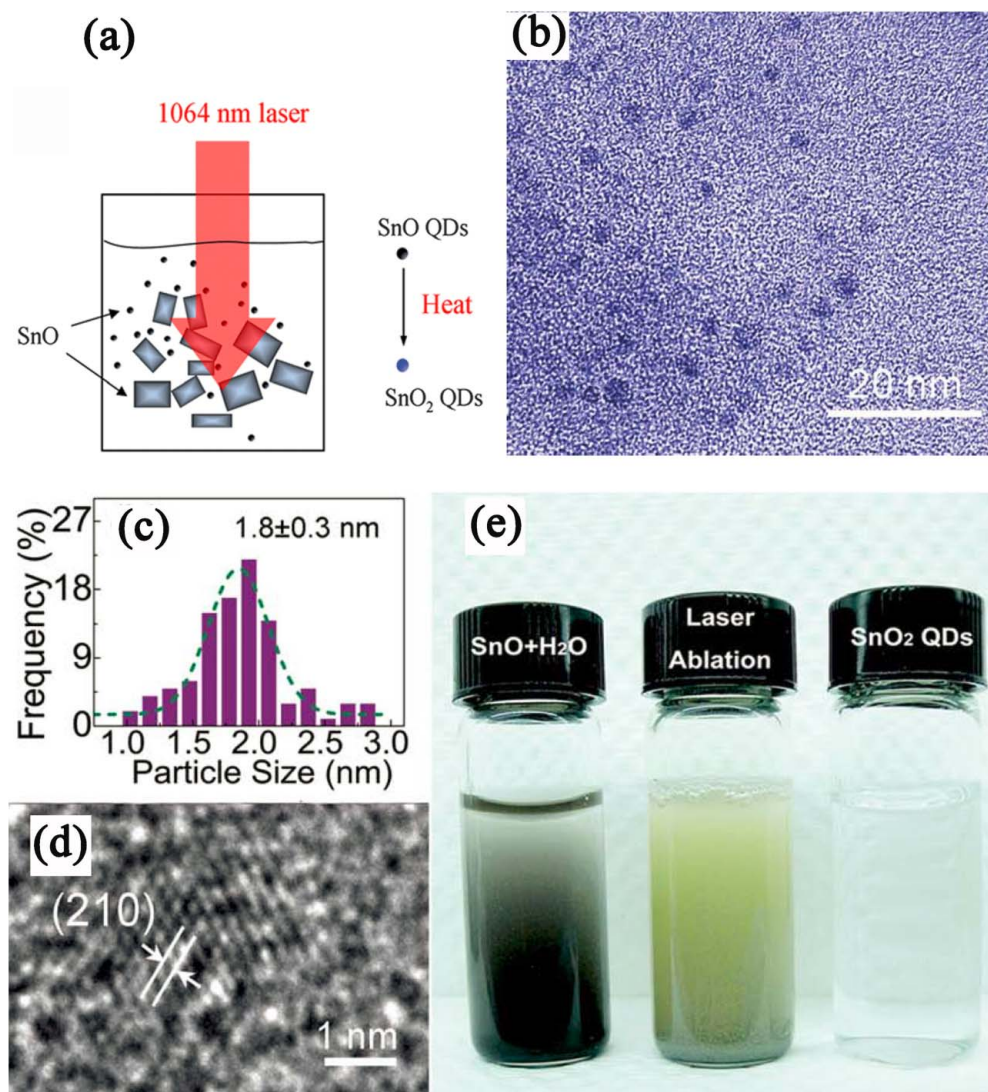


Figure 5. (a) Schematic illustration of the formation of the SnO_2 QDs using SnO as precursors by the pulsed laser ablation process; (b) TEM image, (c) histogram of diameter distribution, and (d) HRTEM of the SnO_2 QDs in water; (f) Photos of the mixture of SnO powder and H_2O (left), the mixture after laser fragmentation (middle) and the mixture of SnO_2 QDs and water after centrifugation (right). Reprinted with permission from Ref. [59]. Copyright 2010 the Royal Society of Chemistry.

solution under stirring until the pH value of the mixed solution reached 7. The as-prepared SnO_2 samples were spreaded to a thickness of 2–3 mm, which was irradiated by a GJ-2-II dynamitron electron accelerator with an accelerating voltage of 2 MeV and a current of 8 mA at 700, 980, 1260, and 1400 kGy, respectively. Figure 6(a) shows that the SnO_2 QDs irradiated at 1400 kGy have a better crystallinity compared to that of the unirradiated one. In addition, it was found that the surface area of the irradiated SnO_2 QDs is higher than that of unirradiated one as shown in Figure 6(b). When the irradiated dose increased to 700 kGy, the BET surface area of the SnO_2 QDs increased from 105.39 to 170.47 m^2/g . However, the BET value has slightly decreased to 165.42 m^2/g at 980 kGy radiation dose. With increasing irradiated

doses to 1260 and 1400 kGy, the BET values increased. It was reasonable to speculate that the electron-beam irradiation is favorable for the formation of more SnO_2 crystal nucleus in SnO_2 QDs. This speculation can also be proved by the HRTEM results as shown in Figure 6(c,d). The research results reveal that the electron-beam irradiation is a potentially powerful technique to achieve SnO_2 nucleation and QD growth.

2.6. Other synthesis strategies

In addition to those above mentioned commonly used methods to prepare SnO_2 QDs, there are some other ones, such as sonication [65], solution combustion [66], interfacial reaction [67], liquid phase refluxing [68],

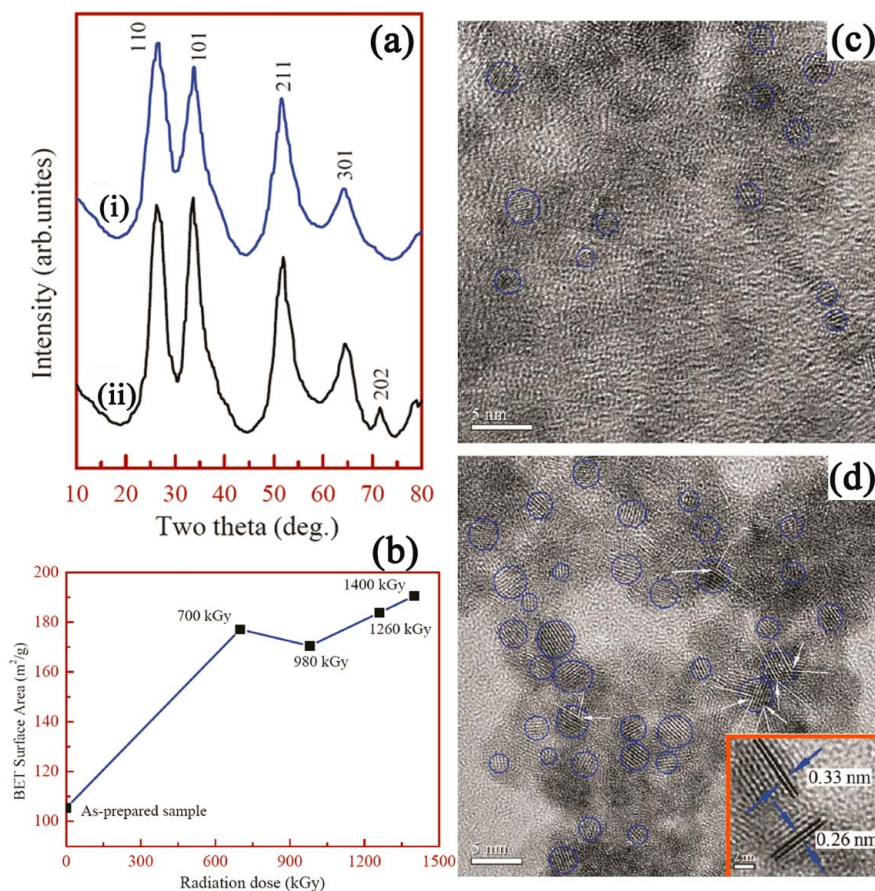


Figure 6. Typical XRD patterns (a) of SnO₂ QDs: (i) unirradiated SnO₂ QDs, (ii) irradiated SnO₂ QDs which was irradiated at 1400 kGy; Specific surface area (b) of unirradiated SnO₂ QDs and irradiated SnO₂ QDs at 700, 980, 1260, and 1400 kGy, respectively. HRTEM images of (c) unirradiated SnO₂ QDs, (d) irradiated SnO₂ QDs which was irradiated at 1400 kGy. Scale bar = 5 nm. Reprinted with permission from Ref. [63]. Copyright 2011 American Chemical Society.

grinding [69]. Lee et al. [67] have fabricated a series of SnO₂ QDs with average diameters from 2 to 2.7 nm, energy band gaps between 5.70 and 4.39 eV through the interfacial reaction of Sn⁴⁺ and OH⁻ in interface between water and chloroform. Kamble et al. [66] have synthesized the SnO₂ QDs with average crystallite size of 7 nm by heating tin nitrate solution with fuel (urea) at 500°C. Kida et al. [68] have prepared monodispersed SnO₂ QDs with size of 3.5 nm by refluxing tin (IV) acetylacetonate in dibenzyl ether at 280°C under the aid of oleylamine and oleic acid. Cui et al. [69] have produced

SnO₂ QDs with particle size of about 1.2 nm at an ultra large scale by grinding the solid mixture of SnCl₂·H₂O, ammonium persulphate and morpholine in a mortar at room temperature. Although these methods have the uniquely attractive advantages of facility, such as large scale, room temperature, and surfactant-free, the explorations of these approaches have just begun and thus will be a subject of future studies.

SnO₂ QDs have been successfully fabricated *via* a variety of methods mentioned above. Being conducted in different conditions, these synthesis strategies

Table 1. Advantages and disadvantages of synthesis strategies for the fabrication of SnO₂ QDs.

Method	Advantages	Disadvantages	Ref.
Hydrothermal synthesis	Simplicity, high-efficiency, environmentally friendly, without organic solvent	High temperature, long synthetic period, uncontrollable dispersion	[34–37]
Solvothermal synthesis	Simplicity, well dispersion	High temperature, long-time duration period, environmental damage, with organic solvent	[45,47,48]
Microwave-assisted synthesis	Short synthesis time (1–10 min), narrow size distribution, well dispersion	Low yield, special equipment is needed, high cost	[52,54]
Pulsed laser ablation	Time-saving (20–60 min), room temperature	Low yield, special device is needed, high cost	[58–60]
Electron-beam irradiation	Convenience, room temperature, time-saving, mass production, the crystallinity can be adjusted by changing the irradiation dose	Special device is needed, high cost	[63]

have their own advantages and disadvantages (Table 1). These methods usually require harsh conditions, complex procedures and/or special devices, high cost, time-consuming and/or environmental pollution. It is necessary to further explore facile, room temperature, environment-friendly approaches for the fabrication of SnO_2 QDs. In addition, these methods are normally low yield. In order to facilitate their practical application, it is of great importance to develop large scale synthesis of SnO_2 QDs.

3. Modified SnO_2 QDs

3.1. Doped SnO_2 QDs

Many applications of SnO_2 QDs are related to their physical properties, such as optical, electrical and magnetic properties. To extend their applications, the enhancement of these properties of SnO_2 QDs is very important. Doping the pure SnO_2 QDs with extrinsic dopants is a facile and effective way to promote their physical properties. In the doping process, the stannum or oxygen component in the SnO_2 QDs can be partially replaced to modify the physical properties of SnO_2 QDs. Recently, some efforts have been devoted to the doped SnO_2 QDs.

3.1.1. Metal-doped SnO_2 QDs

Some metals, including transition and rare earth metals, have been successfully doped into SnO_2 QDs [18,70–83]. The fabrications of metal-doped SnO_2 QDs are very similar to those of pure SnO_2 QDs, which can also be divided into the following types: hydrothermal, solvothermal, sol–gel method and microwave-assisted synthesis strategies, etc.

Some transition metals, such as Ti [83], Mn [77], Pd [70], Cu [84], Cr [85] and Zn [18], have also been successfully doped into SnO_2 QDs. Sakthiraj et al. [83] have performed a systematic study of the SnO_2 QDs, which were doped with different amount of titanium by sol–gel method, and investigated their room temperature ferromagnetism. Figure 7 shows that different amount of titanium ion dopants significantly influences the room temperature ferromagnetism (RTFM) of the SnO_2 QDs. The undoped and 2% titanium doped SnO_2 QDs (i.e. undoped SnO_2 and $\text{Sn}_{0.98}\text{Ti}_{0.02}\text{O}_2$) show perfect RTFM, but the 5% and 7% of titanium doped SnO_2 QDs (namely $\text{Sn}_{0.95}\text{Ti}_{0.05}\text{O}_2$ and $\text{Sn}_{0.93}\text{Ti}_{0.07}\text{O}_2$) exhibit a weak ferromagnetism with diamagnetic contribution. It is obvious that the RTFM of the doped SnO_2 becomes weak with the increase of titanium dopants. The researchers believed that the amount of oxygen vacancies in SnO_2 QDs greatly influence the ferromagnetic property of the samples. Li

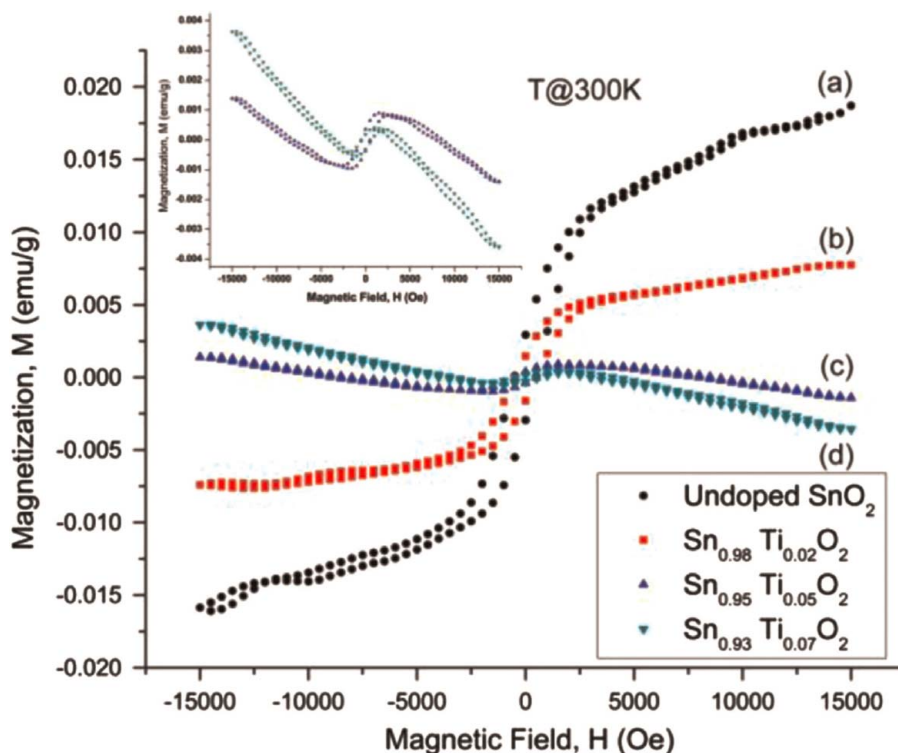


Figure 7. M-H magnetic hysteresis loop of (a) undoped SnO_2 nanoparticles, (b) 2% Ti doped sample, (c) 5% Ti doped sample and (d) 7% Ti doped sample. Inset of the figure shows the focused view of 5% and 7% Ti doped samples. Reprinted with permission from Ref. [83]. Copyright 2015 Elsevier.

et al. [18] have synthesized undoped and zinc-doped SnO_2 QDs by a simple hydrothermal method. The doping with zinc into SnO_2 induced a negative shift in the flat-band potential and increased the isoelectric point. As a result, the dye-sensitized solar cells based on the zinc-doped SnO_2 QDs showed higher dye loading and longer electron lifetimes compared to that based on pure SnO_2 QDs. Sabergharesou et al. [77] have reported the sub-3 nm diameter manganese-doped SnO_2 QDs, synthesized from $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and MnCl_2 precursors. The manganese ions in the SnO_2 QDs exhibit two different oxidation states (i.e. Mn^{2+} and Mn^{3+}); Mn^{2+} species dominated at low doping levels, however, the fraction of Mn^{3+} species increased with doping concentrations. The electronic structure and magnetic properties of the samples were also studied in detail. Both the electronic structure and magnetic properties of the SnO_2 QDs were primarily determined by the density ratio of the two different Mn oxidation states.

Several kind of SnO_2 QDs doped with rare earth metals, such as Eu [72], Cs [75] and Gd [80], have also been fabricated by some research groups. Using microwave synthesis method, Patria et al. [72] have prepared the pure and Eu^{3+} doped SnO_2 QDs and studied their optical and electrical properties. Figure 8 displays the absorption spectra of 1.0 mol% Eu-doped SnO_2 QDs annealed at different temperatures. With the increasing temperatures, the quantum size effect results in the red shift in the absorption edge. The doped SnO_2 QDs showed higher conductivity than that of pure SnO_2 QDs. Using oleic acid as a stabilizing agent, Yang et al. [80] have prepared pure SnO_2 QDs and doped the SnO_2 QDs with

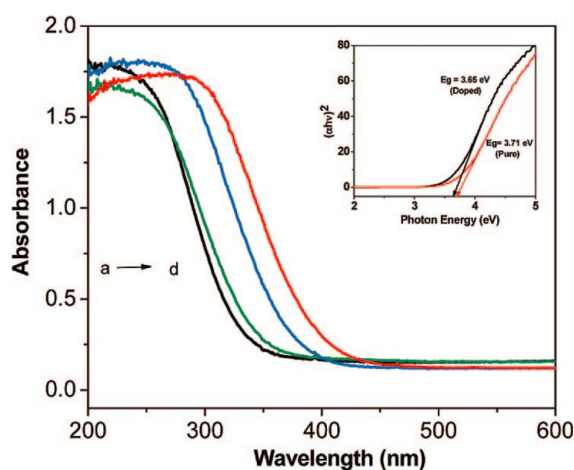


Figure 8. UV-vis spectra of 1.0 mol % Eu^{3+} -doped SnO_2 QDs at different temperatures, (a) 100°C, (b) 200°C, (c) 400°C and (d) 800°C. Inset shows $(Rh\nu)$ vs. photon energy plot of pure and Eu^{3+} -doped SnO_2 nanocrystals. Reprinted with permission from Ref. [72]. Copyright 2009 American Chemical Society.

Gd ions *via* a solvothermal method. The pure SnO_2 QDs with quasi-sphere morphology can be converted to dope SnO_2 QDs with nanorods shape due to Gd^{3+} doping. The absorption edge of the SnO_2 QDs exhibited an obvious blue shift with increasing Gd^{3+} dopant concentration. They attributed the blue shift to size effect induced by the reduced average size of the Gd^{3+} doped SnO_2 QDs.

Some other metals, such as Sb [71], Mg [78], and Sn [81] have also been doped into SnO_2 QDs. For example, Fan et al. [81] have fabricated a series of Sn^{2+} self-doped SnO_{2-x} QDs (with different molar ratios (r) of Sn/SnCl_4 , $r = 1:16, 1:8, 1:4$, and $1:2$, respectively) via a facile one-pot temperature synproportionation reaction, and also studied the self-doping effects on the particle size and band gap modification. The particle size of Sn^{2+} self-doped SnO_{2-x} QDs decreased a little with the increase in the molar ratios (r) of Sn/SnCl_4 . The size of Sn^{2+} self-doped SnO_{2-x} QDs ($r = 1:4$) was about 5 nm. With the increase of tin powder proportion, the absorption edges for the different Sn^{2+} self-doped SnO_{2-x} QDs were red-shifted relative to stoichiometric SnO_2 QDs. This self-doping effect on these absorption edges was attributed to the incorporation of Sn^{2+} into the SnO_{2-x} lattice and accompanying oxygen vacancies, which can lead to significant narrowing of the band gap.

3.1.2. Nonmetal-doped SnO_2 QDs

It is found that two nonmetal elements, namely nitrogen [79], fluorine [73,74,76], have also been doped into SnO_2 QDs. For instance, Zhou et al. [79] have fabricated nitrogen-doped SnO_2 QDs with sizes of 2.2, 5.4 nm by continuously stirring the solution of tin powers, nitric acid and deionized water for 40 h, followed by annealing in O_2 atmosphere at 500, 700°C, respectively. Compared with bare SnO_2 QDs, the PL peaks of nitrogen-doped SnO_2 QDs are blueshifted with the increasing of annealing temperature from 500 to 700°C. Infrared and Raman spectra showed the existence of local disorder and oxygen vacancies in the samples. Spectral analysis and theoretical calculation suggested that the PL band of the nitrogen-doped SnO_2 QDs originates from the mutual effects of nitrogen dopants and oxygen vacancies. Wu et al. [73] have prepared fluorine-doped SnO_2 QDs by a sol-gel procedure accompanied by a hydrothermal process using NH_4F as fluorine dopant. The precursor of SnO_2 QDs was obtained by refluxing the precipitation of $\text{Sn}(\text{OH})_4$ in oxalic acid at 100°C for 4 h. Subsequently, the resulted solution was added with NH_4F , and hydrothermally treated at 180°C for 72 h. The electrical resistivity properties of the fluorine-doped SnO_2 QDs are dependent on the $\text{NH}_4\text{F}/\text{Sn}$ molar ratio. The sheet resistances of fluorine-doped SnO_2 QDs decline with improving the $\text{NH}_4\text{F}/\text{Sn}$ molar ratio from 0 to 2. However, the

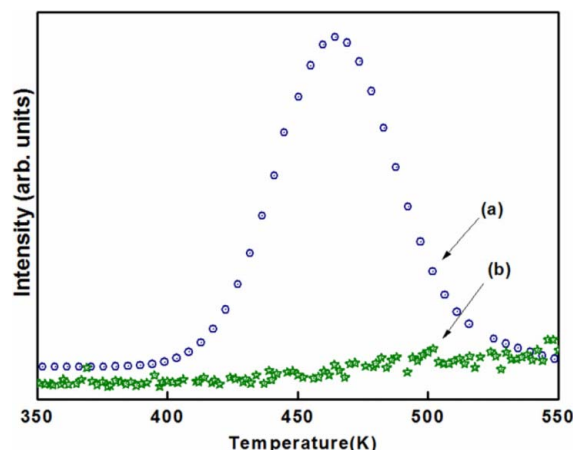


Figure 9. Thermoluminescence glow curve of (a) F-doped SnO_2 QDs and (b) pure SnO_2 QDs. Reprinted with permission from Ref. [76]. Copyright 2012 Elsevier.

sheet resistances of fluorine-doped SnO_2 QDs increase with further improving $\text{NH}_4\text{F}/\text{Sn}$ molar ratio from 2 to 5. When $\text{NH}_4\text{F}/\text{Sn}$ molar ratio is 2, the sheet resistances of fluorine-doped SnO_2 QDs is $110\ \Omega$. Nagarajan et al. [74,76] have successfully fabricated heavily fluorine-doped (up to 21 mol%) SnO_2 QDs using air-stable KSnF_3 as single-source precursor and investigated their optical and photocatalytic properties. A blue shift of the exciton absorption, estimated from the Kubelka–Munk function, was observed from 3.52 to 3.87 eV in the fluorine-doped SnO_2 QDs. The fluorine-doped SnO_2 QDs displayed a broad green emission arising from the singly ionized oxygen vacancies created by high dopant concentration. One year later, Nagarajan et al. [76] have also prepared heavily F-doped SnO_2 QDs by a similar method and studied their thermoluminescence property. As shown in Figure 9, an intense broad thermoluminescence is detected in the fluorine-doped SnO_2 QDs in the temperature range of 350–550 K, signifying the presence of trapped states, but no glow peak is observed for the pure SnO_2 QDs. These results indicate that it is easier to substitute the Sn^{4+} in SnO_2 with extrinsic metals, and it is more difficult to replace the O^{2-} with other anions which may be due to their differences in ionic radii and charge states.

3.2. SnO_2 QDs embedded nanocomposites

Nanocomposites can achieve advantageous optical, electronic, magnetic and mechanic properties due to their potential to combine desirable properties of different components. In recent years, many efforts on SnO_2 QDs have been focused on the preparation of SnO_2 QDs embedded nanocomposites, including SnO_2 QDs embedded reduced graphene oxide (SnO_2 QDs/RGO), SnO_2 QDs embedded carbon nanotubes

(SnO_2 QDs/CNTs), SnO_2 QDs embedded amorphous carbon (SnO_2 QDs/AC), and SnO_2 QDs embedded metal oxide, and so on.

3.2.1. SnO_2 QDs/RGO

3.2.1.1. Strategy for embedding SnO_2 QDs into graphene.

Graphene is a single atomic layer of sp^2 hybridized carbon atoms arranged in a honeycomb lattice. It has attracted widespread attention because of their large specific surface area, outstanding mechanical flexibility, and excellent optical, electronic and electrochemical properties. Embedding SnO_2 QDs into graphene matrix is a facile, efficient way to enhance their physical and chemical properties. An increasing amount of effort is being dedicated to embedding SnO_2 QDs into graphene by using various methods, such as hydrothermal method [86–96], refluxing method [97,98], microwave-assisted approaches [99], ultrasonic method [100].

At present, the hydrothermal method is one of the most commonly used approaches to assembly SnO_2 QDs onto graphene. Mishra et al. [91] have anchored the SnO_2 QDs with a size less than 6 nm on the surface of RGO by a surfactant assisted hydrothermal method. In this process, firstly, RGO (1.0 mg) was added to a transparent colorless aqueous solution containing $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (10 mmol). Subsequently, hexamethyldisilazane (1 mL) was added to the above solution with mild stirring. Next, the pH of the solution was adjusted to 8.5 by adding a NaOH aqueous solution. The resulted solution was transferred to a teflon-lined stainless steel autoclave (100 mL) and treated at 120°C for 20 h. The structural characterizations confirmed that the SnO_2 QDs with a size less than 6 nm have been anchored on the surface of RGO. Using $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ or $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ as precursor, Li et al. [92] have respectively prepared two type of SnO_2 QDs/RGO aerogels by hydrothermally treating the solution containing graphene oxide and precursor at 180°C for 16 h, and then freeze-dried the obtained samples under -50°C . The SnO_2 QDs/RGO aerogel prepared from $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ showed a 3D column-like freestanding structure. However, the SnO_2 QDs/RGO aerogel prepared from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ exhibited a fragile structure. The aerogel prepared from $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ has plentiful nanopores and thus exhibited extremely large surface area ($441.9\ \text{m}^2/\text{g}$), which could be beneficial for its applications. Li et al. [94] have also successfully planted the well dispersed SnO_2 QDs with size of 3–5 nm into nitrogen-doped graphene (containing 18 at% N atoms) *via* hydrothermally treating the homogeneous mixture of graphene oxide, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, dicyandiamide and sulphurea. In the hydrothermally treating process, graphene oxide was modified by dicyandiamide to produce N-doped graphene, which was then planted with the SnO_2

QDs derived from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Here, the sulfoarea was applied to decrease the size of the SnO_2 QDs, simultaneously enhance their uniformity, and also facilitate the combination of the SnO_2 QDs with nitrogen-doped graphene.

Compared with the convenient hydrothermal method, the microwave-assisted method for the fabrication of SnO_2 QDs planted-RGO is more effective in energy and time saving. Zhou et al. [99] have densely anchored the SnO_2 QDs with an average size of about 3 nm on N-doped graphene by radiating a solution containing 60 mg graphite oxide, 1 g urea, 0.3 g $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 10 mL ethylene glycol by microwave at 180°C for 5 min. In this process, Sn^{4+} ions were firstly anchored into graphene oxide because of electrostatic attraction. Subsequently, the urea acted as an N source for doping graphene and the synthesis of $\text{Sn}(\text{OH})_4$ was facilitated by ammonia which was released from the decomposition of urea. Then, ethylene glycol reduced graphene oxide to RGO.

The above mentioned approach for embedding SnO_2 QDs into graphene is usually time-consuming, often carried out in high pressure and temperature and suffered from poor manipulation. Therefore, it is meaningful to develop a novel facile route to obtain SnO_2 QDs embedded-RGO with favored microstructures and performances. By using a facile one-step ultrasonication, our group has assembled SnO_2 QDs into graphene

nanosheets at room temperature [100]. The mechanism of planting SnO_2 QDs into graphene nanosheets is illustrated in Figure 10. In a typical synthesis, 100 mL GO solution was dispersed in 50 mL distilled water to form a suspension. Then, 10 mL aqueous solution of 0.45 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was added into the above suspension and mixed with the suspension. The resulting mixture was treated by ultrasonic wave for 60 min at ambient temperature. We have discovered that the SnO_2 QDs were uniformly dispersed on both sides of the graphene. The size of SnO_2 QDs ranged from 4 to 6 nm and their average size was about 4.8 ± 0.2 nm. In this ultrasonic method, the loading of SnO_2 QDs was an effective approach to prevent graphene nanosheets from self-restacking during the reduction. On the other hand, the graphene nanosheets distributed between SnO_2 QDs have also prevented the SnO_2 QDs from agglomerating.

3.2.1.2. Microstructural evolution of SnO_2 QDs embedded into graphene. The size, morphology and microstructure evolution of SnO_2 QDs on graphene greatly affect their physical and chemical properties as well as their applications in many fields. For instance, the decrease in the size of the particle will lead to increase in its band gap and surface-volume ratio. This effect will finally result in the improvement of the sensitivity of gas sensors. In order to study the microstructural

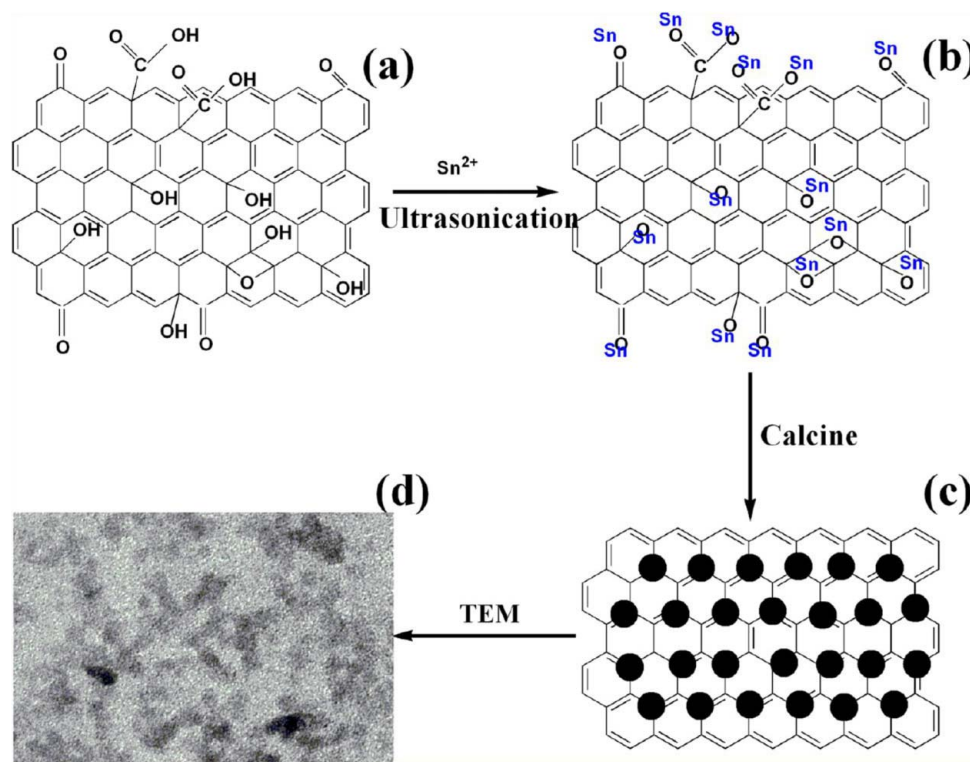


Figure 10. Schematic formation mechanism of SnO_2 QDs/GNS composites: (a) GO, (b) electrostatic interaction between oxide functional groups of GO and Sn^{2+} , (c) graphene decorated with SnO_2 QDs (filled circles) after the calcine treatment, and (d) TEM image of SQDs/GNS composites. Reprinted with permission from Ref. [100]. Copyright 2013 American Chemical Society.

evolution and enhance the performance of SnO₂ QDs anchored on graphene, our group has intentionally applied an electron beam to modify the surface structure of graphene and studied the microstructural evolution of SnO₂ QDs which was loaded graphene [64]. In this work, firstly, four identical suspensions of graphene nanosheets were respectively irradiated by an electron accelerator with four different absorbed doses (70, 140, 210, and 280 kGy) at room temperature. Then, certain amount of cetyltrimethylammonium bromide, SnCl₄·5H₂O and NaOH were added to the irradiated suspensions under stirring. The resulted mixtures were continuously stirred for 30 min. Subsequently, the black suspensions were heated in a Teflon vessel at 160°C for 20 h. Electron beam can create lattice defects or damage in the graphene nanosheets. Since lattice defects and grain boundaries are favorable nucleation sites, these defects and damage are beneficial for the formation of more and smaller SnO₂ QDs. From the Figure 11(b,e,h,k,n), it can be seen that a large amount of SnO₂ QDs are loaded on the surface of graphene nanosheets. As shown in Figure 11(k), the SnO₂ QDs loaded on graphene nanosheets irradiated at 210 kGy exhibits much smaller size distribution and much better homogeneous distribution. These can be attributed to the influences of the radiation dose on the grain boundaries, defects, and oxygen-containing groups in the graphene nanosheets (Figure 11(d,g,j)). Figure 11(n) indicated that the SnO₂ QDs planted on graphene nanosheets irradiated at 280 kGy have large agglomeration. The reason is that the high radiation dose causes deterioration or collapse of the graphene nanosheets as shown in Figure 11(m), resulting in agglomeration of SnO₂ QDs.

3.2.2. SnO₂ QDs/CNTs

Owing to the high aspect ratio and excellent electrical conductivity, the carbon nanotubes (CNTs) are attractive. Some efforts have been devoted to embed SnO₂ QDs into CNTs to form SnO₂ QDs/CNTs nanocomposites [101–106]. The methods of embedding SnO₂ QDs into CNTs can be divided into two classes that is in-situ and ex-situ assembly. Jin et al. [102] have prepared SnO₂ QDs/MWCNTs by a in-situ assembly method. Firstly, MWCNTs were treated with H₂SO₄/HNO₃ (3:1 ratio). Then, the treated MWCNTs were mixed with SnCl₄·5H₂O, N₂H₄ and deionized water to form a homogeneous solution, followed by heating at 150°C for 24 h. The SnO₂ QDs (less than 3 nm) were uniformly planted onto the MWCNT, providing a large BET surface area (240 m² g⁻¹). Compared with the pure SnO₂ QDs, there is a smaller decline in the redox peaks of the SnO₂ QDs/MWCNT until the tenth cycle, implying its improved cyclability in lithium storage. Song et al. [103]

have also embedded SnO₂ QDs into MWCNTs using a similar method. In the process, the ethanol suspension of SnCl₄, activated MWCNTs and deionized water was hydrothermally treated at 100°C for 6 h. Eventually, monodisperse SnO₂ QDs (~3 nm) are firmly embedded into the MWCNTs. This hybrid displayed excellent cycling performance with high reversible capacity about 700 mAh g⁻¹ after 150 cycles at 0.1 A g⁻¹, surpassing both bare SnO₂ QDs and MWCNTs. The ex-situ assembly is another way to anchor SnO₂ QDs onto MWCNTs. Lu et al. [105] have developed a facile ex-situ method of loading SnO₂ QDs on carbon nanotubes. In this method, colloidal SnO₂ QDs with average size of ~3.5 nm have been successfully fabricated using thiourea as stabilizing and accelerating agent at room temperature. For the ex-situ loading of SnO₂ QDs on CNTs, the colloidal SnO₂ QDs solution was added into the suspension of acid-treated CNTs under magnetic stirring. During this process, the SnO₂ QDs were ex-situ loaded on CNTs, forming SnO₂ QDs/CNTs. The SnO₂ QDs/CNTs displayed excellent lithium storage properties, with a discharge capacity of 845 mAh/g at 100 mA/g after 90 cycles. Liu et al. [104] have also loaded SnO₂ QDs on the surface of MWCNT by mixing chloroform suspension of MWCNT and toluene solution of SnO₂ QDs under magnetic stirring at room temperature. They investigated their gas sensing performance for H₂S. Compared to the pure SnO₂ QDs, the sensor based on the SnO₂ QDs/MWCNT displayed a higher response upon H₂S.

3.2.3. SnO₂ QDs/AC

SnO₂ is a good anode material for lithium ion batteries (LIBs) due to its relatively high theoretical reversible capacity. However, the poor cycling stability of SnO₂ is caused by its volume swell during lithium releasing and storing. An effective approach to avoid the volume swell is embedding SnO₂ QDs into amorphous carbon (AC) to form SnO₂ QDs/AC nanocomposites [107–110]. The SnO₂ QDs can be easily embedded in amorphous carbon by a one-step hydrothermal route. Song et al. [109] have encapsulated SnO₂ QDs with a size of 2 nm into mesotunnels of mesoporous carbon by this method. In a typical process, the ethanol suspension containing certain amounts of SnCl₄, mesoporous carbon and deionized water was heated to 100°C and maintained for 6 h. The ultrafine SnO₂ QDs of 2 nm have been evenly encapsulated in the mesotunnels of mesoporous carbon and anchored on the surface of mesoporous carbon. These SnO₂ QDs in mesoporous carbon showed excellent cycling performance with high reversible capacity retention above 95% for 200 cycles, which was superior to that of bare SnO₂ QDs. As shown in Table 2, these SnO₂ QDs in mesoporous carbon also showed

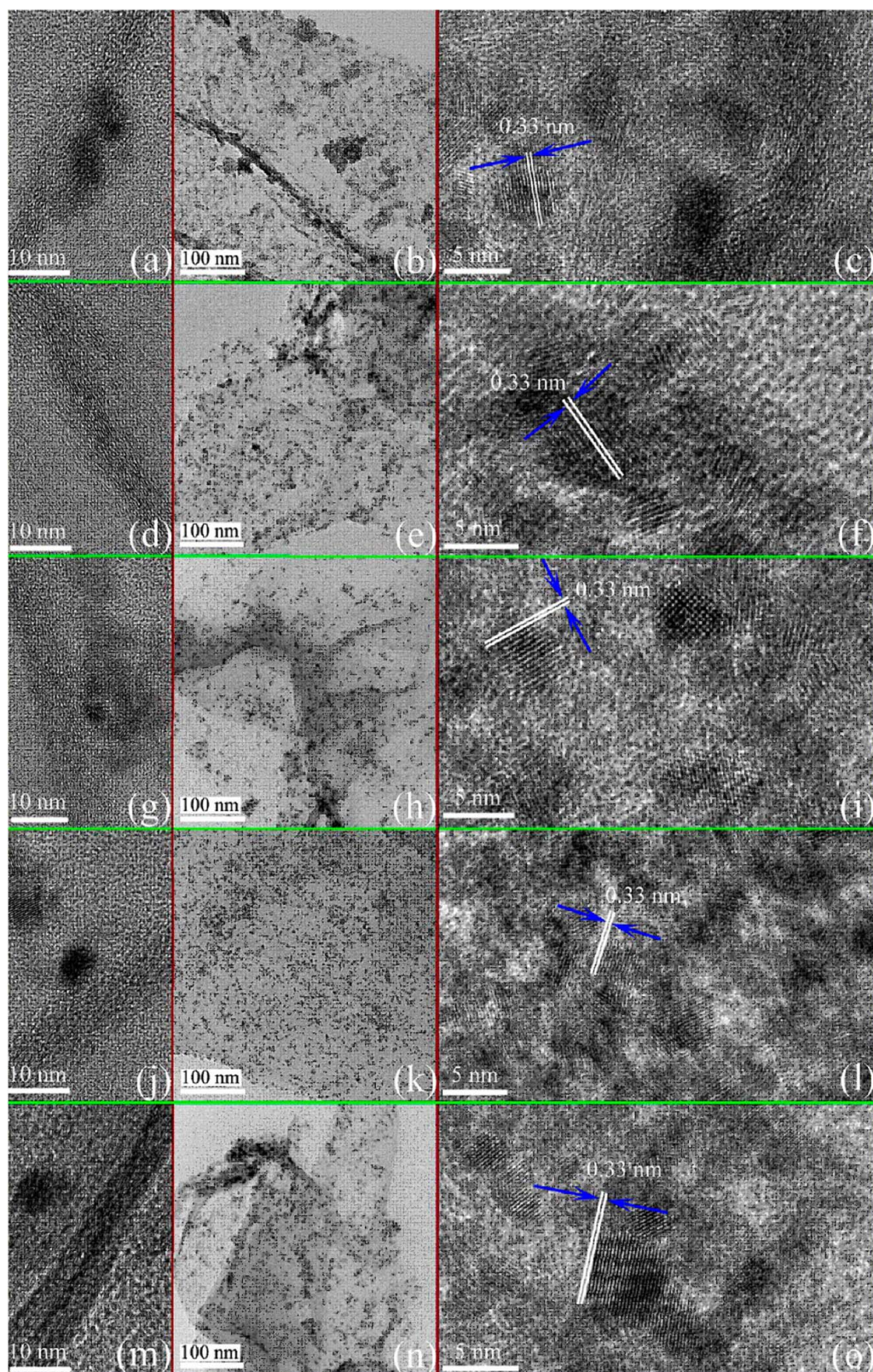


Figure 11. HRTEM images of (a) an unirradiated GNS and an irradiated GNS under different irradiation doses: (d) 70, (g) 140, (j) 210, and (m) 280 kGy; TEM images of (b) an unirradiated SGNS and an irradiated SGNS under different irradiation doses: (e) 70, (h) 140, (k) 210, and (n) 280 kGy; HRTEM image of (c) an unirradiated SGNS and an irradiated SGNS under different irradiation doses: (f) 70, (i) 140, (l) 210, and (o) 280 kGy. Reprinted with permission from Ref. [64]. Copyright 2015 American Chemical Society.

Table 2. Comparisons of electrochemical properties of SnO₂ QDs encapsulated in mesoporous carbon with larger-sized SnO₂ nanoparticles encapsulated in mesoporous carbon ('C' is 'capacity'; '—' is null).

Work	Size of SnO ₂ (nm)	Cycling performance			Rate performance		
		Initial C (mAh g ⁻¹)	Reversible C (mAh g ⁻¹)	Cycles (times)	Retention (%)	Rates (A g ⁻¹)	Initial C recoverable (%)
Yu et al. [111]	7–16	830	448	30	54	0.5	—
Wang [112]	> 10	1661	440	60	—	1.6	39
Fan et al. [113]	15	1473	640	150	—	0.5	43.4
Song et al. [109]	2	1500	800	150	94%	10	100

much better cycling and rate performances than that of larger-sized SnO₂ nanoparticle encapsulated in mesoporous carbon. This improved cycling performance can be ascribed to two factors: redox capacitance and interfacial capacitance. A two-step method has also been developed to embed SnO₂ QDs in amorphous carbon. Jin et al. [106] have embedded SnO₂ QDs into amorphous carbon (SnO₂ QDs/AC) by a solvothermal method accompanied by calcination process in a high temperature. Firstly, the precursor of SnO₂ QDs was obtained by heating aqueous solution of SnCl₄, glucose and urea at 180°C for 12 h. Then, SnO₂ QDs of 3–5 nm were embedded in amorphous carbon through calcinating the resulted precursor in argon atmosphere. This hybrid composite exhibits excellent cycle stability and high rate capability with the capacities of 364 mAh g⁻¹ at the current density of 5 A g⁻¹ after 300 cycles. Wang et al. [107] have coated SnO₂ QDs of 5 nm with amorphous carbon by refluxing Sn⁴⁺ and Bovine Serum Albumin (BSA), followed by a carbonization process. In the refluxing process, the BSA promotes the formation of SnO₂ QDs and simultaneously restricts the size of SnO₂ to quantum dot scale. In the following carbonization process, the BSA acts as a carbon source to form amorphous carbon. The carbon-coated SnO₂ QDs exhibited a markedly improved cycle performance in lithium storage with charge capacity of 473.1 mAh g⁻¹ at the current rates of 250 mA g⁻¹. Hu et al. [108] have planted SnO₂ QDs of 5 nm into amorphous carbon matrix by boiling Sn powders and crystal sugar in deionized water, followed by carbonizing the precursor in Ar atmosphere. Planting SnO₂ QDs in amorphous carbon matrix can well accommodate the volume change of Li⁺ insertion/extraction in SnO₂ anode materials. The SnO₂ QDs planted carbon matrix exhibited stable reversible capacity of 400 mAh/g after 100th cycle at a high current rate of 3.3 A g⁻¹.

3.2.4. Other SnO₂ QDs based hybrid

In order to improve its electrochemical or photocatalytic property, SnO₂ QDs have also successfully been bonded with some other matrix, such as TiO₂ [67,114,115], ZnO [116], MgO [117], Li₄Ti₅O₁₂ [118], SnS₂ [119], amorphous silica [120,121], conducting polymer [122,123], C₃N₄ [124] and polyvinylpyrrolidone (PVP) [125]. For

example, using Zn(NO₃)₂·6H₂O and SnCl₄·5H₂O as precursor, our group has successfully prepared ZnO/SnO₂ heterojunctions by sol-gel method and supercritical fluid drying processes [116]. These ZnO/SnO₂ heterojunctions were adorned uniformly with SnO₂ QDs and ZnO quantum dots (ZnO QDs), whose size varied from 3 to 7 nm. The optical properties of the ZnO/SnO₂ heterojunctions were affected by calcination temperature. When the calcination temperature was increased from 500 to 700°C, the photoluminescence (PL) intensity of the heterojunctions increased. This increase in PL intensity can be attributed to the decrease in the number of surface dangling bonds of ZnO and SnO₂ QDs. Ma et al. [119] have successfully loaded SnO₂ QDs with sizes of 4 nm on the surface of SnS₂ nanosheets by hydrothermal treating a aqueous suspension, which was composed of SnS₂ nanosheets, SnCl₄, ascorbic acid (Ac) and Na₂CO₃. In this method, the Ac acted as a stabilizer to enhance the stability of Sn⁴⁺ ions in solution by forming Sn⁴⁺-Ac complex. The Sn⁴⁺-Ac can gradually separate to release Sn⁴⁺ under hydrothermal process. As a precipitator, the Na₂CO₃ can react with the Sn⁴⁺ to form SnO₂ QDs. These SnO₂ QDs loaded on SnS₂ nanosheet through intermolecular forces or electrostatic gravitation. The SnO₂ QDs/SnS₂ hybrids demonstrated obviously higher photocatalytic activities than both the bare SnO₂ QDs and SnS₂ nanosheets for the reduction of Cr (VI) under visible light. Lee et al. [67] have decorated TiO₂ nanoparticles with SnO₂ QDs through stirring the mixture of ethanol suspension of SnO₂ QDs and ethanol suspension of P25 TiO₂ at room temperature. The SnO₂ QDs decorated TiO₂ nanoparticles showed much enhanced photocatalytic activity for the degradation of Rhodamine B. The reaction rate constant was significantly enhanced from 0.025 to 0.055 min⁻¹ by decorating SnO₂ QDs on TiO₂ nanoparticles. Du et al. [122] have loaded SnO₂ QDs with size less than 10 nm onto polypyrrole (PPy) nanowires by a electrodeposition. The PPy nanowires can accommodate the volumetric change of SnO₂ QDs and increase the interface of electrode/electrolyte. So, the SnO₂ QDs/PPy nanowires delivered enhanced Li⁺ storage performance with a reversible capacity of 690 mAh/g after 80 cycles at a rate of 0.3 C.

4. Applications of SnO₂ QDs

4.1. Applications in lithium-ion batteries

Compared with commercially used graphite with an theoretical lithium storage of 372 mAh/g, SnO₂ is a promising anode material for next-generation lithium-ion batteries (LIBs) due to its low cost, safety, natural abundance and high theoretical lithium storage capacity (about 782 mAh/g). However, the lithiation and delithiation processes cause large volume expansion and severe particle aggregation, and inevitably bring on the pulverization, loss of interparticle contact and blocking of the electrical contact pathways, which consequently result in a rapid capacity fading and poor cycling stability [90,122,126,127]. To eliminate these problems, two strategies have been explored. One strategy is to minimize the particle size of SnO₂ and optimize their dispersity [44,49], which can suppress the huge volume expansion during Li⁺ insertion and extraction processes. Chen et al. [49] have reported that the electrode constructed from ultrasmall pure SnO₂ QDs exhibited an improved cyclic capacity and a better rate capacity. The discharge capacity was about 718 mAh g⁻¹ after 60 cycles at 0.1 C. The electrode also showed excellent discharge ability at a high current density. Even after 200 cycles, the discharge capacities at 1 and 5 C were respectively maintained at 454 and 376 mAh g⁻¹. These excellent performances of the ultrasmall SnO₂ QDs electrode for lithium-ion batteries can be attributed to the reduction of the SnO₂ particle size and optimization of their dispersity, which can shorten the distance for Li⁺ diffusion and enlarge electrode-electrolyte contact area for a high Li flux across interface.

Another strategy is to combine ultrasmall SnO₂ with other nanomaterials, which can buffer the volume expansion or enhance the electronic conductivity of the electrodes. The currently used nanomaterials in this aspect include various carbonaceous materials, such as graphene nanosheets [66,69–73,128], carbon nanotubes [75–77], amorphous carbon [107,109,129]; several kind of metal oxide, such as TiO₂ [114,115], and Li₄Ti₅O₁₂ [86]; conducting high polymer [122] and amorphous silica [120]. Song et al. [86] have loaded the SnO₂ QDs with particle size below 5 nm onto graphene oxide (GO) to form a SnO₂ QDs/GO hybrid as shown in Figure 12(a,b). As shown in Figure 12(c), the charge-discharge curve for the SnO₂ QDs/GO electrode exhibited an obviously high initial discharging capacity (about 2000 mA h g⁻¹). This composite electrode also displayed a high reversible capacity of 800 mAh g⁻¹ at the rate of 100 mA/g as shown in Figure 12(d), maintaining about 90% of its initial capacity after 200 cycles. More importantly, the composite electrode based on SnO₂ QDs/GO hybrid also delivers

superior rate performance. Figure 12(d) also shows that the composite electrode exhibited a superior rate performance at the high rates of 1 A g⁻¹ and 2 g⁻¹, retaining capacities of 600 mAh g⁻¹ and 400 mAh g⁻¹, respectively. As exhibited in Figure 12(e), increasing rates from 100 mA g⁻¹, 500 mA g⁻¹ to 5 A g⁻¹, 10 A g⁻¹ and then returning to 100 mA g⁻¹ were performed for galvanostatic cycling. Even under these harsh conditions, the electrode fabricated from SnO₂ QDs/GO hybrid can still recover to its initial capacity. The long term cycling testing at 5 A g⁻¹ (Figure 12(f)) exhibited a stable cycling performance for 1000 cycles with a capacity similar to that of the 2nd cycle. Compared with the electrode fabricated from the graphene loaded with different morphologies of SnO₂, such as SnO₂ nanosheets [30,130], SnO₂ nanorods [131,132], SnO₂ hollow nanospheres [133], SnO₂ mesoporous spheres [134] or SnO₂ nanotubes [135], the electrode fabricated from SnO₂ QDs/GO has displayed much improved cycling and rate performances for lithium-ion storage. The reasons for these excellent electrochemical performances are as follows: (1) the extremely small size of SnO₂ QDs makes the process of redox reaction between SnO₂ and Sn partially reversible; (2) the large specific surface area and good distribution of the SnO₂ QDs on graphene guarantee the abundant active sites for Li⁺ insertion and extraction, and the efficient utilization of the active sites in the electrode materials; (3) the intimate contact of the conductive graphene with the SnO₂ QDs provides transport pathway for the alloying-dealloying of Li⁺; (4) the graphene sheets withstand the volume expansion of the electrode materials and prevent the aggregation of SnO₂ QDs. Ren et al. [101] have applied multiwalled carbon nanotubes uniformly loaded with 3–5 nm SnO₂ QDs as the electrode materials. The electrode exhibited a superior cycling stability with a capacity of 800 mAh g⁻¹ after 300 cycles. It can be explained as follows: (1) the MWCNTs, as a conductive nanomaterial, facilitate transportation of Li⁺ and electrons during charge and discharge; (2) the MWCNTs serve as volume buffers in the electrode. Wang et al. [107] have reported that the 5 nm SnO₂ QDs with a 16 wt% carbon coating exhibited a high discharge capacity of 502 mAh g⁻¹ at current rate of 100 mA g⁻¹ after 100 cycles. They ascribed high discharge capacity to the carbon coating on the surface of SnO₂ QDs. The carbon coating can resist the volume expansion/contraction during Li-Sn alloying-dealloying.

It is well known that the TiO₂ has a volume variation of less than 4% with a very low capacity (170 mAh/g) during lithium intercalation. However, SnO₂ has a relatively higher capacity (784 mAh/g) with a volume change of more than 250%. Du et al. [115] have prepared a three-dimensional SnO₂/TiO₂ anodes for

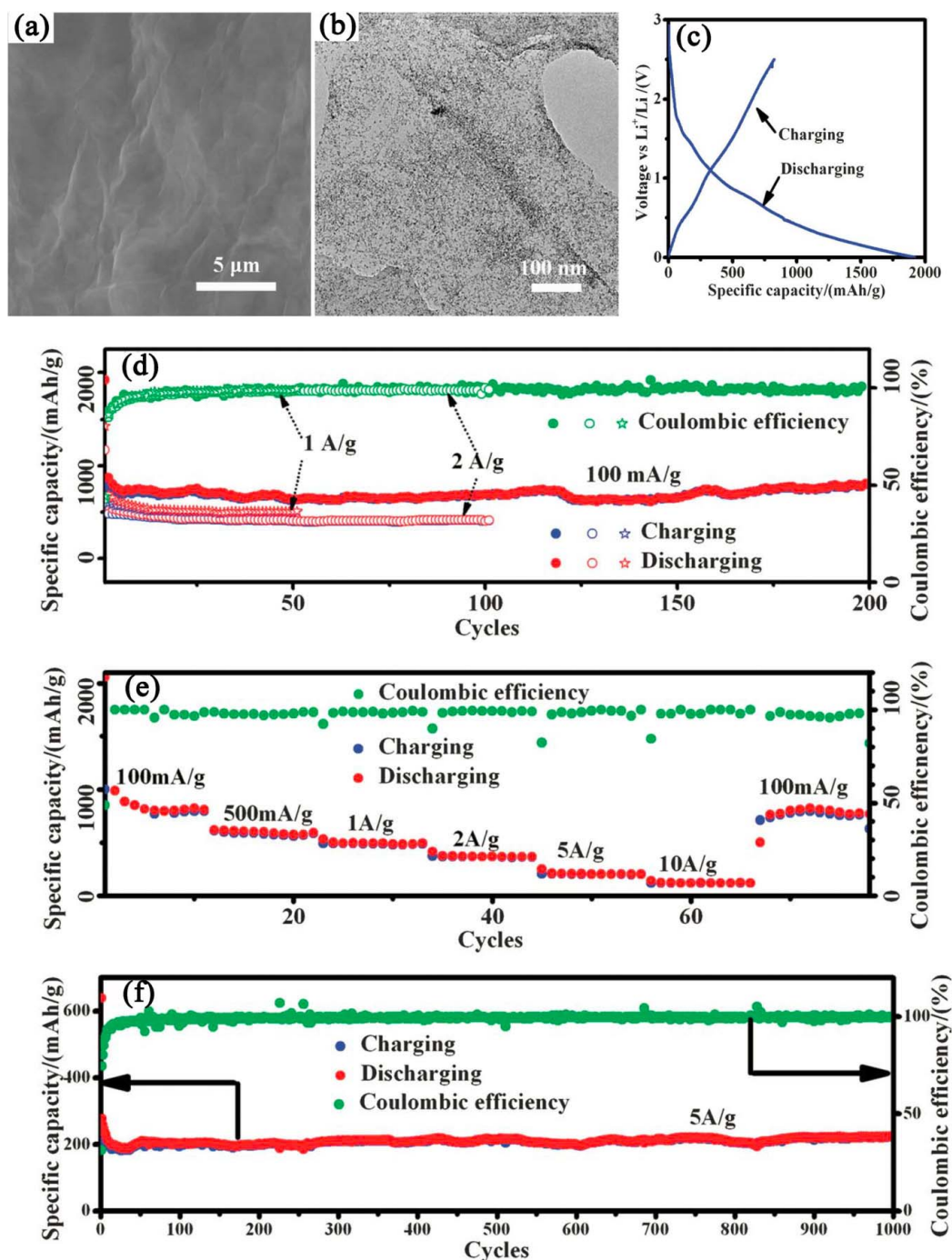


Figure 12. (a) SEM and (b) TEM image of the SnO₂ QDs-GO hybrid; (c) Typical charge-discharge curve for the composite electrode tested at 100 mA g⁻¹ in a voltage window of 0.005–2.5 V; (d) Cycling performance for the composite electrode galvanostatically tested at different rates; (e) Rate performance for the composite electrode discharging at various rates from 100 mA g⁻¹ to 10 A g⁻¹; (f) Long term cycling for the composite electrode discharging at 5 A g⁻¹ for 1000 cycles. Reprinted with permission from Ref. [86]. Copyright 2013 the Royal Society of Chemistry.

lithium-ion battery by planting SnO₂ QDs (diameters < 5 nm) into TiO₂ nanotube arrays. The three-dimensional anodes displayed an excellent capacity retention of 70.8% after 100 cycles in the voltage range of 0.05–2.5 V. This may contribute by the synergistic

effect between the SnO₂ QDs and TiO₂ nanotube arrays. The SnO₂ QDs can improve the capacity of the electrode, while the TiO₂ nanotube array can sustain the volume change and maintain the structural integrity of the electrode.

4.2. Application in photocatalysis

SnO₂ is considered to be one of the most efficient and nontoxic photocatalysts. Their photocatalytic mechanisms are summarized as following: (1) upon irradiation by a light with photons energy larger than the band gap of SnO₂, the electrons from the SnO₂ are excited and jump from the valence band (VB) to the conduction band (CB), producing electron–hole pairs; (2) the charge carriers produced by photons move from interior to the surface of photocatalyst; (3) the charge carriers promote the formation of hydroxyl radicals ($\cdot\text{OH}$) and superoxide radical anions ($\cdot\text{O}_2^-$); (4) the organic pollutants are adsorbed on the surface of photocatalyst, then are decomposed by the powerful hydroxyl radicals ($\cdot\text{OH}$) and superoxide radical anions ($\cdot\text{O}_2^-$). The photocatalytic performance of SnO₂ is significantly influenced by (1) the light absorption properties of catalytic agent, (2) reduction and oxidation rates on the surface by the electron and hole, and (3) the electron–hole recombination rate [136]. These influence factors depend on particle size, crystallinity, specific surface area, and so on.

It is known that the smaller SnO₂ particles have the higher specific surface area. The higher the specific surface area has, the more the active sites locate in the surface. The active sites can improve the photocatalytic activity. The catalytic activity of SnO₂ QDs is higher than that of the one with larger particles size. In recent years, many groups have dedicated themselves to the photocatalytic performances of pure SnO₂ QDs [50,53,54,57,137–140]. Liu et al. [57] have studied the photocatalytic activity of SnO₂ QDs with diameters of 3–5 nm on the degradation of methylene blue under visible light irradiation. The SnO₂ QDs exhibited a good photocatalytic activity with a degradation rate of 90% on methylene blue after 240 min. However, at the same condition, the commercial SnO₂ photocatalyst showed very low photocatalytic activity with degradation rate of 3% after 240 min. Jia et al. [138] have fabricated the SnO₂ QDs with a size of 6.7 nm and investigated their photocatalytic activity on degradation of Rhodamine B (RhB) under UV light irradiation. The SnO₂ QDs showed high photocatalytic activities, photodegrading 100% after exposure to UV light for 80 min. The photocatalytic activity of the SnO₂ QDs was superior to that of SnO₂ nanorods [31], SnO₂ nanoflowers [141,142], SnO₂ nanospheres [45] and SnO₂ films [28]. This enhanced photocatalytic activity of SnO₂ QDs may be ascribed to: (1) a easier adsorption of methylene blue on the surface, (2) a higher visible light absorption intensity, and (3) a lower rate of electron–hole pair recombination. Shajira et al. [139] have investigated the photocatalytic

performances of the SnO₂ with three different particle sizes (2.5, 5 and 12 nm) on the decomposition of methyl orange. Their investigation indicated that the smaller particle shows the better photocatalytic activity. For example, after 6 h of sunlight irradiation, the SnO₂ with 2.5 nm particle size decomposed the aqueous vanillin solution (0.01 mM) to 93% of its initial concentration. In contrast, the SnO₂ with 5 and 12 nm particle sizes only decomposed the solution to 51% and 35% of its initial concentration, respectively. Two factors may donate the better photocatalytic activity of the SnO₂ with smaller particle size. The decrease of crystallite size leads to the increase in the specific surface area, which facilitates the absorption of methyl orange. On the other hand, the decrease of crystallite size results in the increase in population of defects, which accelerates the reaction between electron–hole pairs and methyl orange.

The photocatalytic activity of the SnO₂ QDs is significantly hindered by the high recombination rate of electron–hole pairs. It is worth noting how to manipulate the chemical composition and surface chemistry of SnO₂ QDs. Metal-ion dopants in the SnO₂ QDs significantly influence the recombination rate of electron–hole pairs and interfacial electron transfer rates. Fan et al. [81] have discussed that the optical response of Sn²⁺ self-doped SnO₂ QDs and their catalytic activity on photodegradation of methyl orange. The UV-vis diffuse reflectance spectra illustrated in Figure 13(a) reveal that with the increase in the added tin powder, the absorption edges for the each samples of Sn²⁺ self-doped SnO_{2-x} QDs are red-shifted compared to bare SnO₂ QDs. This improved visible-light absorbance of the Sn²⁺ self-doped SnO_{2-x} QDs is beneficial for their photocatalytic applications in visible light range. Figure 13(b) exhibits that the calculated band gaps for SnO_{2-x} (1:2), SnO_{2-x} (1:4), SnO_{2-x} (1:8) and SnO_{2-x} (1:16) are 2.6, 2.65, 2.8 and 2.9 eV, respectively, which are all obviously narrowed relative to that of the bare SnO₂ QDs (3.5 eV). These narrowed band gaps are crucial for the applications of the doped SnO_{2-x} QDs samples in the photodecolorization of organic dyes in visible light illumination, since the bare SnO₂ QDs sample can only respond to ultraviolet light. Compared with the bare SnO₂ QDs, the Sn²⁺ doped SnO_{2-x} QDs (1:4) showed an excellent photocatalytic activity on methyl orange (MO) in visible light illumination. As shown in Figure 13(e), the Sn²⁺ doped SnO_{2-x} QDs (1:4) decompose 99.5% of methyl MO after irradiated by visible light for 15 min. However, the bare SnO₂ QDs show no photocatalytic activity on the degradation of MO at the same experimental conditions. This superior photocatalytic activity in the Sn²⁺ doped SnO_{2-x} QDs sample can be attributed to the self-doping of Sn²⁺ into

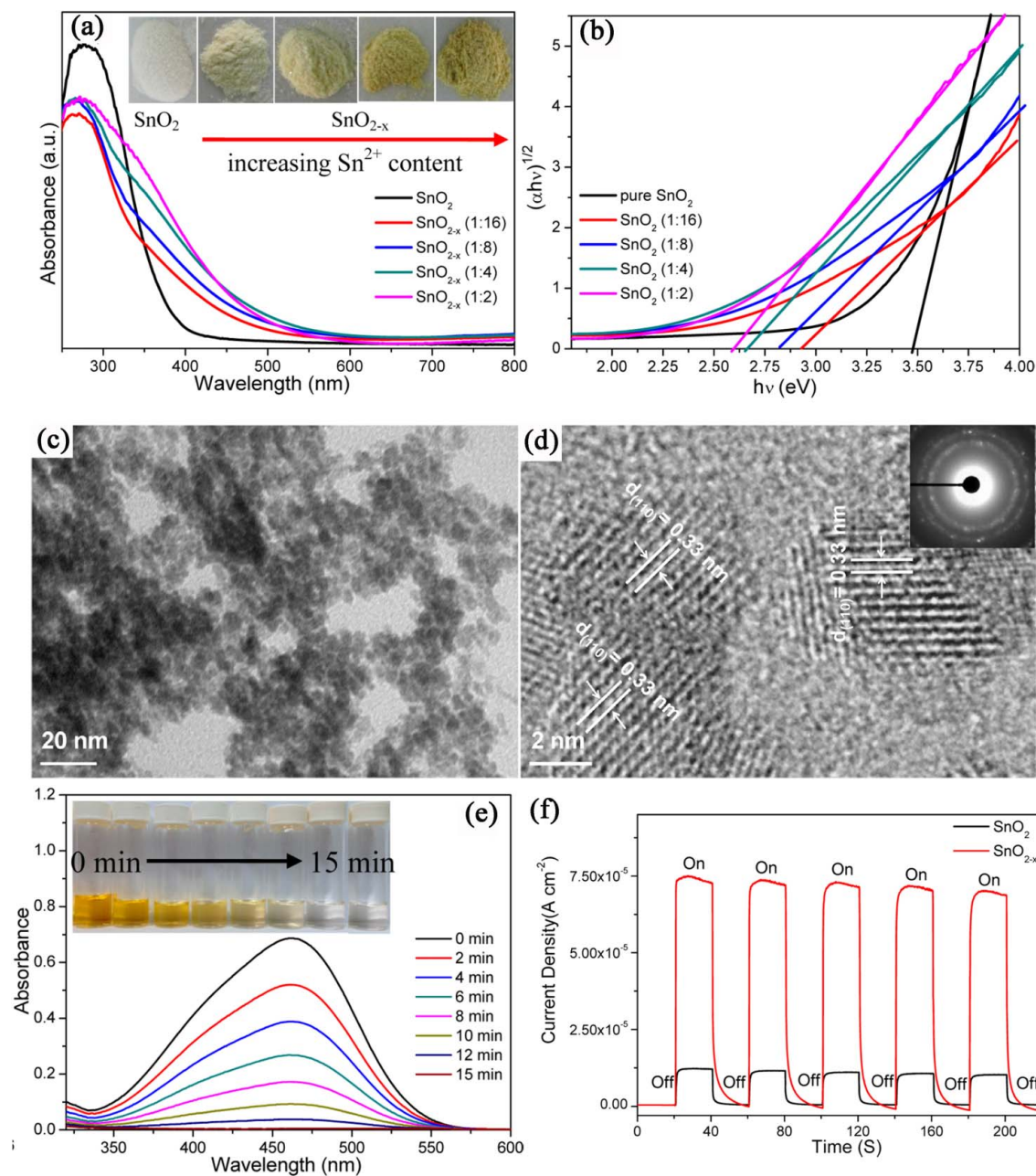


Figure 13. UV-vis diffuse reflectance spectra (a) and band gap evaluation (b) of the SnO₂ QDs and Sn²⁺ self-doped SnO_{2-x} QDs with different molar ratios of Sn/SnCl₄; TEM (c) and HRTEM (d) images of Sn²⁺ self-doped SnO_{2-x} QDs (1:4), the inset in (d) is the corresponding SAED pattern; UV-vis spectra (e) of MO in aqueous Sn²⁺ self-doped SnO_{2-x} QDs (1:4) dispersions as a function of irradiation time with visible light irradiation ($\lambda \geq 400$ nm); Current density response vs time (f) for the Sn²⁺ self-doped SnO_{2-x} (1:4) QDs and SnO₂ QDs under chopped irradiation at a bias potential of 0.5 V vs Ag/AgCl ($\lambda \geq 400$ nm). Reprinted with permission from Ref. [81]. Copyright 2013 American Chemical Society.

the lattice of SnO₂ QDs and accompaniment of oxygen vacancies, which can narrow the band gap and separate the electron-hole pairs in SnO₂ QDs. As is exhibited in the photocurrent response experiments (Figure 13(f)), the photocurrent of the Sn²⁺ doped SnO_{2-x} QDs (1:4) is more stable and higher than that of the bare SnO₂ QDs. This confirms the decrease of the band gap due to the Sn²⁺ doping and oxygen vacancies. Kumar et al. [74] has

studied the photocatalytic properties of heavily F-doped SnO₂ QDs with an average diameter of 5–7 nm. The F-doped SnO₂ QDs displayed much better photocatalytic properties on the degradation of Rhodamine B compared to pure SnO₂ QDs. In the presence of F-doped SnO₂ QDs, the Rhodamine B aqueous solution turns colorless within 20 min after irradiated by UV light. They ascribed this enhancement to the large pore diameter and very high

concentration of oxygen vacancies in SnO_2 produced by F doping.

Planting SnO_2 QDs onto other nanomaterials, e.g. TiO_2 [67,143], silica [121] and poly (ethylene glycol methyl ether) [123], are another efficient way to improve the photocatalytic properties on the degradation of organic pollutant. For example, Lee et al. [67] have compared the photocatalytic performances of undecorated P25 TiO_2 and the P25 TiO_2 decorated with SnO_2 QDs on the degradation toward Rhodamine B. Compared with undecorated P25 TiO_2 , the P25 TiO_2 decorated with SnO_2 QDs with size of about 5.3 nm showed an improved photocatalytic performance on the degradation of toward Rhodamine B under UV light illumination. The apparent reaction rate constant of the P25 TiO_2 planted with SnO_2 QDs (0.055 min^{-1}) is much higher than that of unplanted P25 TiO_2 (0.025 min^{-1}). Through planting of the SnO_2 QDs, the photon-induced charges (namely, electrons and holes) separation in the P25 TiO_2 is much boosted, which is beneficial for the enhancing in the photocatalytic performances. Babu et al. [124] have reported the improved photocatalytic activities of SnO_2 QDs/ $\text{g-C}_3\text{N}_4$ for degradation of MO under illuminated by sunlight. The SnO_2 QDs below 3 nm are well dispersed on $\text{g-C}_3\text{N}_4$ layers. At the same conditions, the photodegradation efficiency of SnO_2 QDs/ $\text{g-C}_3\text{N}_4$ for the degradation of MO is about 94%, which is obviously larger than that of bare SnO_2 QDs (21%). Figure 14 displays the mechanism of SnO_2 QDs/ $\text{g-C}_3\text{N}_4$ with improved photocatalytic activities under illumination sunlight. The CB level of $\text{g-C}_3\text{N}_4$ is negative than that of SnO_2 QDs, therefore, the electrons generated by photons move from CB of $\text{g-C}_3\text{N}_4$ to

that of SnO_2 QDs. The VB level of SnO_2 QDs is positive than that of $\text{g-C}_3\text{N}_4$, therefore, the holes generated by photons still stay at the VB of $\text{g-C}_3\text{N}_4$. So, the electrons and holes generated by photons are efficiently separated and promote the formation of hydroxyl radicals ($\cdot\text{OH}$) and superoxide radical anions ($\cdot\text{O}_2^-$). These $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ are powerful enough to oxidize the toxic MO molecules adsorbed on the surface of SnO_2 QDs/ $\text{g-C}_3\text{N}_4$ to nontoxic H_2O and CO_2 .

4.3. Application in gas sensors

It is important that the working mechanism of the semiconductor oxide gas sensors. Upon exposure to target gases, the resistance of semiconductor oxide may significantly change. This resistance change reflects the gas sensing performance of semiconductor oxides. SnO_2 , as an n-type semiconductor, possesses an electron-depletion layer on the surface due to the chemisorbed oxygen, which lead to the structure with resistive shell and semiconducting core. When the oxygen species with negative charges are adsorbed on the surface of SnO_2 , the resistive shell is oxidized by these oxygen species. The conductivity of SnO_2 increases with the increase of electrons induced by the oxidation reactions. On the contrary, the conductivity of SnO_2 will decrease when it is exposed in reducing gas. In order to boost gas sensing performances, it is of importance to fabricate SnO_2 with large surface areas or large porosity, which can ensure its easy access to target gases.

Some researchers have discovered that the SnO_2 QDs have gas sensing performance [44,144,145]. Ma et al.

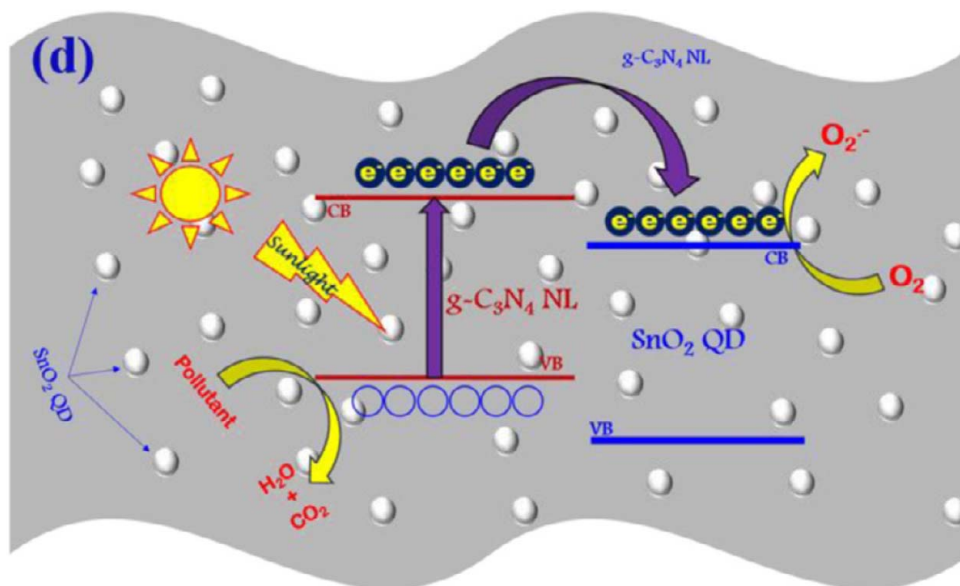


Figure 14. The mechanism of SnO_2 QDs/ $\text{g-C}_3\text{N}_4$ with improved photocatalytic activities. Reprinted with permission from Ref. [124]. Copyright 2018 Elsevier.

[44] have reported the ethanol sensing behavior by using the sensor based on the SnO₂ QDs with a small size of 2.5–4.1 nm. It was found that the sensor response is enhanced obviously with the increase of ethanol concentration from 5 to 100 ppm. The sensor based on 2.5–4.1 nm SnO₂ QDs also showed good repeatability at 100 ppm ethanol concentration. In addition, this sensor showed more superior response and recovery speeds performances than that based on the SnO₂ with size of 20–110 nm. Two factors significantly contribute to this strongly improved gas sensing activities. Firstly, the SnO₂ QDs with smaller size have a higher BET surface area (189.4 m² g⁻¹), which can supply more active sites for sensing reactions. Secondly, the SnO₂ QDs have a small size of 2.5–4.1 nm, which is smaller than the thickness of the electron depletion layer. It has been demonstrated that the gas sensing properties can be enhanced if the size of an active material is smaller than the thickness of the electron depletion layer. He et al. [145] have fabricated the SnO₂ QDs with different size by annealing primal SnO₂ QDs, and studied their gas sensing properties towards ethanol. It was found that the SnO₂ QDs with smaller size exhibited higher sensing activities. Moreover, the SnO₂ QDs with a size of 3.7 nm showed fast response (1 s) and recovery (1 s) toward ethanol. These excellent gas sensing properties may be contributed to the fast adsorption of ethanol on the surface of SnO₂, which is promoted by the small size of the SnO₂ QDs.

It is known that the bare SnO₂ QDs have an undesirable tendency to aggregate because of their ultrasmall size. This agglomeration will seriously abate the specific surface area and thus degrade the gas sensing performances. In order to improve the gas sensing property, it is necessary to conquer the above mentioned drawbacks. The dispersion of SnO₂ QDs can be significantly enhanced by planting them on a conductive and stable matrix. Carbon materials, especially graphene [87,91,92,146] and carbon nanotubes [92], have been used as the matrix to support SnO₂ QDs due to their superior stability and conductivity. Li et al. [92] have planted the SnO₂ QDs with an average size of 2–7 nm into three-dimensional mesoporous graphene aerogel (SnO₂ QDs/rGO-4), and studied the NO₂ gas sensing performance of obtained SnO₂ QDs/rGO-4. At 55°C, the optimal operating temperature, the sensor displayed low detection limit (2 ppm), high sensitivity (0.001 ppm⁻¹), an excellent linearity in a wide NO₂ gas concentration (from 14 to 110 ppm). These excellent sensing performances for NO₂ gas result from the supporting effect of graphene, such as the 3D graphene aerogel, which boost the dispersity of SnO₂ QDs, enhance the electron transfer to target gas as well as improve the gas diffusion. The sensor also showed high sensing selectivity for NO₂ gas

in the presence of other vapors (~110 ppm) at 55°C, including CO, ethanol, phenylcarbinol, ethylene glycol, toluene, acetone, trihalomethanes (THMS) ammonia, and formaldehyde. In addition, due to the flammable nature of liquefied petroleum gas (LPG), some groups have focused on the LPG gas sensing by using SnO₂ QDs/rGO. Mishra et al. [91] have reported the LPG gas sensing behavior of SnO₂ QDs/RGO. This sensor showed a high response of ~92.4% to 500 ppm LPG at temperatures of 250°C, and good selectivity for LPG upon exposure to various volatile gases, including LPG, ammonia, toluene, chloroform, benzene, n-butylacetate, acetone, formic acid, and acetic acid. The response for LPG was 17.8 times higher than that for formic acid. Nemade et al. [146] have investigated the LPG gas sensing behavior of the SnO₂ QDs/RGO at low temperatures. They found that the response increased with the wt% of graphene at room temperature. When exposed to towards 50 ppm LPG during 30 days, the 1.6 wt% graphene/SnO₂ QDs show a fast response time of 16 s, good recovery time of 16 s, and good stability. Liu et al. [104] have studied the gas sensing property of SnO₂ QDs/MWCNTs towards H₂S. The sensor based on SnO₂ QDs/MWCNT was fabricated by spin-coating method as shown in Figure 15(a). As is shown in Figure 15(b), in the SnO₂ QDs/MWCNT, ultrasmall SnO₂ QDs are efficiently attached and covered on MWCNT. As is exhibited in the response curves (Figure 15(c)), the sensor based on SnO₂ QDs/MWCNT was more sensitive to H₂S gas detection than that fabricated from the pristine SnO₂ QDs at the same experiment conditions. For example, at the gas concentration of 100 ppm, the response of the SnO₂ QDs/MWCNT sensor reached to 181, while that of pristine SnO₂ QDs sensor only was 47. The response performances of the SnO₂ QDs/MWCNT gas sensors toward H₂S, NH₃, SO₂, and NO₂ were compared in Figure 15(d). The sensors were highly selective toward H₂S with response value of 108 at 70°C, while with very small response values of 0.28, 4.3 and 1.0 for NO₂, NH₃, and SO₂, respectively. In addition to the excellent access of H₂S molecules to SnO₂ QDs surfaces and the electron transport in MWCNTs, they ascribed this higher response toward H₂S to the synergetic effect between SnO₂ QDs and MWCNTs. The favorable energy band alignment of SnO₂ QDs/MWCNT facilitates the electron transport, thereby boosts the H₂S sensing performance.

4.4. Applications in some other domains

Up to now, the applications of bare SnO₂ QDs and their modified ones mainly focus on the above discussed lithium-ion batteries, photocatalysis and gas sensors domains. However, researchers have also explored their

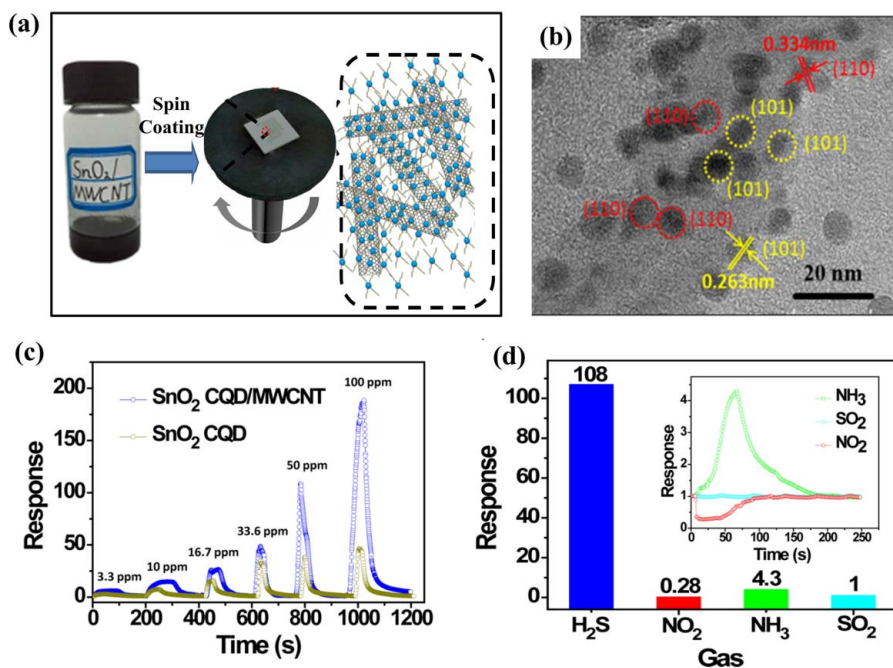


Figure 15. (a) Sensor fabrication from the SnO₂ QDs/MWCNT; (b) HRTEM image of the SnO₂ QDs/MWCNT; (c) Response curves of the sensors fabricated from SnO₂ QDs/MWCNT and pristine SnO₂ QDs upon H₂S exposure/release cycles at 70°C; (d) Selectivity of the SnO₂ QDs/MWCNT gas sensor at 70°C. Reprinted with permission from Ref. [104]. Copyright 2013 American Chemical Society.

applications in some other domains, such as fast adsorption of methylene blue (MB) [121], nano light emitting [125], microwave absorbing [147] and resonance imaging [148]. Dutta et al. [121] have loaded the SnO₂ QDs with size of 3 nm on mesoporous SiO₂ nanoparticles (MSN) and investigated their adsorption performances of MB. The SnO₂ QDs/MSN nanocomposite showed fast adsorption performances of MB adsorbing 100% of MB in 5 min at room temperature. The SnO₂ QDs/MSN nanocomposite also displayed excellent regenerated performance with no obvious loss in adsorption capacity of MB after four cycles. Nath et al. [125] have embedded the SnO₂ QDs with size of 8 nm in polyvinylpyrrolidone (PVP) and explored their light emitting performances as a diodes. At room temperature, the SnO₂ QDs displayed obvious electroluminescence (EL) intensity at 580 nm. Moreover, the EL intensities were linear with applied voltage (up to 20 V). It is believed that the EL originated from the oxygen vacancies in SnO₂ QDs. Lin et al. [147] have anchored the Ni doped SnO₂ QDs with a diameter from 3 to 5 nm on MWCNTs and investigated their microwave absorption properties. It is found that the Ni-doped SnO₂ QDs/MWCNTs with 28.2% (molar percentage) Ni exhibited the best microwave absorbing performances. Dutta et al. [148] have embedded the 3 nm SnO₂ QDs in 30 nm γ -Fe₂O₃ nanoparticles (NPs) and studied their magnetic resonance imaging properties at room temperature. The SnO₂ QDs/ γ -Fe₂O₃ NPs inherit not only the optical properties of SnO₂ QDs but also the

superparamagnetic property derived from γ -Fe₂O₃ NPs. Here, the introduction of superparamagnetic γ -Fe₂O₃ NPs extend the applications of SnO₂ QDs to the magnetic resonance imaging. The SnO₂ QDs/ γ -Fe₂O₃ NPs were used to image hela cells. Laser scanning confocal microscope (LSCM) of hela cells shows the cellular uptake of SnO₂ QDs/ γ -Fe₂O₃ NPs after incubation for 6 h.

5. Conclusions and outlook

In summary, our efforts putted into the SnO₂ QDs have resulted in a rich database for the synthesis, modifications, and applications for SnO₂ QDs over the past years. Many specified ways can be employed to achieve SnO₂ QDs, in which the reaction conditions, including reaction temperature, duration of time and pH influence on the sizes and morphologies. Doping the SnO₂ QDs with extrinsic dopants is an effective way to adjust their physical and chemical properties. Strategies for embedding SnO₂ QDs into graphene have intentionally been summarized. Electron-beam irradiation can create lattice defects or damage in the graphene nanosheets, which is beneficial for their potential applications. The SnO₂ QDs and their modified ones showed improved performances in lithium-ion storage, photochemical catalysis, and gas sensing.

Although significant review has been made in SnO₂ QDs, including their synthesis, modifications, and applications, further efforts are still required in the following

aspects: (1) in order to make their high-volume production more viable, the explore in the synthesis methods of SnO₂ QDs in atmospheric pressure, room temperature is necessary; (2) doping multi-elements into SnO₂ QDs may be an appropriate method to optimize their physical and chemical properties; (3) more efforts should be focused on the improvement in the selectivity of SnO₂ QDs based sensors through further exploring the fundamental sensing mechanisms; (4) the application of SnO₂ QDs and their modified ones can be extended over a much wider fields, such as sodium-ion batteries, dye-sensitized solar cells, photo detection, photocatalytic hydrogen production and electrochemical sensing of heavy metals and organic pollutants. This review will stimulate further development in the synthesis and modification of SnO₂ QDs, as well as further studies on their applications in the environment and energy fields.

Disclosure statement

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