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Abstract

Composite material with uniform size and structure is a critical asset that decides its properties like charge transfer, thermal, photoluminescence, mechanical, etc. and consequently the applications. Here for the first time, we report the concept of flame/combustion at liquid-liquid interface to synthesize in situ, thin film formation of composite consisting of two or more quantum dots. Synthesis of thin films of a composite containing C and SnO₂ QDs having particle sizes below 2 nm was successfully done. As compared to a single quantum dots system, the formed composite showed significantly improved specific capacitance due to the synergistic effect arising from strong interaction between C and SnO₂ QDs. This was confirmed by XPS, UV visible spectroscopy and photoluminescence spectra. Moreover, it was confirmed that even after 1000 charge/discharge cycles, the interaction between C and Sn remained unaltered; indicating significant stability of capacitance. Some of the advantages of this method include one step, eco-friendly process at ambient conditions. The generality of the method was established by synthesizing C-ZnO and C-TiO₂ composite thin film. This new approach can be extended to form many other valuable composite thin films for various applications.

Introduction

Composite materials such as carbon/metal oxide, metal/metal oxide, polymer/metal oxide have wide range of applications in various fields such as catalysis, sensing, electrocatalysis, batteries, bioimaging, solar cells etc.^{1,2} Moreover, if particle sizes of the respective components are in nanometer range, bulk properties of the material get modified which become suitable for contemporary applications.³⁻⁶ Therefore, the methods to obtain solid materials in nanometer sizes are of a sustaining interest of researchers for last four decades.³⁻⁶ In this regard, quantum dots (QDs) are of significant importance as their respective particle sizes are smaller than their respective Bohr radius which then generate exclusive properties.⁷⁻¹⁰

In the recent times, rather than pure single phase materials, composite consisting of QDs of different components are found to be more beneficial for various applications. Such composite formation normally requires more than one step for a single phase end product and hence necessitates an

innovative procedure altogether. Large number of composite materials e.g. TiO₂/SnO₂,¹¹ CdS/TiO₂,¹² TiO₂/GO,¹³ CdS/ZnO¹⁴, CuO/Co_3O_4 ,¹⁵ rGO/Au¹⁶, Ge/TiO₂, PbSe/ZnSe¹⁷ etc., have been synthesized and studied. However synthesizing composite materials suffer from drawbacks such as (i) a chronological addition of different precursors, (ii) higher temperature, (iii) costly instruments, (iv) use of dispersing/capping agents, (v) inert atmospheric conditions by employing N₂/Argon surrounding etc. which render the synthesis cumbersome, multi-step and time consuming. Such methods may be also specific to the product and cannot be generalized, for wide range of applications. Equally important is the reproducibility of thin film formation required for their applications such as supercapacitor. Since nanomaterials/QDs are formed normally in powder form, additional steps also may be needed to fabricate a film.¹⁸

Therefore, the development of a rapid, one-pot, eco-friendly, low cost, generalized method of QDs composite thin film formation involving minimum number of steps is still required. Previously, we have reported a method to make thin films of QDs of various singular semiconductors.¹⁰ In the present work we describe for the first time, one-pot method of simultaneous synthesis of a thin film of the composite comprising QDs of carbon and SnO₂, at liquid-liquid interface. Compared to our previous work on single component QDs, this new route is more efficient and applicable to a wider variety of simultaneous synthesis of more than single component QDs. Other, important advantages of this method are; (i)

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simultaneous synthesis of QDs of both C and SnO_2 at room temperature, (ii) the QDs formed on the surface can be transformed into thin film on a suitable substrate, (iii) possibility to tailor the composition of various components in the final composite, (iv) deposited composite is found to have good adherence to the substrate without the use of binders or additives, (iv) eco-friendly, in-situ, low cost synthesis without requiring harsh post treatment with better control over parameters like film thickness etc. The generality of this method of QDs was established by synthesizing C-ZnO and C-TiO₂ composite thin films. The end-product formed following our method showed properties suitable for one of the most sought after application for supercapacitor.

Experimental

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The materials used in the present work were all of analytical grade. Anthracene ($C_{14}H_{10}$, 99%), Tin (II) chloride dihydrate (SnCl₂.2H₂O, 98%), hydrochloric acid (HCl), petrol (Sulfur free), zinc acetylacetonate (Zn($C_5H_7O_2$)₂.xH₂O 99%), ammonium titanium oxalate ((NH₄)₂TiO(C_2O_4)₂.H₂O 99%) were purchased from Sigma-Aldrich and castor oil from local market. For the synthesis of QDs films, all the chemicals were used as received, without further purification. Throughout all the experiments double-distilled, deionized water was used. The substrates used are glass slides, quartz plates and silicon wafers. Glass and quartz substrates were cleaned by pre-treating them with freshly prepared piranha solution ($H_2SO_4/H_2O_2 = 70:30$, v/v) at $70^{\circ}C$ for 15 min, thoroughly rinsed with deionized water and dried in nitrogen flow.

Synthesis of Quantum dots thin film

Synthesis of SnO₂ QDs thin films

To synthesize SnO₂ QDs, SnCl₂.2H₂O was used as a precursor. Petrol (sulfur free) was used as a fuel for the combustion of SnCl₂.2H₂O for the formation of SnO₂. The experimental procedure is essentially the same as given earlier (Scheme S1).¹⁰

In a typical procedure, 10⁻⁴ M solution of SnCl₂.2H₂O is formed by dissolving tin (II) chloride in distilled water. A whitish solution was formed. To this solution, few drops of HCl were added until a clear solution was formed. This solution was placed in a Teflon tray (15 X 15 X 2 cm) in such a way that a meniscus formed above the edges of the tray. The surface of the solution was cleaned by sweeping the Teflon barrier to avoid any dust contamination on the surface. Surface of subphase was divided into two compartments by fixing a teflon thread barrier on the edges of the tray. In one of the compartments, petrol was allowed to spread on the subphase with the help of a micro-syringe. In this process, stretching of the thread formed the uniform layer of petrol which was immediately set on fire. During this process, sufficient heat was generated to form SnO_2 at the interface. The formed product was then compressed laterally by spreading a drop of castor oil on the surface of the subphase in the other compartment. The as-formed compressed film on the surface was transferred on to suitable substrate by immersing the substrate vertically in the solution at a constant rate of 0.5 cm/min and lifting it vertically at the same rate (Blodgett technique). The operation was repeated several times to get the desired film thickness.

Synthesis of C QDs thin films

To prepare carbon QDs, 10^{-3} M anthracene, 1.8 mg of anthracene was dissolved in 1 ml alcohol. A clear solution was formed in which 9 ml petrol was added. From this solution, 10^{-4} M anthracene was prepared by adding proper amount of alcohol/petrol. This solution was spread on the surface of the distilled water and immediately set on fire. The combustion of anthracene led to the formation of thin layer of carbon on the surface of the subphase. In this way, carbon QDs was formed at the surface. To form a compact film, same procedure was followed as used to make SnO₂ films.

Synthesis of C-SnO₂ QDs thin films

For the preparation of carbon-SnO₂ QDs composite thin films, 10^{-4} M solution of SnCl₂.2H₂O was used as a subphase. A precursor solution of carbon, 10^{-4} M of anthracene in petrol which was spread on the subphase and subsequently followed the same procedure as described above to obtain a composite thin film.

Synthesis of C-ZnO, C-TiO₂ QDs thin films

For the preparation of C-ZnO and C-TiO₂ QDs composite thin films, 10^{-4} M solutions of Zinc acetyl acetonate and Ammonium titanium oxalate were used as a subphases respectively; and the same procedure was followed as described for C-SnO₂ QDs composite thin film formation.

Characterization

The size distribution and morphologies of as-prepared products were examined by transmission electron microscopy (TEM, FEI Tecnai F-20) at an acceleration voltage of 200 kV. High resolution transmission electron microscopy (HRTEM, FEI Tecnai F-30) was used at an acceleration voltage of 300 kV. Specimens for TEM and HRTEM analysis, were prepared on carbon coated copper grids by depositing the respective film by the above described procedure by dipping it twice in the solution followed by drying at room temperature. The electron diffraction facility was employed for assessment of the structure and the phases present. The absorption in the UVvis. region was studied (JASCO dual beam spectrophotometer (JASCO V-570 operated at a resolution of 1 nm). The chemical analysis of the film was done by surface characterization by XPS analysis (ESCA-3000, VG Scientific Ltd, UK) with a base pressure of lower than 1.0×10^{-9} Pa. Mg K α radiation (1253.6 eV) was used as a X-ray source and operated at 150 W. The peak shift due to charging was corrected using the C1s level at 285 eV as an internal standard. The photoluminescence film were recorded on Fluorescence spectra of spectrophotometer (F-2500) using UV blocking filters to cut down the scattered light from the sample. Fourier transform infrared spectra (FTIR) were acquired with Perkin Elmer spectrum.

Electrochemical Properties of SnO_2 , C and C- SnO_2 QDs thin film

Thin film synthesized by combustion at liquid-liquid interface was studied on an Autolab PGSTAT 30 (Ecochemie) electrochemical workstation using cyclic voltammetry, chronopotentiometry and electrochemical impedance test. Published on 30 March 2018. Downloaded by Stockholms Universitet on 31/03/2018 06:16:19

The measurement was performed by configuring the samples into a two electrodes system, where the sample used as the working electrode as well as counter electrode. The working electrodes were prepared as follows: C QDs or SnO₂ QDs or C-SnO₂ QDs composite at the interface of the liquid was collected on the FTO and used as it is without the use of any binder or further processing. The electrolyte used was 1 M Na₂SO₄ aqueous solution at room temperature. The electrochemical properties and capacitive behaviour of the supercapacitor electrodes were evaluated by cyclic voltammetry (CV) and galvanostatic charge–discharge (CD).

The specific capacitance values of the samples are calculated from the CV curves using following equation: 19

Where, Csp is the specific capacitance in farads per gram (Fg⁻¹), m is the active mass of the electrode material (g) obtained from quartz crystal microbalance (QCM-200), I is the response current density (Ag⁻¹) and v is the potential scan rate in (Vs⁻¹) and V is potential (V). The specific capacitance, C (Fg⁻¹), of the electrode material was calculated from the galvanostatic charge-discharge according to the following equation

$$C_{sp} = \frac{(1 \times \Delta t)}{(\Delta E \times m)} \dots \dots 2$$

Where, m is the active mass of the electrode material obtained from quartz crystal microbalance (QCM-200) (10.4, 10.5 and 11.5 μ g for SnO₂, C and C-SnO₂ composite respectively), i is the response current density (Ag⁻¹), Δ t is discharge time (s), Δ E is a voltage difference in (V).

Results and Discussion

The growth mechanism of QDs is normally controlled by thermodynamics wherein lowering of surface energy of particles formed becomes more important. However, in the present method, growth of particles by this method is prevented by the surface tension forces at the interface which controls direct contact of particles. Also, practically the particle formation process takes place at room temperature with insufficient energy for growth of the particles in spite of small particles' active nature. Thus, kinetics must be considered to explain control of growth/size of particles. Exactly at this the present method differs from iuncture. other combustion/flame methods. Most of the methods in the literature allow sufficient time for reaction to go to its completion which allows changes in the characteristics of particle morphology and growth of particle due to agglomeration. As against this in the present method, although reaction leads to end products, the time of reaction is so small (few seconds) that kinetic effect on particle morphology of end products, namely, growth in sizes/agglomeration is restricted. Moreover, it occurs by the inherent parameters (very small time span) of the method and therefore it is

independent of the reaction/s, provided it takes place spontaneously at the temperature developed by the flame/combustion and within the time span of combustion. Also, the particle characteristic morphology is independent of precursors used, its concentration, small changes in the ratio of precursor to fuel, number of simultaneous reactions, etc.

The thin films of QDs of SnO₂, C and composite C-SnO₂ prepared by flame/combustion at liquid-liquid interface were characterized by XRD analysis. A multilayered film did not show XRD pattern. The absence of XRD signal may be due to the very small particle size and insufficient material concentration of the samples.²⁰

Further, each sample was examined by XPS analysis to know elemental composition and purity of the material (Fig. 1). Fig. 1a and Table S1 indicate the absence of peaks other than expected elements after the combustion of precursors. It was obvious to expect carbon formation from organic precursors and metal compounds leading to the formation of respective oxides by high temperature combustion process. The elemental mapping of the C, SnO₂ and C-SnO₂ QDs composites, images are shown in Fig. S1, confirming this conclusion.



Fig. 1 XPS spectra of a) survey scan b) Sn 3d c and d) deconvoluted peak of C1s for C QDs and C-SnO₂ composite.

The high-resolution XPS spectra of SnO₂ and C-SnO₂ composites showed two distinct peaks at 486.5 and 495 eV attributed to Sn 3d_{5/2} and Sn 3d_{3/2}, respectively, arising due to spin-orbit splitting (Fig. 1b). The peak positions were in agreement with the expected spin orbit separation of 8.5 eV assignable to Sn⁺⁴, a formal oxidation state of Sn.²¹ However, a slight shift in the peak for the composite was observed for Sn 3d; which could be assigned to the interaction between C and SnO₂. The high resolution spectra of C 1s (Fig. 1c) showed four peaks at 284.2, 285.5, 286.5 and 288.2 eV which are attributed to C-C sp², C-C sp³, C-O and C=O species, respectively present in the carbon QDs.²² The graphitic carbon (sp²) might be formed during carbonization of aromatic carbon precursor namely, anthracene wherein large number of sp² carbon bonds exist in the precursor itself; so that no rearrangement in the product was needed at the expense of high energy. This

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may be seen on the background of reported carbonization products formed in non-aromatic carbon precursor such as sucrose.^{23,24} This outcome is important as graphitic carbon provides higher electronic conductivity to a composite which is vital for various relevant applications.²⁵ Thus, the choice of aromatic precursor for the formation of C QDs and composite based on it turned out to be the most appropriate one. Two other peaks at 286.5 and 288.2 eV were assigned to the presence of COOH and C=O groups of C QDs respectively. The presence of such functional groups on 'C' based nanomaterials is reported in the literature.²⁶ In the present case, where the reaction medium was water and reaction time was very short so as to eliminate 'C' completely as CO₂.

The deconvolution of 'C' peak revealed the intricacies of the functionalization of products. A peak at 282.3 eV in the composite was a newly formed peak which could be assigned to metal-carbon bond formation (Fig. 1c).²⁷ Simultaneously, C=C i.e. C sp² bond formation decreased while, C-C bond formation seemed to rise. This may be accounted for by considering that many double bonds might have been transformed during the formation of Sn-O-C or/and Sn-C bonds. This was supported by the peak observed at 282.3 eV, attributable to M-C bond (Fig. 1c).²⁷ Moreover, it was observed that during composite formation, the area under intensity curve of C=O bond gradually deceased as compared to that observed for its counterpart in C QDs. Two important inferences drawn from these observations were, 1) Composite with less C sp² contribution in bonding, and 2) an interaction between metal and carbon; directly or through oxygen.



Fig. 2 FTIR spectra for Anthracene, C, ${\rm SnO}_2$ and ${\rm C-SnO}_2$ composite.

Fourier transform infrared (FTIR) spectrum for the $C-SnO_2$ composite sample was compared with the corresponding spectra of C QDs, SnO_2 QDs and pure anthracene as presented in Fig. 2. Pure anthracene showed more number of absorption peaks due to the various sp^2 and sp^3 stretching vibrations in benzene ring. The peaks around 1625-1575 cm⁻¹ and 1525-1475 cm⁻¹ were attributed to the C=C stretching in benzene ring. The peak in anthracene around 3554 cm⁻¹ for aromatic -H bond disappeared after its combustion. Moreover, the

intensity of most of the peaks decreased considerably to the extent that some peaks vanished. This was obvious as during the carbonization process, most of the anthracene structure collapsed. The end product was expected to be a solid carbon having mostly C-C bonds in its structure. However, the reaction time was small to restrict the growth resulting in bigger carbon particles. Thus, the end product was the formation of 'C' QDs. The presence of peaks around 2924 and 2846 cm⁻¹ were assigned to C-H stretching, 1589 cm⁻¹ for C=C stretching and the peak around 1571 cm⁻¹ further confirmed the presence of the sp^2 and sp^3 C in C QDs. Since the reaction takes place at liquid-liquid interface, some C-OH or C-OO⁻ type bonds are expected to be formed on the surface of QDs which also need to be considered. The presence of C=O stretching around 1743 cm⁻¹ in C and C-SnO₂ composite confirmed that some of the C QDs were oxidized during the formation. These results were consistent with the XPS studies. The peak at 575 and 663 cm⁻¹ were assigned to the O-Sn-O and Sn-O vibrational modes, respectively; which further confirmed the presence of SnO_2 .

UV- visible absorption spectra of SnO₂, C and C-SnO₂ QDs composite thin films on quartz plate are shown in Fig. 3. SnO₂ QDs showed the peak at around 225 nm, which was at much lower wavelength than the reported optical absorption edge for bulk SnO_2 (~344 nm, 3.6 eV).²⁸ This blue shift could be ascribed to the smaller size of the particles in the film.²⁹ C QDs showed a broad absorption peak from 270 to 300 nm, which was similar to that of the typical C QDs.³⁰ The absorption peak at 270 nm corresponded to the $\pi \rightarrow \pi^*$ transition of the aromatic sp² hybrid orbital and small peak around 300 nm corresponded to $n \rightarrow \pi^*$ transitions of the sp³ hybrid orbital, respectively.^{31,32} For the composite $C-SnO_2$ QDs thin film, a clear shift in the peak was observed. A shift in peak of composite suggests that there was an interaction between C QDs with SnO₂. Moreover, from the graph it was clear that the intensity of the peak at ~300 nm increased in case of composite film which confirmed increase in concentration of sp^3 C in the composite.²²⁻²⁴ These results are consistent with XPS and IR. All these results confirmed that there was an interaction between C and SnO₂ QDs.



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The optical band gap was calculated using the Kubelka–Munk equation. From Fig. S2, it can be seen that the band gaps for the C, SnO_2 , C- SnO_2 QDs composite and SnO_2 bulk were about 5.7, 4.24, 4.14, 4.76, and 3.67 eV respectively, which was higher than the respective bulk materials. It is not surprising that we observed two absorption band edges for composite, which is similar to observed and explained by Umarao et al. for TiO₂ GO composite.³³

The size distribution of the particles in the samples under consideration was examined by using transmission electron microscopy (Fig. 4). Typical TEM images for SnO₂, C and C-SnO₂ QDs composite showed the presence of un-agglomerated, spherical shaped, distinct nanoparticles of C QDs and SnO₂ with a size below 1.5 nm (bottom inset of histogram). In the TEM of the composite sample, the darker particles represent SnO₂ and the lighter particle C QDs. Excellent dispersion of C QDs and SnO₂ QDs confirmed that agglomeration/ aggregation/growth of particles was restricted during the synthesis process. This observation was important as no dispersion or capping agents were employed in the process. Two fundamental causes of preventing the particle growth appear to be 1) liquid-liquid interface of few nanometer widths imposed confinement to the reaction zone, and 2) very fast reaction time of few seconds. The selected area electron diffraction (SAED) pattern of the film formed by two dips for SnO₂, C and C- SnO₂ QDs composite films on copper grid are shown at the bottom inset of each Fig. S3. SnO₂ QDs show the distinct spots on ring pattern which were indexed to tetragonal SnO₂ structure (JCPDS Card No. 77-0452). However, C QDs shows ring pattern and C-SnO₂ showed ring pattern with spots indexed to tetragonal SnO₂ structure (JCPDS Card No. 77-0452).



Fig. 4 Low magnification TEM image of SnO_2 QDs (a), C QDs (b) and C-SnO₂ QDs composite (c); the insets shows particle size histogram of respective sample (bottom).

The high-resolution TEM (HRTEM) provided as insets of Fig. S3 for SnO₂ and C-SnO₂ QDs composite exhibited clear lattice fringes with a *d*-spacing of 0.26 nm corresponding to (101) lattice planes of SnO₂. The lattice fringe spacing (in C and C-SnO₂ composite QDs) was 0.24 nm corresponding to the inplane lattice constant in sp² carbon or graphene like structures.³⁴ The SnO₂ QDs and C QDs were found to be evenly distributed on the substrate. During the formation of C-SnO₂ QDs composite, it was proposed that chemical/physical bonds formed between SnO2 and C would lead to the formation of interface between them. This tight coupling would be favorable for the charge transfer between C and SnO₂ Moreover, it is likely to promote the separation of electronhole pairs formed by exciting the semiconductor which is important for catalytic, sensor and other applications. All the above characterizations confirmed that C- SnO₂ is not a physical mixture of two separate phases of C and SnO₂ but a real composite.

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The weight fraction of C QDs in C-SnO₂ QDs composite was determined by themogravimetric analysis (TGA) (Fig. S4). The TGA curve shows a total weight loss of 32.4% at 400°C due to the combustion of carbon component in composite. After reaching 800°C, the total fraction of SnO₂ content in the composite is calculated to be 67.6%.

Further, we could also show that the developed method was potentially useful for the applications. It occurred to us that conducting C QDs and SnO₂ having high capacitance can form a composite which can be an electrode for value-added energy storage devices. Therefore, the capacitive performance of the as-prepared SnO₂, C and C-SnO₂ composite QDs thin films on conducting glass was evaluated as an electrode material by using standard cyclic voltammetry (CV) and charge-discharge in two-electrode system. The CV measurements were done in 1 M Na_2SO_4 as an electrolyte. During fabrication of the electrode, no binder material like Nafion was used, which is an advantage of the procedural part of present method of depositing film on conducting glass and using it as working electrode. The galvanostatic charge-discharge technique was used to check the stability and recycling of electrodes. Figs. 5 a, b and c shows the cyclic voltammogram (CV) of SnO₂, C and C- SnO₂ QDs composite thin films at various scan rates ranging from 20 to 200 mVs⁻¹. The voltammogram of the C-SnO₂ electrode was just about an ideal rectangle with a greater area and better shape symmetrical shape than voltammogram of pure carbon and SnO₂ thin films respectively. This indicated the enhanced capacitance of the hybrid matrix. Moreover, the shape at high scan rates were similar to those at low scan rate, indicating better energy storage performance of the C-SnO₂ composite with excellent ionic and electronic transport concerned with electrode material.³⁵

The specific capacitance (Csp) of C, SnO_2 and $C-SnO_2$ QDs calculated from the CV curves using equation 1, is shown in (Table S2 in ESI⁺).¹⁹ The calculated Csp for the C, SnO_2 and C- SnO_2 QDs thin films were 185, 220 and 576 Fg⁻¹ at the scan rate of 20 mVs⁻¹ and 138, 159 and 547 Fg⁻¹ at the scan rate of 200 mVs⁻¹, respectively. Fig. 5d and Table S2, showed clearly

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Fig. 5 Typical CV curves of SnO_2 QDs (a), C QDs (b) and C- SnO_2 QDs composite (c) at different scan rates 20 to 200 mVs⁻¹. (d) Specific capacitance values calculated from eqn. (1) for SnO_2 , C, and C- SnO_2 composite as a function of scan rates mVs⁻¹.

Moreover, it was clearly seen that as the scan rate increased, the specific capacitance (Csp) decreased. The decreasing Csp was observed due to part inaccessibility of electrode surface for holding charge at high charging–discharging rates. This might arise due to the presence of secluded active sites that could not sustain the higher frequency of redox transitions.³⁶



Fig. 6 Typical galvanostatic charge discharge profile of SnO_2 QDs (a), CQDs (b) and C-SnO₂ QDs composite (c) device at different current densities, (d) the specific capacitance of SnO_2 , C, and C-SnO₂ QDs composite as a function of current density.

The specific capacitance of the composite was 576–547 Fg⁻¹, nearly three times higher than that of the carbon QDs (185 Fg⁻¹) and almost two times higher than that of pure SnO_2 (220 Fg⁻¹)

¹). The capacitance (576–547 Fg^{-1}) obtained in the present study is considerably higher than those of Sn-based carbon hybrid composites reported earlier (Table 1). These results indicate that the potential of the composite C-SnO₂ QDs thin film can offer high performance supercapacitors. The percent retention of Csp in the case of composite is 95 which were higher than the singular components of the hybrid namely, C and SnO₂.

The galvanostatic charge/discharge curves of the QDs thin film of the samples measured at different current densities are shown in Fig. 6. A symmetrical charge/discharge characteristics and linear voltage vs. time profiles were observed which represent the excellent capacitive characteristics of these supercapacitors. The charge–discharge curves (Figs. 6 a to c) were nearly symmetric, revealing a good capacitive behavior. In addition, no voltage drop was observed indicating that the electrode had low internal resistance. Csp values calculated on the basis of charge/discharge results for SnO₂, at 20 and 100 μ A were 225 and 167 Fg⁻¹, respectively. Moreover, the hybrid electrode showed high values of 578 Fg⁻¹ to 552 Fg⁻¹ at the high current densities from 20 μ A to 100 μ A, (Table S3, ESI⁺). The observed Csp from the calculations of both CV and charge/discharge study were found to be consistent.

Table 1 Comparison of the electrochemical performance of the Carbon, SnO_2 and C-SnO₂ composites.

Electrode	Specific capacitance	Reference and
Materials	(Fg ⁻¹)	year
C QDs	185.0	Present work
SnO ₂ QDs	220.0	Present work
C-SnO ₂ (QDs)	576.0	Present work
composite film		
SnO ₂ QDs	241	2014 ³⁷
SnO ₂ thin film	119	2016 ³⁸
C QDs	106	2016 ³⁹
SnO ₂ @C	247	2015 ⁴⁰
SnO₂@C	420	2014 ⁴¹

From Table 1, a significant value addition was observed by making $C-SnO_2$ QDs composite in terms of higher capacitance at high current density with good retention over the individual components of the composite.



Fig. 7 Electrochemical impedance spectroscopy for SnO₂, C and C-SnO₂ QDs composite.

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Electrochemical impedance (EIS) spectroscopy gives information regarding the internal resistance of an electrode material as well as the resistance between the electrode and the electrolyte (Fig. 7). The spectra were analyzed using Nyquist plots. The solution resistance (Rs) for the C, SnO₂ and C-SnO₂ QDs composite was found to be 75.4, 60.3 and 47.6 Ω , respectively. The charge transfer resistance (Rct) for SnO₂, C, and C-SnO₂ QDs composite was measured to be 11.3, 15.4 and 8.03 Ω , respectively. The equivalent series resistance (R_e) can be obtained from the X-intercept of the Nyquist plots, which is a combined resistance comprising ionic resistance of electrolyte, contact resistance of active material/current collector interface and intrinsic resistance of substrate. This indicates that the C-SnO₂ hybrid electrode possessed low charge transfer impedance, and therefore, the composite showed higher capacitance than shown by the SnO₂ and C electrode respectively. These results are consistent with those obtained by the CV measurements.



Fig. 8 Stability performances for SnO_2 , C and C- SnO_2 QDs composite.

The stability of the performance of the composite was also studied up to 5000 cycles of charge–discharge processes (Fig. 8) which showed the retention of Csp up to 96% at high current density of 20 μ A. The higher percentage of SnO₂ in composite ensured a higher reversible capacity for composite.⁴² Also it can be seen that in case of C-SnO₂ composite, the specific capacitance decreased only by 4% at current density 20 μ A. Thus, it was relatively more stable at higher current density as well as at higher number of cycles, and can be useful for specific applications.

To understand the encouraging electrochemical performance of C-SnO₂ QDs composites, their microstructure and morphology was also examined by TEM after 1000 charge/discharge cycles. The TEM image (Fig. S5) clearly showed that the distinct particles of C and SnO₂ QDs were visible even after electrochemical cycling. However, some increase in particle size was also observed, which might be responsible for the capacitance loss during cycling.⁴³ Nevertheless, the size of most of the particles was found to be less than 2.5 nm (histogram shown as inset of Fig. S5). The stability of the composite after cycling was further confirmed by UV-visible, FTIR and XPS studies. The UV-visible and FTIR spectra of C-SnO₂ composites after charge/discharge cycle clearly showed that the peaks were unaltered (Fig. S6). However, slight broad range of peak from 230 to 350 nm in UV-visible spectrum was seen, which might be due to the presence of broad particle size range. XPS analysis in Fig. S7 and Table S1 clearly showed the presence of peaks after charge/discharge cycle of C-SnO₂ composites. The peaks at 282.1, 283.6, 284.7, 286.5 and 287.8 eV of deconvoluted C 1s (Fig. S7 (a)) spectrum could be assigned to metal-carbon, C-C sp³, C=C sp² and carbon bonded to -OH and -COOH groups, respectively. The presence of peak M-C after charge/discharge cycles confirmed the strong interaction between C and Sn (Fig. S7 b) and thus confirmed the stability of the composite.

The enhanced electrochemical performance of the composite could be attributed to the following features.

i) The small size of component (QDs/OD) resulted in high surface area, shorter diffusion path and lower charge-transfer resistance. These features improved the access of the electrolyte and enhanced the capacitance of the material. Therefore, the electrode easily absorbed the electrolyte cations (Na⁺) on the surface from the electrode:⁴⁴

 $(SnO_2)_{surface} + Na^+ + e^- \leftrightarrow (SnO_2 - Na^+)_{surface}$

This provides more charge storage and easy access of $SO_3^{2^-}$. Therefore, both Na⁺ and $SO_3^{2^-}$ from the electrolyte are fully utilized in SnO₂ electrode.

ii) The composite prepared by our method offers more stable, binder free (e.g. Nafion etc.) electrode for the capacitance application than most of the methods reported earlier (Table 1). This method is also useful to synthesize other composites as shown by the synthesis of C-ZnO and C-TiO₂ composites for which the detail characterization is given in supporting information (Figs. S8-S10).

Conclusions

In summary, simultaneous synthesis of two materials in QD form viz. C QDs and SnO₂/ZnO/TiO₂ QDs for the first time, was achieved by an easy, low cost, eco-friendly, single step flame/combustion at liquid-liquid interface without using any surfactant. It was shown that a thin film of composite was formed during the synthesis and the HRTEM of C-SnO₂ composite showed uniformly well dispersed C and SnO₂ QDs on the substrate with particle size < 2 nm. UV-visible, FTIR and XPS characterization evidenced the presence of sp^2 and sp^3 form of C in C QDs. Moreover, systematic investigation by XPS, FTIR, TEM of C, SnO₂ and C-SnO₂ QDs composite showed the successive interaction between C and SnO₂ QDs. An electrode of C-SnO₂ composite exhibited high capacity, excellent rate capability, and long cycle life revealed from its CV studies. The maximum specific capacitance for the C-SnO₂ QDs composite film achieved was 576 Fg^{-1} at a scan rate of 20 mVs^{-1} and for SnO_2 and bare carbon; it was only 220 and 185 Fg^{-1} , respectively. TEM image of the composite after 1000 charge/discharge cycles showed distinct particles of both carbon and SnO₂. Moreover, UV-visible, FTIR and XPS study of the composite after electrochemical measurements showed

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the strong interactions between carbon and tin establishing the excellent stability at higher current density as well as at higher number of cycles. The general applicability of our methodology was proven for the formation of few other composites of C-ZnO and C-TiO₂.

Conflicts of interest

There are no conflicts to declare.

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TOC/ Graphical Abstract

Composite thin film of simultaneously formed carbon and SnO₂ QDs for supercapacitance application

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A simple, one step, low cost combustion method for simultaneous formation of two/more components QDs thin film