



# Hollow carbon sphere/metal oxide nanocomposites anodes for lithium-ion batteries



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## ABSTRACT

HCS (Hollow carbon spheres) covered with metal oxide nanoparticles (SnO<sub>2</sub> and MnO<sub>2</sub>, respectively) were successfully synthesized and investigated regarding their potential as anode materials for lithium-ion batteries. Raman spectroscopy shows a high degree of graphitization for the HCS host structure. The mesoporous nature of the nanocomposites is confirmed by Brunauer–Emmett–Teller analysis. For both metal oxides under study, the metal oxide functionalization of HCS yields a significant increase of electrochemical performance. The charge capacity of HCS/SnO<sub>2</sub> is 370 mA hg<sup>-1</sup> after 45 cycles (266 mA hg<sup>-1</sup> in HCS/MnO<sub>2</sub>) which clearly exceeds the value of 188 mA hg<sup>-1</sup> in pristine HCS. Remarkably, the data imply excellent long term cycling stability after 100 cycles in both cases. The results hence show that mesoporous HCS/metal oxide nanocomposites enable exploiting the potential of metal oxide anode materials in Lithium-ion batteries by providing a HCS host structure which is both conductive and stable enough to accommodate big volume change effects.

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## 1. Introduction

Rechargeable LIBs (Li-ion batteries) are currently the dominant energy storage technology for portable electronic devices. Despite their enormous commercial success in this field, for more demanding high power and high energy applications new materials have to be developed which enable significantly improved specific energy densities, capacities, and power rates in combination with long life time and cycling stability [1–3]. In case of the anodes, the most commonly used reference is graphite, which is a low-cost material with good cyclic stability but rather low electrochemical potential. Its limited reversible intercalation capacity (theoretically 372 mA hg<sup>-1</sup>) and poor rate performance hinder its application in high-performance LIBs [4–6]. Accordingly, extensive efforts have been done to develop new high-performance anode materials for next-generation LIBs. One promising approach aims at utilizing redox-active metal oxides such as Fe<sub>2</sub>O<sub>3</sub> [7], SnO<sub>2</sub> [8], and Co<sub>3</sub>O<sub>4</sub> [9] which exhibit very high theoretical specific capacities as they are

capable of converting up to 6 Li per formula unit [10–13]. Despite significant progress, however, metal oxide-based anodes do not yet reach their full potential which is mainly caused by their low conductivity and by large volume changes during dis-/charge cycling [14,15]. Hence, during electrochemical cycling, metal oxides typically break into small metal clusters, resulting in a large volume expansion and a loss of reversible capacity [16,17].

A materials-science based answer to these issues applies nanoscaled metal oxides embedded into conductive carbon structures. Such nanocomposites have indeed emerged as a promising method towards high-performance anode materials [18,19]. On the one hand, downscaling the active material yields short transport lengths for both, electrons and Li-ions, higher specific surface areas, and better accommodation of strain upon Li insertion/extraction [20,21]. To date, such composites are commonly prepared by simply coating pyrolytic carbon species on nanoscaled oxides [22,23]. However, while increasing the overall electronic conductivity of the materials, pyrolytic carbon does provide an effective host structure for accommodating the strain due to large volume expansion and such materials hence offer only limited cycling stability. Alternatively, creating composites with porous characteristics has been proposed to overcome these limitations [24–27]. Such composites can be achieved either by preparing hybrid composites or by producing nanostructured composites. Here, we report a facile

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impregnation method [28] to synthesize HCS (hollow carbon spheres) covered with SnO<sub>2</sub> and MnO<sub>2</sub> nanoparticles as advanced anode material for high performance LIBs (see Fig. 1). The resulting nanocomposite materials displays reversible capacities larger than pristine HCS as well as good cycling performance.

## 2. Experimental section

Synthesis of solid SiO<sub>2</sub> nanospheres (SiO<sub>2</sub>). SiO<sub>2</sub> spheres were prepared in a modified Stober process [29]. TEOS (Tetraethyl orthosilicate) (1.5 ml) was added to a mixture of ethanol (50 ml) and concentrated ammonia (28 wt%, 2.5 ml). Then the solution was stirred for 24 h. Afterwards, the product was separated by filtration, washed with ethanol and dried [30].

Synthesis of mesoporous silica spheres (SiO<sub>2</sub>@m-SiO<sub>2</sub>). In a typical synthesis, 100 mg of SiO<sub>2</sub> was dispersed in a solution containing CTAB (cetyltrimethylammonium bromide 0.8 g), deionized water, concentrated ammonia (28 wt%), and 60 ml ethanol. The suspension was sonicated and stirred for 60 min, then 1.43 ml of TEOS was added dropwise while stirring. The suspension was stirred for another 6 h, and afterwards, the product was filtered, washed with ethanol and water several times. Finally, the sample was dried in air at 100 °C for 24 h.

Carbonization of SiO<sub>2</sub>@m-SiO<sub>2</sub> and removal of silica (HCS). The dried SiO<sub>2</sub>@m-SiO<sub>2</sub>-CTAB spheres were used as a template to prepare the hollow mesoporous carbon spheres using CVD (chemical vapor deposition). The silica spheres were placed in an alumina boat and put into a tube furnace. Argon and ethylene were introduced at a flow rate of 100 and 30 sccm, respectively. The temperature was raised to 800 °C, and the CVD reaction time was 3 h. Afterwards, the resulting SiO<sub>2</sub>@m-SiO<sub>2</sub>-C spheres were thoroughly washed with hydrofluoric acid to remove the silica components and finally hollow carbon spheres (HCS) were obtained.

Functionalization of HCS with metal oxide nanoparticles. Two samples of HCS modified by metal oxide nanoparticles (HCS/SnO<sub>2</sub> and HCS/MnO<sub>2</sub>, respectively) were prepared according to the following procedure: 150 mg of HCS and 150 mg manganese acetate (product referred to as HCS/MnO<sub>2</sub>) or tin chloride (product referred to as HCS/SnO<sub>2</sub>) were dispersed in 250 ml of ethanol and sonicated for 2 h. Afterwards, the mixture was stirred for another 24 h. Finally, the product was dried in air at 100 °C for 24 h.

Characterization. The morphology of the samples was investigated by a FEI Tecnai F30 TEM (transmission electron microscope) with a field emission gun operating at 200 kV and EDX (Energy-dispersive X-ray spectroscopy) as one mode. Powder XRD (X-ray diffraction) was performed on a Philips diffractometer using Cu-K<sub>α</sub> radiation. Raman scattering was studied on a Renishaw micro-Raman spectrometer (λ = 720 nm). N<sub>2</sub> adsorption/desorption isotherms were acquired at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2010 M instrument, and the specific surface area was calculated by the BET (Brunauer Emmett Teller) method. TGA (Thermogravimetric analysis) was carried out on 10 mg samples using the DTA-Q600 SDT TA at a heating rate of 10 °C/min from room temperature to 900 °C in air flow (100 ml/min).

Electrochemical studies by means of cyclic voltammetry and galvanostatic cycling were carried out in Swagelok-type two-electrode cells by a VMP3 (Bio-Logic) potentiostat (see Ref. [30]). The working electrodes were prepared from a mixture of pristine material with carbon black (Super P, Timal) and PVDF (polyvinylidene fluoride) binder (Solvay Plastics) in a weight ratio of 70:15:15. Additional carbon black was added in order to assure the mechanical stability of the electrodes. PVDF was dissolved in NMP (N-Methyl-2-pyrrolidone) and subsequently the active material and carbon black were mixed with the solution. The resulting slurry was pasted on circular copper plates and dried at 100 °C in a vacuum furnace (<5 mbar) over night. After mechanical pressing at 10 MPa, the electrodes were dried again. The Swagelok-type cells were assembled in an argon atmosphere glovebox (H<sub>2</sub>O, O<sub>2</sub> < 1 ppm) with the working electrode, a lithium metal (Alfa Aesar) counter electrode, which had been pressed on a circular nickel plate, and two layers of glass microfibre separator (GF/D, Whatman). 200 μl of a 1 M solution of LiPF<sub>6</sub> in 1:1 EC (ethylene carbonate) and DMC (dimethyl carbonate) was used as electrolyte (LP30, Merck). While measuring, the cells were held at 25 °C in a climate chamber. For the CVs, the scan rate was fixed at 0.1 mV/s in the voltage range of 0.01–3.00 V and GCPL (Galvanostatic cycling with Potential Limitation) measurements were done at current densities of 100–1000 mA h/g.

## 3. Results and discussion

Fig. 2 shows TEM images of pristine hollow carbon spheres and of HCS/metal oxide composites with different metal oxide loading. As observed in Fig. 2(a,b), the pristine HCS are uniform in diameter which amounts about 250 nm. The shell thickness is about 90 nm. Functionalization with SnO<sub>2</sub> nanoparticles yields HCS/SnO<sub>2</sub> with a small metal oxide particle size distribution ranging from 3 to 5 nm. The particle sizes have been derived from averaging over 100 nanoparticles observed in the TEM image (Fig. 2(c,d)). SnO<sub>2</sub> nanoparticles are distributed on the surface of HCS homogeneously. Similar results are obtained for HCS/MnO<sub>2</sub> (Fig. 2(e, f)). However, the diameter of MnO<sub>2</sub> nanoparticles is smaller, ranging from 1 to 3 nm. As shown in Fig. 3, EDX elemental mapping clearly reveals that the elements Sn, O, and C are evenly distributed throughout the HCS/SnO<sub>2</sub> nanocomposite. Similarly, the elemental mappings of HCS/MnO<sub>2</sub> indicate the presence of Mn, O, and C. All detected elements seem to be rather homogeneously distributed in the sample. In summary, the EDS data clearly show that SnO<sub>2</sub> and MnO<sub>2</sub> are located both in the core and the shell of the hollow carbon spheres.

The carbon content and the quality of the materials are evaluated by TGA (thermogravimetric analysis) (Fig. 4) and Raman spectroscopy (Fig. 5). The thermogravimetric analyses of the HCS, HCS/SnO<sub>2</sub>, and HCS/MnO<sub>2</sub> samples present the thermal stability by monitoring the change of weight during heating. From the TGA results (Fig. 4), the pristine HCS start to oxidize around 550 °C [31]. The HCS are completely exhausted when the temperature is increased to ~700 °C in air, which indicates high purity of the HCS. TGA measurements for HCS with metal oxide nanoparticles show ash contents of 24 wt% and 37 wt% for MnO<sub>2</sub> and SnO<sub>2</sub>, respectively. In comparison to the pristine HCS, the stabilities of both metal



**Fig. 1.** Synthesis schematic of hollow carbon spheres (black) decorated with metal oxide nanoparticles (blue). Mesoporous silica spheres (grey) are being carbonized (step 2). After removal of silica (step 3), the resulting hollow carbon sphere is functionalized by metal oxide nanoparticles (step 4). (See the text.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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