



# Hollow nanospheres composed of titanium dioxide nanocrystals modified with carbon and gold for high performance lithium ion batteries



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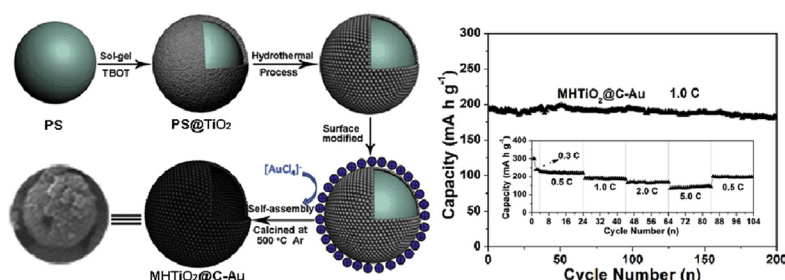
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## HIGHLIGHTS

- TiO<sub>2</sub> hollow spheres modified with carbon and Au were fabricated *via* a facile and controllable route.
- The high porosity of the composite could shorten the diffusion path of electrons and lithium ions.
- The inner carbon and superficial Au coating could improve the conductivity and stability of the structures.
- The composites could provide excellent electrochemical performance.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Herein, we reported a facile route to fabricate carbon and Au treated TiO<sub>2</sub> mesoporous hollow spheres (MHTiO<sub>2</sub>@C–Au) as high performance anode materials for lithium ion batteries. The high porosity of the hollow spheres, together with the inner carbon supporting and superficial Au coating, enhanced the cycling stability and rate performance of the MHTiO<sub>2</sub>@C–Au electrode significantly. The MHTiO<sub>2</sub>@C–Au composite exhibits a high reversible specific capacity of 186.6 mA h g<sup>−1</sup> after 200 cycles at the current density of 1.0C, superior rate performances of around 151.0 mA h g<sup>−1</sup> at the current rate of 5.0C. The outstanding electrochemical property is attributed to the overall structural features of the MHTiO<sub>2</sub>@C–Au, which can not only shorten the diffusion path of lithium ions and electrons, but also improve the stability of the hollow structures during the lithium ion insertion and extraction process.

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## 1. Introduction

Rechargeable lithium ion batteries (LIBs) with various merits of environmental benignity, low cost and high energy and power densities, have attracted considerable attention as promising power devices for future applications [1–4]. The ever-increasing

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performance demands of LIBs largely depend on the selection of electrode materials [5,6]. Therefore, considerable efforts have been focused on the rational design of electrode materials with diverse morphologies and structures, which can deliver superior cycling performance and rate properties [7,8]. However, as conventional anode materials, the application of graphite and carbon-based materials have been still limited by their low lithium insertion potential and lithium diffusion coefficient, which always leads to the formation of lithium dendrites on the surface of electrodes after consecutive cycles, as well as the rapid capacity fading. As a result, those drawbacks impede the practical application of LIBs [9–11]. Therefore numerous efforts in fabricating distinct electrode materials with suitable voltage and enhanced diffusion kinetics are required to satisfy the development of next generation of LIBs [12–14].

Over the past years, fabrication of electrode materials with hollow micro-/nanostructures has been ubiquitous since their widespread characteristics including high surface areas and void ratios can effectively improve the diffusion kinetics by reducing the penetration pathways of electrolyte and lithium ions into the electrode materials, allowing these materials to exhibit remarkable cycling and rate capability [15,16]. Generally, the universal strategies for the controllable generation of hollow structures have been based on the templating methods, by encapsulating various templates (e.g. silica, polymer and carbon spheres) with designed products and subsequent removal of interior materials [17–19]. However, insufficient efforts have been focused on addressing these crucial challenges, such as the difficulty of controlling the uniformity of the coating layer in size and morphology, as well as the crack and fracture of the architecture resulting from the calcination, dissolution or etching treatment during removing the interior templates [20]. Therefore, construction of high-quality hollow structures still remains a considerable challenge.

Titanium oxide ( $\text{TiO}_2$ ) has been demonstrated to be very promising electrode materials for the LIBs in recent years because of its abundance, chemical stability and environmental benignity. Particularly, the suitable voltage of  $\text{TiO}_2$  ( $>1.5$  V vs. Li) which effectively suppresses the lithium plating can largely enhanced the safety of LIBs [21–24]. However, the intrinsically low ionic and electrical conductivity always occurs in  $\text{TiO}_2$ -based materials during the charging and discharging cycles, which results in poor cycling performance and further hinders its practical applications [25,26]. To date, considerable efforts have been devoted to overcoming such obstacles. It has been demonstrated that  $\text{TiO}_2$  hollow structures with rich porosity can not only provide a short Li-ion insertion and extraction distance, but also improve the contact with the electrolyte [27–29]. Unfortunately, the space among the active particles which may increase the possibility of electrical disconnection during cycling will give rise to its capacity decline [18]. To improve the electrical contact among the active sites and further stabilize the hollow structures of  $\text{TiO}_2$ , carbon and carbon-based materials were explored [30,31]. In particular, the introduction of template derived carbon can be used as an ideal support for strengthening the hollow architecture of materials, which can generate complex hollow structure with novel properties [32]. In addition, the utilization of conductive metal particles (e.g. silver, gold) can serve as excellent electrical transfer medium and reduce the distance of charge transport [33–35]. For example, the structure of silver-treated hollow porous silicon spheres exhibited much enhanced performance compared to silicon nanoparticles, which is mainly attributed to improved diffusion kinetics from the good conductivity of silver [36]. Therefore, it is highly desirable to optimize  $\text{TiO}_2$  hollow structures with conductive metal particles and template derived carbon to form hybrid materials with superior electrochemical features.

Herein, we propose a facile strategy to synthesize a superior anode material for lithium-ion batteries by combining gold and template derived carbon with mesoporous  $\text{TiO}_2$  hollow spheres ( $\text{MHTiO}_2\text{@C-Au}$ ). The as-prepared composite could possess the instincts of hollow structures with high void ratios, which offer both the large contact area with electrolyte and the convenient diffusion pathway of lithium ions during insertion/extraction. Moreover,  $\text{TiO}_2$  hollow spheres modified by the gold and template derived carbon can also significantly improve the structural stability and electric conductivity. Benefiting from the optimal design of the unique architecture, the  $\text{MHTiO}_2\text{@C-Au}$  composite can exhibit superior cycling and rate performances, such as a high specific capacity of  $299.2 \text{ mA h g}^{-1}$  at the current rate of 0.3C, an excellent cyclic performance of  $186.6 \text{ mA h g}^{-1}$  after 200 cycles at the current rate of 1.0C, and a good rate performance of around  $151.0 \text{ mA h g}^{-1}$  at the current rate of 5.0C ( $1.0\text{C} = 168 \text{ mA g}^{-1}$ ).

## 2. Results and discussion

The strategy for the preparation of the  $\text{MHTiO}_2\text{@C-Au}$  composite was illustrated in Fig. 1. The synthesis technique was first based on sol-gel and hydrothermal process to fabricate mesoporous  $\text{TiO}_2$  shells on polystyrene (PS) nanospheres ( $\text{PS@m-TiO}_2$ ) [37]. In the sol-gel growth process, a compact  $\text{TiO}_2$  layer was directly formed on the surface of PS spheres ( $\text{PS@a-TiO}_2$ ). After the hydrothermal treatment, the  $\text{TiO}_2$  layer was converted into mesoporous structure ( $\text{PS@m-TiO}_2$ ). Then the  $\text{PS@m-TiO}_2$  hybrid was modified to acquire positive charged followed by self-assembly of  $[\text{AuCl}_4]^-$  in solution driven by electrostatic interaction ( $\text{PS@m-TiO}_2-[\text{AuCl}_4]^-$ ). Finally, the composite was treated in Ar atmosphere at  $500^\circ\text{C}$  for 4 h to give rise to template derived carbon and Au treated  $\text{TiO}_2$  spheres ( $\text{MHTiO}_2\text{@C-Au}$ ). The resultant  $\text{MHTiO}_2\text{@C-Au}$  composite composed of carbon supported  $\text{TiO}_2$  as well as Au surface modification together was expected to show particular advantages.

The size and morphology of the pristine PS spheres were demonstrated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images as shown in Figure S1. The PS spheres were nearly monodisperse with relatively smooth surface and diameters of around 400 nm. Then the PS spheres were coated with amorphous  $\text{TiO}_2$  layer through controlled hydrolysis of TBOT in ethanol/acetonitrile solution, resulting in the formation of  $\text{PS@amorphous TiO}_2$  ( $\text{PS@a-TiO}_2$ ) core-shell architecture (Fig. 2A and C). Meanwhile, as shown in Fig. 2C, the existence of the amorphous  $\text{TiO}_2$  shell with an average thickness of about 40 nm can be further evidenced by the clear boundaries between core and shell. Subsequently, the  $\text{TiO}_2$  shells underwent an evolution from a compact layer to a mesoporous one by hydrothermal reaction in the ethanol/water solvent, and still maintained the original spherical shape ( $\text{PS@m-TiO}_2$ ). The surface of the spheres consisted of rough particles, upon closer scrutiny, revealing highly ordered arrangement (Fig. 2B and D). Benefiting from the tight coupling of the PS spheres and  $\text{TiO}_2$  layer, the overall spherical morphology of the  $\text{PS@m-TiO}_2-[\text{AuCl}_4]^-$  was well preserved with mesoporous shells (Figure S2). The space among the active  $\text{TiO}_2$  particles gave rise to the porosity in the well-designed structure, which could facilitate the migration of lithium ions and the permeation of electrolyte into electrode materials during electrochemical cycling [19].

The obtained  $\text{PS@m-TiO}_2-[\text{AuCl}_4]^-$  nanospheres were calcined to convert PS spheres and  $[\text{AuCl}_4]^-$  into carbon and Au, respectively. As shown in Fig. 3, the X-ray diffraction (XRD) pattern was used to analyze the structural composition of  $\text{MHTiO}_2\text{@C-Au}$ . The peaks at  $25.3^\circ$ ,  $37.8^\circ$ ,  $48.0^\circ$ ,  $53.9^\circ$ ,  $55.1^\circ$ ,  $62.7^\circ$ ,  $68.8^\circ$ ,  $70.3^\circ$  and  $75.0^\circ$  can be ascribed to the anatase phase of (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes, which is similar to the results of previous investigation [35]. In addition, four peaks corresponding

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