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RAPID COMMUNICATION

Design a novel kind of open-ended carbon sphere for a highly effective counter electrode catalyst in dye-sensitized solar cells

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Abstract
A new kind of carbon sphere (denoted as OCS) with an open end on the surface has been synthesized successfully. The designed OCS shows higher electrocatalytic activity than the conventional solid and hollow carbon sphere (denoted as SCS and HCS) as counter electrode (CE) catalyst for the regeneration of both iodide (I^-/I_3^-) and sulfide (T^-/T_2) redox shuttles in dye-sensitized solar cells (DSCs). For the iodide electrolyte, the DSCs using SCS, OCS, and HCS CEs yield high power conversion efficiency (PCE) values of 7.8, 8.7, and 8.1%, respectively, indicating the potential to replace expensive Pt CE. Most importantly, the carbon sphere catalysts exhibit obvious advantages when applied in sulfide redox shuttle. The OCS-CE based DSCs produces a high PCE of 6.4%, much higher than that for Pt-CE based DSCs (4.1%). The high catalytic activity of OCS benefits from the sufficient contact between the redox shuttle with the external and internal surfaces of OCS because an open end exists on the surface of OCS, which provide a diffusion channel for the electrolyte into the inner of OCS. This strategy for designing open-ended structure is highly important for the fields of drug delivery, nanodevice, and adsorption, but not confined to catalysis.

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Introduction

Significant breakthroughs in science and technology often benefit from the application of new functional materials. For instance, the development of dye-sensitized solar cells (DSCs) with power conversion efficiency (PCE) exceeding 7% can be attributed to the application of mesoporous TiO_2 semiconductor film, which can absorb more dye molecule than compact TiO_2 film [1]. Recently, another breakthrough was made by combining new sensitizers and new redox shuttle, resulting in a high PCE over 12% [2]. Although great advancements in the dye, semiconductor, and redox shuttle components have been made for DSCs, the long-term development and practical application of DSCs still requires a robust increase in PCE and a significant decrease in the production cost [3-8]. Unlike the semiconductor, dye, and redox shuttle components, counter electrode (CE) catalysts are often overlooked. Fortunately, CE catalysts begun to attract increasing attention, as a class of new CE catalysts, such as carbon materials, [9-12] organic polymers, [13-16] and metal compounds [17-30] have been applied to replace conventional noble Pt CE. Among these Pt-free materials, carbon is a promising CE catalyst for use in DSCs because of its low cost, high conductivity, high catalytic activity, ready availability, high thermal stability, and corrosion resistance. To date, several carbon materials have been used as CE catalysts, such as activated carbon (Ca), carbon black (Cb), carbon fiber (Cf), mesoporous carbon, CNTs, and grapheme [31-36].

We conducted a comprehensive study on the catalytic performance of nine types of carbon materials, namely, Ca, Cb, conducive carbon (Cc), carbon dye (Cd), Cf, CNTs, ordered mesoporous carbon (Com), discarded toner (Cp), and C_{60}, as CE catalysts in DSCs [37]. The traditional carbon materials (Ca, Cb, Cc, CNTs, and Cf) showed decent catalytic activity and the corresponding DSCs showed PCE values of 6.3% to 7.0%. Com and Cd showed the highest catalytic activity and the devices achieved a PCE of 7.5%. In addition to the abovementioned carbon materials, carbon sphere (CS) is also an attractive candidate for functional materials because of their uniformity, high thermal stability, large surface-to-volume ratios, and excellent conductivity. Thus, CS has been widely studied in various applications, including adsorbents, catalysts, fuel cells, drug delivery systems, nanodevice, and lithium ion batteries, and the common used CSs are the solid CS (SCS) and hollow CS (HCS) [38-43]. However, no study to date has reported on the use of CS as CE catalyst for DSCs.

In this study, we reported the design and synthesis of SCS and HCS. Further, the authors think that design an open end on the surface of CS is meaningful for solid-liquid catalysis, because the reaction can be realized on the external surface as well as on the internal surface of CS simultaneously. Thus, we further design an open end on the surface of CS, achieving a novel kind of open-ended CS (denoted as OCS). The prepared SCS, OCS, and HCS were subsequently introduced into DSCs as CE catalysts to replace the expensive Pt for the regeneration of the conventional iodide and novel sulfide redox shuttles. For the regeneration of iodide redox shuttle, the catalytic activity of OCS was higher than those of Pt and the other two CSs as we expected. Moreover, SCS, OCS, and HCS all performed better than Pt in terms of sulfide redox shuttle regeneration. The superior catalytic performance of OCS stemmed from its open-ended structure, which provided a channel for the electrolyte diffusing into the inner of OCS, resulting in sufficient contact between the redox shuttle with both the external and internal surfaces of OCS. Finally, after long-term stability testing, the PCE of the DSCs using SCS, OCS, and HCS maintained 86.5, 88.7, and 89.2% of their initial values, respectively, proving that the three types of CSs exhibit high stability under working conditions.

Experimental

Fabrication of solid carbon sphere (SCS)

Resorcinol (220 mg) was first dissolved in deionized water (400 mL) under stirring at 25 °C, followed by the addition of F127 (100 mg) and formaldehyde (37 wt%, 300 μL), producing a clear solution. Next, 1,2- diaminohexane (DAH, 60 mg) was added, and the clear solution became a white colloidal colour. The resultant solution was further heated to 80 °C under vigorous stirring for 12 h, and a polymer product was collected. The polymer product was purified several times with water by centrifugation. SCS was achieved by pyrolysis of the polymer product at 800 °C for 2 h under a N_2 atmosphere.

Fabrication of open-ended and hollow carbon spheres (OCS and HCS)

(1) Synthesis of polystyrene (PS) spheres. All steps were carried out under N_2 atmosphere. First, 80 μL of oleic acid and 1.6 mL of styrene were dissolved in 120 mL of deionized water. The resultant solution was stirred at 50 °C for 30 min. Next, 70 mg of potassium persulphate was added to the solution, which was then heated to 60 °C under stirring for 4 h. After centrifugation and washing with water, the PS spheres were collected. (2) Synthesis of PS@PR spheres. First, 100 mg of PS spheres was dispersed in 80 mL of water, followed by the addition of formaldehyde (100 μL, 37 wt%), resorcinol (120 mg), and ammonium hydroxide (100 μL, 28 wt%). Next, the solution was transferred into a 150 mL Teflon-lined autoclave and heated at 150 °C for 4 h. After centrifugation and several repetitions of washing with deionized water and ethanol, the PS@PR spheres were obtained. (3) Synthesis of PS@PR@SiO_2 spheres. First, 360 mg of cetyltrimethylammonium bromide (CTAB) was stirred with water (15 mL) for approximately 1 h at 30 °C. Next, the CTAB solution was added to a mixture of PS@PR (90 mg), pure ethanol (20 mL), deionized water (60 mL), and ammonia solution (28%; 1.0 mL) and stirred for 30 min, after which tetraethyl orthosilicate (0.63 mL) was added. The reaction mixture was maintained at 30 °C for 10 h, and the PS@PR@SiO_2 was collected by centrifugation and dried at 60 °C for 5 h. (4) Synthesis of OCS. The as-prepared PS@PR was sintered at 800 °C under a N_2 flow for 2 h, yielding OCS. (5) Synthesis of HCS. The as-prepared PS@PR@SiO_2 was heated at 800 °C under a N_2 flow for 2 h, producing the pyrolysed product. The pyrolysed product was treated with aqueous NaOH solution to remove the silica coating, yielding HCS.

Fabrication of dye-sensitized solar cells

The carbon sphere electrodes were prepared by spray-coating method. For example, to prepare the SCS (OCS or