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RAPID COMMUNICATION

Hierarchical TiO_2 nanowire/graphite fiber photoelectrocatalysis setup powered by a wind-driven nanogenerator: A highly efficient photoelectrocatalytic device entirely based on renewable energy

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Abstract
Photoelectrocatalysis is an efficient approach for the degradation of organic pollutants as well as for water splitting. However, an external power source supplying a direct current (DC) is essential to enhance the separation of photo-induced carriers. In this paper, a fully-functional photoelectrocatalysis device was constructed by connecting single crystalline TiO_2 nanowires assembled on graphite microfibers (TiO_2 nanowire/graphite fiber, TNGF) to a wind-driven triboelectric nanogenerator (WDTENG). The excellent photocatalytic and photoelectrocatalytic properties of TNGF originate from the ability of graphite fibers to transport rapidly the charge carriers, the high photocatalytic activity of TiO_2 nanowires and the photo-induced carrier separation enhancement created by the zero band gap of graphite. When this system is used for hydrogen generation via photoelectrocatalytic water splitting, the hydrogen evolution of the TNGF is significantly increased under assistance of the WDTENG. Photoelectrochemical analysis demonstrates that the separation and recombination of photo-induced charge carriers in the 7TNGF composite is dependent on the applied voltage bias. Thus, the wind driven generator

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provides large enough voltage bias for efficient charge separation, leading to a highly enhanced photocatalytic performance. This work is the first instance of high performance photoelectrocatalysis device aimed either at depollution or at hydrogen production which is entirely based on renewable energy.

Introduction

The rapid technological development as well as the demographic expansion of our world is responsible for a series of imminent environmental problems as well as an ineluctable energy crisis. The use of photocatalytic processes either for the degradation of contaminants in water or for the generation of hydrogen as clean fuel is a very practical and effective approach to alleviate these problems [1]. Therefore, it is urgent to develop highly active photocatalysts coupled to efficient photocatalysis techniques [2]. However, most of the existing photocatalysts still suffer from high recombination rate of the photo-induced charge carriers, which largely limits the photocatalytic performance. Separating such carriers is one of the key elements to achieve high photocatalytic efficiency [3]. The main factors causing this recombination process are thought to be related to the presence of crystal defects and to low transfer rates [4]. The concentration of electrons and holes significantly decreases due to the trapping of the charge carriers by the defects whereas low carrier mobilities associated to short diffusion lengths induce fast recombination rates. The presence of defects can be minimized through the improvement of the crystallinity, for example by growing single-crystalline nanomaterials. Recent works have shown that heterostructured nanomaterials constructed with different semiconductor or semiconductor/metal nanoparticles can promote photo-induced carrier separation based on p-n heterojunction [5], Schottky heterojunction [6] and band structure matching physical mechanism [7]. Most recently, a new methodology for enhanced separation of photo-induced carriers was proposed by applying a small electric field to drive the positive or negative charge out of the structure and suppress the recombination process [8]. However, most photoelectrocatalytic devices are based on a film-like working electrode, which is built by coating a layer of photocatalytic powder at the surface of a conductive substrate/electrode. This configuration leads to two obvious flaws. First, the semiconductor nanoparticles are just in physical contact with the surface of the electrode, the electrode – photocatalytic film contact resistivity is too large and it impedes the charge transfer. Second, the film-like geometry of the photocatalytic layer offers only a low surface area which is insufficient to promote high activity, as the reaction is confined to a 2-D and not a 3-D environment.

TiO_2 has been widely used in the fields of solar cell, photocatalysis, gas sensor and biosensor because of its low cost, high chemical stability and environmental friendliness [9]. TiO_2 possesses a wide bandgap of about 3.2 eV and thus excellent photocatalytic activity under UV light illumination [10]. Normally, the use of single phase crystalline TiO_2 nanoparticles as photocatalyst is hampered by photo-induced carrier recombination. As mentioned above, assembling TiO_2 nanoparticles on an conductive substrate is a practical method to enhance the separation of photo-induced carriers by a photoelectrocatalysis technique [11]. In 1972, Fujishima and Honda discovered the phenomenon of photocatalytic splitting of water under a certain bias [12]. Up to now, the most popular photoelectrocatalysis method consists in coating the TiO_2 powder at the surface of conductive metal [8] to form a working electrode, and in applying a constant direct voltage to export photo-induced electrons from the photocatalyst to the electrode, leaving the holes to oxidize the organic pollutant or the water in the case of water splitting [13]. It has been confirmed that under a certain bias, TiO_2 electrodes as anodes can photodegrade formic acid [14], 4-chlorophenol [15], as well as dyes and other organics. Although functional, the efficiency of this two dimensional TiO_2 coated electrode remains low because the photodegradation reaction only occurs at the surface of the electrode. Therefore, it is necessary to develop 3-D stereo photoelectrocatalysts for highly efficient photodegradation and hydrogen generation via water splitting.

As a nontoxic, eco-friendly, low-cost, electrically conductive and chemically and physically stable one-dimensional material, graphite fibers have been used in dye-sensitized solar cells [16], supercapacitors [17], and biosensors [18]. Because graphite fibers are highly graphitized materials with a graphite content higher than 99% [19], they possess numerous advantages compared to amorphous carbon fibers. These advantages make graphite fibers an ideal building block for constructing hierarchical nanostructures for energy storage and photo-electronic transfer materials, in which the electron transfer can be significantly speeded up due to the high electric conductivity of the graphite fibers. Furthermore, their good mechanical properties make them excellent candidates to efficiently support nanostructured catalysts which can be recycled and reused. Therefore, we envision that assembling TiO_2 nanoparticles on graphite micro-fibers to form graphite–TiO_2 nanostructure arrays should lead to high performance photocatalysts.

Most recently, triboelectric nanogenerators (TENG) [20], with their ability to harvest energy from the environment, have attracted much attention because they are easily fabricated, very reliable and efficient, they offer a large output power, and they are low-cost [21]. TENG driven by renewable energy sources, such as light wind [22], water flow [23] and even body movement [24] have been designed and realized. For photoelectrocatalysis, if electricity can be supplied by a wind-driven nanogenerator, systems aiming at the degradation of organic pollutants or the generation of hydrogen should be self-powered. This strategy is efficient and simple, and the resulting device becomes portable and