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A solar storable fuel cell with efficient photo-degradation of organic waste for direct electricity generation

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ABSTRACT

Solar fuels and fuel cells are two of the key enabling technologies for clean and sustainable electricity generation. However, photo-synthesis of hydrocarbon or hydrogen fuels is kinetically slow and low efficient, while the current fuel cells use pure hydrogen fuel and precious metal electro-catalysts, which pose severe cost and resource restraints for commercial application. Here, we propose and construct a solar storable fuel cell (SSFC) based on the photo-oxidation of organic wastes and the oxygen reduction reaction at the MnO_2 air cathode, which generates electricity with simultaneous photo-degradation of organic contaminants in waste water. As a proof-of-principle device, the SSFC delivers a stable voltage of $+0.6$ V at constant current of 20 μA cm^{-2} with almost complete degradation of methyl orange in aqueous solution in an hour, demonstrating an effective utilization of the organic waste for direct electricity generation.

1. Introduction

Increasing concerns over the future availability of global fossil energy resources and the environmental contamination by pollutant emission produced massively in modern society have stimulated the development of new energy technologies with minimal ecological footprint [1]. In such a pursuit of clean energy and healthy environment, many types of fuel cells have been actively investigated to generate electricity from renewable energy resources [2], among which polymer electrolyte membrane fuel cells (PEMFCs). This are developed with great success, demonstrating viable applications for zero-emission vehicles and distributed electric stations [3,4]. However, these PEMFCs are mostly based on pure hydrogen fuel and precious metal electro-catalysts, which pose severe cost and resource restraints for commercial applications. If organic wastes could be served as anodic fuels for fuel cells, it would bring about great benefits for clean electricity generation with simultaneous environmental remediation. This idea is originally applied in microbial fuel cells (MFCs) [5–8] with bacteria as biocatalysts to decompose organic matter for generating bioelectricity simultaneously. However, the low power output and bacterial instability in the solution with a variety of hazardous organic compounds have largely limited the commercial development of MFCs [9,10].

Photo-catalysis may provide an alternative way to utilize the organic wastes as anode fuels for electricity generation. Photo-degradation of chemical pollutes has been known for half a century [11–13], and is extensively investigated for wastewater treatment and environmental remediation [14,15]. Typically, the photo-catalytic fuel cells (PFCs) show advantages in organics degradation and electricity production [16]. Unfortunately, the poor visible light response [17–22], weak stability of the photo-anode [23–25], and the uneconomic of the cathode materials [26–28] are the main defects for overcoming in PFCs. Seeking for cheap cathode materials and excellent utilization of solar energy is necessary for improving the performance of the system. As an efficient way to enhance the light harvesting, dye^{-} sentized TiO_2 photo-anode for electricity generation was first demonstrated in a dye-sensitized solar cell (DSSC) by Gratzel M et al. in 1991 [29,30]. Since then, numerous researches have been devoted for the development of the material design and structural optimization of TiO_2 photo-anode [31,32]. Though a number of dye-sensitized photo-electrochemical cells have been developed for light-to-electric energy conversion and storage [33–38], few of them has been done to use organic wastes as anode fuels for electricity generation [39].

Taking advantages offered by strong photo-oxidation ability of TiO_2 photo-catalyst and clean oxygen reduction of air cathode, we

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propose and construct a solar storable fuel cell (SSFC) by use of a dye-sensitized TiO_2 photo-anode, a MnO_2 air cathode and a degradable organic contaminant as anode fuel. This SSFC is fueled by the photo-oxidation of organic contaminants, thus enabling clean electricity generation with simultaneous degradation of environmental contaminants. Particularly, due to the facile photo-oxidation at the TiO_2 anode and the stable electro-catalysis of the MnO_2 cathode for oxygen reduction, this SSFC can work well without the use of precious metal catalysts, possibly offering an alternative approach to make low cost and highly efficient fuel cells for environmental and energy applications.

2. Experimental

2.1. Electrode preparations and cell construction

The preparation of α-MnO_2 nanofibers air cathode were described in detail in Supporting Information. The photo-anode was fabricated by doctor-blading a commercial TiO_2 sol (CNANE) onto a fluorine-doped tin oxide glass (FTO, 15 $\Omega\,cm^{-2}$, Nippon Sheet Glass) to form a mesoporous TiO_2 film followed by sintering the anode at 500 °C in muffle furnace at a heating rate of 5 °C min^{-1}) for 30 min. The TiO_2 anode was sensitized by immersing it in an ethanol solution containing 5.0×10^{-4} mol L^{-1} Z907 dye (Solaronix, Sweiss) for 24 h at room temperature, then rinsed with anhydrous ethanol and dried for experimental use.

The solar storable fuel cell was composed of a dye-sensitized TiO_2 photo-anode, a MnO_2 air cathode and a Nafion film, tightly clamped together with two plastic spacers inserted into the two sides of the separator to form an anode and a cathode chambers. The anolyte was a 1 mol L^{-1} $LiClO_4$ aqueous solution containing 20 mg L^{-1} methyl orange (MO) and the catholyte was a pure 1 mol L^{-1} $LiClO_4$ solution.

2.2. Structural and photo-electrochemical characterization

The crystalline structure of the as-prepared α-MnO_2 nanofibers was characterized by X-ray diffractometry on a Rigaku MiniFlex II diffractometer. The morphology of the MnO_2 nanofibers was observed by scanning electron microscopy (SEM, Supra 55vp-25-62) and transmission electron microscopy (TEM, FEI Tecnai F20). The cyclic voltammetry and discharge curves of the MnO_2 electrode were recorded on a CHI 600 A electrochemical workstation (Shanghai, China). The photo-electrochemical responses ($I\sim V$ curves) of the solar storable fuel cell were recorded with an IM6ex electrochemical workstation (Zahner, Germany). The light source used in this work was a filtered (500–1100 nm) Xe lamp (Oriel 91,160–1000, USA) and adjusted to give a power density of 100 mW cm^{-2}. The intensity of the incident light was characterized with a radiant power/energy meter (Oriel, 70,260) before each experiment. The optical absorption spectra of the photo-degradation solution at different times were recorded by using a UV–vis spectrophotometer (UV-3600, Shimadzu, Japan). Meanwhile,

3. Results and discussion

Fig. 1 schematically illustrates the cell configuration and working mechanism of the SSFC device built in this work. This SSFC consists of a dye-sensitized TiO_2 photo-anode (DS-TiO_2) and a MnO_2 air cathode, which are separated by a polymer electrolyte membrane to prevent the crossover of the anodic fuel and its degraded product between the anodic and cathodic compartments. The aqueous $LiClO_4$ solution containing methyl orange (MO) is used as the anolyte and organic fuel for the photo-oxidation reaction. The pure neutral solution of $LiClO_4$ is used as catholyte. The selection of MO molecule as a degradable pollute in this work is simply because MO is a representative organic contaminant in industrial wastewater and widely investigated as a model compound for characterizing the degradation kinetics of photo-catalysts [40–42].

As shown in Fig. 1, photo-excitation of the dye adsorbed on the TiO_2 nanoparticles results in an injection of electrons into the conduction band of the oxide under light illumination (Eq. (1)). The oxidized dye (D^{*+}) is subsequently reduced by electron donation of MO molecules in the anolyte, i.e. the MO molecules are photo-electrochemically degraded into smaller radicals and

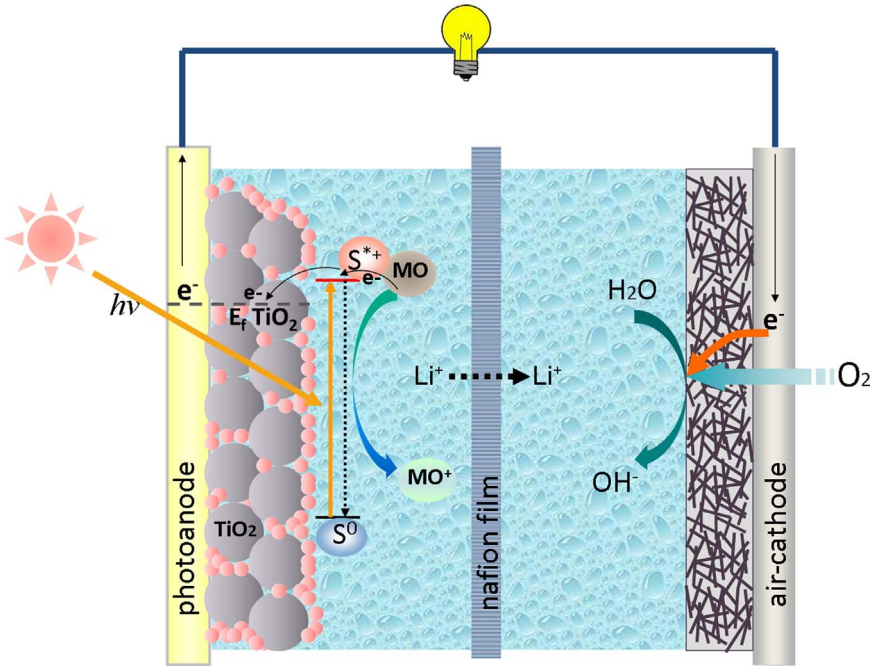

Fig. 1. Schematic representation of the working principle of the SSFC.