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Rain-responsive polypyrrole-graphene/PtCo electrodes for energy harvest

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ABSTRACT

Renewable energy conversion has become one of the major strategies to solve energy crisis and environmental pollution. Tremendous energy is released during the raining process, however rain energy is always considered as a waste energy without further utilization. We present here experimental realization of physical proof-concept rain-response electrodes from polypyrrole (PPy), PPy-graphene and PPy-graphene/PtCo for rain energy harvest. By obeying charging/discharging mechanism of cation (rain)/electron (electrode) electrical double-layer (EDL) pseudocapacitances at rainwater/electrode interfaces, periodical current and voltage signals are produced under the stimulation of simulated rain droplets. The energy conversion device made from PPy-graphene/PtCo achieves a maximized peak current of 4.91 μA/droplet, a peak voltage of 320.62 μV/droplet, yielding a power of 1161.38 pW/droplet. The results demonstrate that the improved current and voltage outputs are highly dependent on increased electron concentration at electrode surface. This work may extend our knowledge to advanced energy conversion devices for waste energy harvest.

1. Introduction

Energy conversion from renewable sources including wind energy [1–5], tidal energy [6–8], solar energy [9–13] and mechanism vibration [14,15] et al. is a promising solution to solve energy crisis and environmental pollution, which has aroused great concerns for realizing sustainable development of human society [16]. As one of the most ideal alternatives, solar power has attracted considerable interests and great achievements have been made through complicated solar-to-electric conversion mechanisms [17–27]. However, solar energy is intermittent, making it a promising strategy to integrate as-developed energy conversion devices with waste energy harvest.

It is worth mentioning that triboelectric nanogenerators made by Wang have significant effects on harvesting energy from sunlight and raindrops [28], an attempt has been made to develop a new technology of converting waste energies into electricity. Since the first experimental realization of rain energy harvest through chemical method proposed by our group [29], the waste energy conversion has been considered as a complement to state-of-the-art energy conversion techniques. For example, the first prototype for harvesting rain energy is from a flexible reduced graphene oxide (rGO) electrode made by a hot-pressing technology, achieving a current over microamps as well as voltage of hundreds of microvolts in response of simulated rain droplets. We demonstrate in previous work that the mechanism for rain energy conversion is the formation of electrical double-layer (EDL) pseudocapacitance at rainwater/rGO interface through the adsorption between cations of raindrops and delocalized electrons of rGO. When dropping rainwater onto the surface of electron-enriched rGO electrode, the pseudocapacitors are charged because cations drag π-electrons at the spreading process. Subsequently, they are discharged by separating electron-cation pairs at shrinking process. At the same time, the π-electrons are released to rGO electrode to participate in the

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next energy conversion cycle. This point of harvesting energies from natural environments into electricity has guided the design of advanced functional devices for addressing the issue of traditional photovoltaics being dysfunctional beyond sunny days [30]. Further studied on graphene tailored coating [31], platinum alloy electrodes [32] and polymer electrode [33] are also performed to increase rain response.

In the current work, we demonstrate a new class of electron-enriched electrodes from conductive polypyrrole (PPy), PPy-graphene complex, and PPy-graphene/PtCo to harvest rain energy. PPy is a typical electron-enriched conductive polymer owing to existence of large conjugated structure in linear molecular chain, therefore it always presents high conductivity, good electrocatalytic activity and film-forming ability [34–40]. Arising from the lower electronegativity of Co (1.88) than Pt (2.2), the free electrons from Co atoms can deviate to Pt surface to form electron-enriched PtCo alloy surface. On the other hand, the Co atoms enter into the Pt lattice due to lower lattice constant of Co than Pt, leading to an inter-atomic extrusion for increased active sites. The complexation of PPy with graphene as well as the combination of PtCo alloys can markedly increase the electron density of these electrodes. In this fashion, three electrochemical technologies including cyclic voltammetry (CV), potentiostatic mode and galvanostatic mode are used to make electrode materials. By optimizing the synthesis technologies and electrode materials, the impacts of electron density of electrodes, injection velocity and cation species on electrical signals are carefully investigated. The optimized electrode is also in response to the real rainwater, extending our knowledge of advanced energy conversion devices for rain energy harvest.

2. Experimental

2.1. Fabrication of electrodes for rain energy harvest

The feasibility of fabricating film-typed PPy, PPy-graphene or PPy-graphene/PtCo was carried on an Electrochemical Workstation (CHI660E) platform using different electrochemical technologies, including cyclic voltammetry (CV), potentiostatic mode and galvanostatic mode in a traditional three-electrode system. A Pt foil, Ag/AgCl electrode and fluorine doped tin oxide (FTO) glass with an active area of $1.5 \times 1.5\ cm^2$ were used as counter electrode, reference electrode and working electrode, respectively. FTO glass was used as a substrate because of its good adhesion toward electrode films. The detailed procedures were shown in the following part.

PPy electrode: 0.7058 mL of pyrrole (Py) and 0.8588 mL of concentrated HCl aqueous solution with a molar Py/HCl ratio of 0.1: 0.1 were mixed to form a homogenous solution, and the total volume of mixture was tuned to 200 mL using deionized water. In terms of cyclic voltammetry method, the electro-polymerization of PPy onto FTO glass was carried out by scanning from −0.2 V to +1.0 V at a scan rate of 100 mV s^{-1} for 100 cycles. Moreover, a constant potential of 3 V was applied for 100 s to deposit PPy at FTO glass using a potentiostatic technology. Besides, a constant current of 0.01 A was used for galvanostatic deposition, and the high and low potentials were set at +3.0 V and −3.0 V for 150 s, respectively.

PPy-graphene electrode: Prior to electrochemical deposition, Py-graphene complex was prepared via a reflux process using Py and graphene (lateral size of graphene is 5 μm) as sources. In details, 10 mL of Py monomer and 0.5, 1, 2, 3, 4 or 5 wt% of graphene were sealed in a three-necked flask and treated by ultrasonification for 30 min to form a homogeneous solution, respectively. Filled with nitrogen gas in the dark atmosphere, the solutions were refluxed at 130 °C for 3, 4, 5 or 6 h, subsequently the products were preserved in an airtight, dark and cool condition. A solution was made by dissolving 0.33 mL of the Py-graphene complex and 0.4015 g of cetyl trimethyl ammonium bromide (CTAB) in 50 mL of deionized water. Finally, the PPy-graphene complex material was made according to the methods similar to that for PPy electrode.

PPy-graphene/PtCo electrode: Prior to electrochemical deposition, 2.63 mL of chloroplatinic acid aqueous solution (1 mM H_2PtCl_6), 0.196 g of cobalt sulfate (7 mM $CoSO_4$) and 0.142 g of sodium sulfate (10 mM Na_2SO_4) were dissolved in 100 mL of deionized water to make a homogeneous solution. PPy-graphene/PtCo material was prepared by electrodepositing PtCo onto above-mentioned PPy-graphene film under a constant potential of −0.6 V for 600 s. Finally, the resultant PPy, PPy-graphene and PPy-graphene/PtCo electrodes were rinsed with deionized water at ambient conditions.

2.2. Device assembly and tests

The device for rain energy harvest was made by covering two copper-based collecting electrodes at electrode surface to form device architecture of substrate/film/collecting electrode. The two

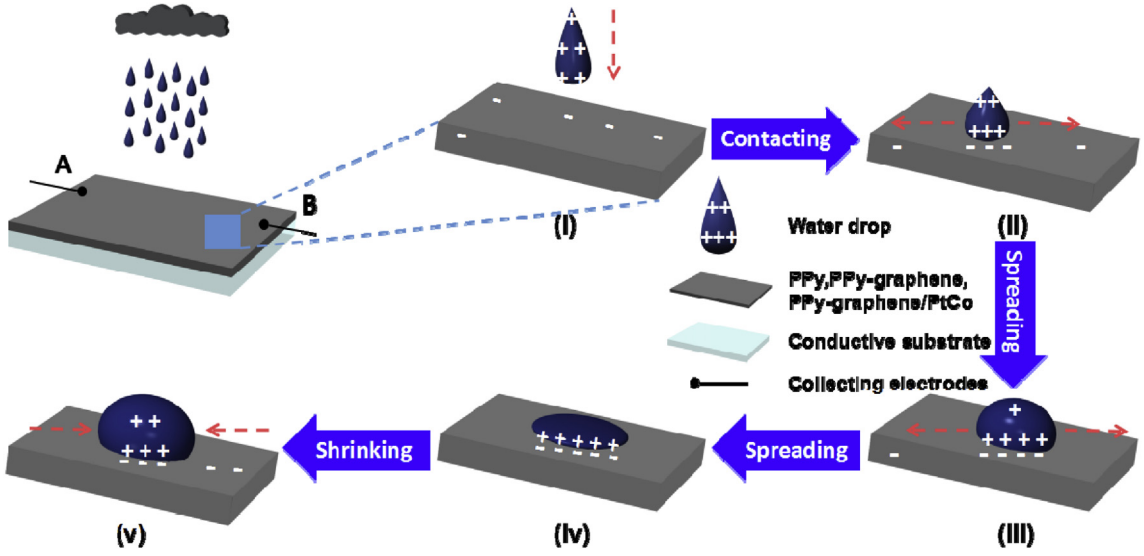

Fig. 1. Schematic illustration of working mechanism for rain-energy harvesting electrode.