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Ultrasound-assisted synthesis of PPyCuS@GOPt nanocomposite and investigation of its electrocatalytic behavior towards photo-hydrogen evolution

Habib Ashassi-Sorkhabi*, Babak Rezaei-moghadam

Electrochemistry Research Laboratory, Department of Physical Chemistry, Faculty of Chemistry, Iran University of Tabriz, Tabriz, Iran

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ABSTRACT

Capability of reducing the overpotential and also increasing the current density of hydrogen evolution reaction, HER, through exposure to light can be aid in the development of effective HER driven by sunlight. With this in mind, herein, the hybrid electrode based on polypyrrole –CuS composite, PPyCuS, is fabricated with the aim to form an electrode photo-electrocatalyst for HER. Therefore, an in situ sonoelectrochemical method was employed to synthesis of hybrid nanocomposite film on copper substrate. The photoelectrochemical performance of PPyCuS@GOPt hetrostructure was investigated in acidic solution under visible light irradiation by linear sweep voltammetry, electrochemical impedance spectroscopy, EIS, and Tafel slopes evaluation. Actually, we could prepare the PPyCuS@GOPt nanocomposite film on Cu_2O nano particles exhibited a much smaller onset overpotential with high current density for photo-HER. It was proven that GO, and Pt can act as effective dual co-catalysts to enhance the photocatalytic H_2 production activity of PPyCuS. The higher photoactivity is attributed to the fact that the photoinduced interfacial charge transfer in the heteronanostructures follow by further transfer in GO sheets. This work is expected to provide a new concept for development of highly efficient polymer-sulfide compounds photoelectrocatalysts for HER under simulated sunlight.

1. Introduction

Regard to limitation in fossil fuels and growing environmental concerns, logically forecasted that the energy demand will be covered by renewable resources [1–3]. Hydrogen evolution under visible light irradiation using semiconductor catalysts is considered to be a promising solution to the global energy requirements [4–8]. In this case, the light–induced generation of fuels encompass processes such as light absorption, energy transfer to catalytic active sites and interfacial reactions at the catalyst–solution interfaces [7,9]. Indeed, if the energy of the photon is suitable, pair of electron and hole per absorbed photon can be generated. In other word, photoinduced charge separation is the key for light-harvesting systems in photoelectrocatalyst performance, which convert light energy into electrical power or chemical fuels.

Conducting polymers such as polypyrrole with extended π-conjugated electron structures have been widely studied due to their rapid photoinduced charge separation and relatively slow charge recombination. Besides as well-known, graphene oxide, GO, due to its high specific surface area, high carrier mobility and also the high content of the oxygen containing functional groups in the basal planes and the edges can provide anchoring groups which caused to bind inorganic materials onto GO [10]. Yu et al. [11] indicated that GO sheets with rich π-conjugation structure can efficiently and quickly separate and transfer the photogenerated electrons. However, in order to improve the photocatalytic efficiency, it is important to reduce the recombination of photogenerated electrons and holes. To solve the above issue, one of the effective ways is to employ co-catalyst on photoelectrocatalyst. Cuprous oxide, Cu_2O, is an attractive p-type oxide for photoelectrochemical hydrogen production with a direct band gap of 2 eV [12]. Also, CuS with narrow band gaps exhibits low reflectance in the visible region which makes it a prime candidate for solar energy adsorption [11,13,14].

It is already proved that the sulfur atoms on the exposed surface of transition metal chalcogenides increases the HER activity of a material. CuS possess layered crystal structure having weak van der Waals interactions between two double layers of Cu. Sulfur present in the CuS have empty 3-p orbitals which further helps to easy capture electrons and promotes electron transportation [15]. However, the low photogenerated charge transfer rate on the photocatalyst surface and high aggregation of CuS nanomaterials significantly degrade the

* Corresponding author.
E-mail addresses: habib.ashassi@gmail.com, habib_ashassi@yahoo.com (H. Ashassi-Sorkhabi).

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photocatalytic performance. In order to overcome these drawbacks, coupling of CuS with other co-catalysts can increase its electron–hole separation yield by the efficient charge carrier dissociation at the interface of the formed heterojunctions [13,16–20]. These studies indicated that CuS particles may expand the light absorption range and prolong the life time of photogenerated charge carriers. Despite all these reports, the efficient nanocomposite still remains a challenge.

Yu' group [11] proposed that under visible-light irradiation, CuS/Cu_2S heterostructures will generate the optoelectronics which are transferred by the carrier of rGO due to effective interfaces constructed of rGO–CuS/CuS. Recently, Dubale et al. [21] have been proposed a Cu_2O/CuO heterostructure modified with CuS (Cu_2O/CuO/CuS) and with both CuS and Pt (Cu_2O/CuO/CuS/Pt) as highly promising and stable photocathode for solar hydrogen production. In our last publication, we presented nanocatalysts based on CoS_2, as non-precious metal catalysts, were directly prepared by a sonoelectrochemical method [22].

Being inspired by all of these reports we have introduced one step sonoelectrochemical synthesis method to prepare PPyCuS@GOPt nanocomposite film. This study highlights the significance of using modified polypyrrole with copper sulfide as a photoelectrocatalyst for HER. To the best of our knowledge, there is no report on photocatalytic hydrogen production over CuS and Pt loaded PPyGO nanocomposite. So, we expect that the favorable properties of GO and PPy can be extended by integrating them with Cu_2O, CuS and Pt nanomaterials to form nanohybrid for improving the hydrogen evolution reaction under visible light irradiation.

2. Experimental

2.1. Materials

Pyrrole was obtained from Merck and was purified by distillation prior to use. All reagents and solvents were of analytical grade and were purchased from commercial sources and were used without further purification.

2.2. Fabrication of electrodes

The working electrode was a 1 × 1 cm^2 copper sheet mounted in a polyester resin in such a way that only one surface with 1 cm^2 area remains uncovered. These electrodes were polished with emery papers to remove the oxides, and then followed by a distilled water rinsing. Copper oxide nanoparticles were prepared by anodizing of the copper substrates in the KOH electrolyte. The anodization was performed using two-electrode cell with copper sheet as the working electrode and platinum as the counter electrode, under constant applied voltage of 10 V at room temperature (approximately 25 °C) for 120s. Both electrodes were immersed in the electrolyte (50 ml) and were spaced 20 mm apart from each other.

2.3. Preparation of photocatalyst

CuS hierarchical flower like nanostructures were synthesized which are consistent with previously reported structural properties [23] and GO was synthesized from natural graphite powder as reported in reference [24]. The catalysts deposited in this study as photocathode were prepared by sonoelectrochemical method. The Cu_2O photoelectrode was immersed into a sonoelectrosynthesis solution was made by dissolving the Pyrrole monomers in oxalic acid solution containing the dodecylbenzenesulfonic acid, DBSA, as doping and dispersing agent. Prior to electropolymerization, the CuS nanoparticles were completely dispersed in the bath by sonication for about 2 h. Sonoelectrochemical synthesis was performed with an Autolab PGSTAT30 Potentiostat/Galvanostat (Netherland Instruments) coupled with a sonication device (Dr. Hielscher S400UP model). The horn tip of the sonication device was inserted about 1 cm into the bath solution. Saturated calomel electrode (SCE) and Pt plate were used as reference and counter electrodes, respectively. The working electrodes were anodized copper with a 1 × 1 cm^2 surface area. Then, the sonoelectrodeposition was conducted at constant current density of 4 $mA.cm^{-2}$. In order to synthesis of PPyCuS@GOPt nanocomposite films, graphene oxide (0.05 g L^{-1}) and H_2PtCl_6,$6H_2O$ (0.01 M) were added in bath solution and were sonicated for 2 h.

The characterization of the CuS nanoflower like structures was obtained using field emission-scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). The HRTEM images were obtained with JEOL JEM-2010F microscopes operating at 200 kV. The morphology of the samples was examined using a MIRA3 FEG-SEM, Tescan field emission scanning electron microscope (FESEM).

Besides, by using a Bruker, Tensor 27 spectrophotometer in the wave number range of 4000–400 cm^{-1}, the Fourier transform infrared (FT-IR) spectra were recorded. Indeed, the prepared nanocomposite films on copper were scratched and mixed with KBr to prepare the FT-IR spectra.

2.4. Evaluation of photoelectrocatalytic activity

The Enhanced photoelectrochemical performance of the modified film electrodes for HER was assessed in 0.5 M H_2SO_4 solution. Three electrode system is consisting of Hg/Hg_2Cl_2 in saturated KCl as reference electrode, a Pt plate as the counter electrode and the prepared Cu_2O/PPyCuS or Cu_2O/PPyCuS@GOPt as working electrode. Besides, for the photoelectrocatalytic measurements a 400 W lamp was used.

Cyclic Voltammetry, CV, chronoamperometry and electrochemical impedance spectroscopy, EIS, tests were carried out at 298 K using GPES and frequency response analyser, FRA, module respectively. The EIS measurements were carried out at open circuit potential, OCP, using a ± 10 mV amplitude voltage in the frequency range of 10 kHz–10 mHz. Consequently, the results of impedance measurements were analyzed by Zview® (II) software and an appropriate equivalent electrochemical circuit was proposed.

3. Results and discussion

3.1. Electrochemical fabrication

As mentioned before, Cu_2O because of its narrow band gap as well as its non- toxicity and relatively low cost is highly desirable material for use in photocatalysis. So, we employed a simple and straightforward approach according to the obtained results by Allam and Grimes [25], to fabricate Cu_2O nanoarchitectures by anodization in KOH aqueous electrolyte. Indeed, Cu_2O nanoparticles were loaded by successive anodizing of copper substrate. The proposed mechanism is that the Cu_2O film growth mechanism includes concurrent processes: a pure electrochemical step and heterogeneous nucleation of Cu_2O from the dissolved Cu and OH, and the solid-state reaction between diffusing Cu and oxygen that causes Cu_2O formation underneath the electrode surface.

Then, we carried out one step synthesis procedure using synchronous physical acoustic cavitation assistance and electrochemical condition, sonoelectrochemical method to synthesize PPyCuS nanocomposite film on anodized copper. Furthermore, in order to investigate the effect of dual co-catalyst of GO and Pt, the PPyCuS@GOPt nanocomposite film was prepared.

3.2. Morphological characterization

Following the synthesis procedure described above for CuS hierarchical structures, characterization was performed by FESEM and high-resolution transmission electron microscopy (HRTEM). As dis-

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