

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Polymers functionalized with 1,2-benzenedithiolate-bridged model compound of [FeFe]-hydrogenase: Synthesis, characterization and their catalytic activity

Xinglong Zhu^a, Wei Zhong^b, Xiaoming Liu^{b,*}

^a School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China

^b College of Biological, Chemical Sciences and Engineering, Jiaying University, Jiaying 314001, China

ARTICLE INFO

Article history:

Received 20 March 2016

Received in revised form

25 April 2016

Accepted 3 June 2016

Available online 18 June 2016

Keywords:

[FeFe]-hydrogenase

Functional polymer

Click chemistry

Membrane electrode

Electrocatalysis

ABSTRACT

Three polymers functionalized with 1,2-benzenedithiolate-bridged diiron carbonyl units, **Polymers 1–3**, were prepared by using three diazide monomers with different organic frames via “click chemistry”. These polymers were characterized by IR spectroscopy, thermal gravimetric analysis, scanning electron microscopy and electrochemistry. Their solubility, morphology and catalysis on proton reduction are largely controlled by the organic moieties of the diazides. The presence of carboxylates in **Polymer 3** causes significant difference both physically and chemically (electrochemically). It is soluble in water but decomposes rapidly in DMSO. Its stability is much improved after being assembled into membrane electrodes. The electrodes assembled from these polymers are relatively robust and all operational in water. The carboxylate in **Polymer 3** turns out a better proton-relay in catalysis by exhibiting higher catalytic efficiency in both solution and solid state (membrane electrode).

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

At the end of the last century, the structure of [FeFe]-hydrogenase was successfully revealed [1,2]. The revelation has attracted a great deal of attention in both synthetic and biological community and initiated enthusiasm in mimicking synthetically the diiron center of the enzyme. It was hoped that the catalytic mechanism of the enzyme could be elucidated at molecular level and further artificial systems could be derived with comparable properties to the natural system. Indeed, over the last 18 years or so, significant progresses have been achieved [3–14]. Notably, the identity of the central atom

of the bridge dithiolate and the essential role of the secondary amine N has finally been established [15,16]. Electrochemically investigating the electron transfer mechanism of diiron models has shed light on understanding how the enzyme performs the two successive electrons redox process of reversible hydrogen evolution without overpotential [6,7,17–27]. Extensive studies in the electron transfer of diiron models reveal that the structural isomerization of the diiron center upon the first electron transfer, which leads to the so-called potential inversion, could be the key for the enzyme to perform the catalyst without acquiring additional energy [6,7,22,27–32].

* Corresponding author. Tel./fax: +86 (0)573 83643937.

E-mail address: xiaoming.liu@mail.zjxu.edu.cn (X. Liu).

<http://dx.doi.org/10.1016/j.ijhydene.2016.06.025>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Among the mimicking chemistry of the enzyme is using macromolecular or polymeric material to mimic, to some extent, the proximal environment around the active center of enzyme [33–38]. By employing host–guest chemistry, the diiron unit was successfully housed in the cavity of β -cyclodextrin (β -CD) [34]. The assembled system exhibited improved catalytic performance on proton reduction and stability. Utilizing the thiols of a short peptide to assemble a diiron mimic is conceptually one step close to mimicking the proximal environment around the metal center of the enzyme [33,38]. But further lengthening the protein chain for assembling a mimicking system has not reported due to properly synthetically challenging. Another approach to assemble an electrocatalytic electrode has been chemically anchoring a diiron unit to a matrix. The matrix could be the chemically modified surface of vitreous carbon and polypyrrole [39–42]. In our group, a number of strategies were employed to incorporate chemically diiron mimics into polymeric materials. For a diiron model bearing alkyne group(s), polymeric materials were obtained by either polymerizing the mimics or reacting it with polymers functionalized with azide on simple organic azide via “click chemistry”. Such polymers could be PVC [43] and PEI [44]. Since the polymers functionalized with diiron mimics contains terminal alkyne group, it could be chemically anchored onto the surface of gold modified with organic azide [45]. For other polymeric materials, spin-coating technique could be employed to assemble a film electrode. To improve conductivity, multi-walled carbon nanotubes (MWCNTs) or graphene could be doped into the films [43,46–48]. In addition to the approaches described above, electrospinning technique could be also used to obtain fibrous membranes functionalized with diiron mimics to fabricate membrane electrodes [47]. Those electrodes exhibited electrochemical response. When the matrix used to support the diiron mimics is hydrophilic, electrode could be operated in water [46,47]. However, the major problem for those electrodes is the bleaching of the active components, the diiron mimics, during the catalysis. In other word, the stability of the mimics in those matrices needs to be improved.

It is well known that diiron mimics with 1,2-benzenedithiolate-bridged as bridging linkage are robust upon reduction. They show perfectly reversible two-electron reduction [20,29,30,49]. Among the complexes of this type is the mimic of the bridging linkage, 1,4-dihydroxybenzene-2,3-dithiolate. The two hydroxyl groups allow chemically grafting additional functional groups, such as alkyne. By reacting the alkyne group with an organic diazide, a linear polymeric containing regularly a diiron unit can be obtained as we described previously [50]. Herein, we further report our continual effort devoted in this chemistry. By varying the functional group of the diazide, the properties of the polymeric material such as hydrophilicity, basicity could be delicately tuned. In this piece of work, the preparation, characterization and electrochemical investigation of three polymers derived from three organic diazide are described. It turns out that carboxylate is the most efficient proton relay in proton reduction catalyzed by the polymers. The carboxylates destabilize also the polymer via substitution reaction in an appropriate solvent (DMSO). But when it is incorporated into Nafion matrix, its stability is improved and the resultant

membrane electrode exhibited much higher efficiency in catalysis compared to the other two.

Experimental section

Material, instruments and general procedures

Reactions and operations related to the organometallic compounds appeared in this work were carried out under argon atmosphere with standard Schlenk techniques when necessary. Solvents were dried and distilled prior to use with appropriate drying agents. The reagents were purchased from Aladdin Reagent Co Ltd. $\text{Fe}(\text{CO})_5$ and the eluents of chromatography on silica gel were purchased from local suppliers and used as received. Compounds $[\text{Fe}_2(\mu\text{-S})_2(\text{CO})_6]$ [51], $[\text{Fe}_2(\mu\text{-S})_2(\text{C}_6\text{H}_2)(\text{OH})_2(\text{CO})_6]$ [52], L_1 [50], L_2 [53] and PEI-RGO [54] were prepared according to literature procedures.

Infrared spectra were measured with Agilent 640 spectrophotometer. ^1H and ^{13}C NMR spectra were collected with a Varian INOVA 400 NMR spectrometer. Scanning electron microscope (SEM) images were obtained on HITACHI S-4800. Thermal gravimetric analysis (TGA) measurement was carried out on NETZSCH Thermische Analyzer at a heating rate of 10 K min^{-1} under nitrogen flow. The iron contents of the polymers were determined by ICP-AES analysis (Varian 710-ES) for iron amount of samples.

Synthesis of Polymers 1–3

A red solution of $[\text{Fe}_2(\mu\text{-S}_2\text{C}_6\text{H}_2(\text{OCH}_2\text{C}\equiv\text{CH})_2)(\text{CO})_6]$ (**1**) (0.33 g, 0.67 mmol) and 2,6-diazidomethylpyridine (L_1) (0.11 g, 0.60 mmol) in CH_3CN (30 mL) was added the catalyst of CuI (15.8 mg, 0.083 mmol) and Et_3N (0.2 mL, 1.4 mmol) in CH_3CN (5 mL). The mixture was stirred at room temperature for overnight. The reaction mixture was filtered to remove any insoluble solids. Removal of the solvents produced a brown crude product. The crude product was dissolved in THF and diethyl ether was added to crush out the polymer, which was repetitively carried out three times to give **Polymer 1** (0.23 g, 52%). **Polymer 2** (0.25 g, 59%) was analogously prepared by using bis(2-azidoethyl)amine (L_2) (0.097 g, 0.62 mmol) and complex **1** (0.352 g, 0.67 mmol).

Polymer 3 was prepared by reaction of sodium bis(2-azidoethyl)glycinate (L_3) (0.14 g, 0.57 mmol) with complex **1** (0.34 g, 0.63 mmol) in methanol at room temperature for overnight. Removal of the solvents produced a brown product, **Polymer 3** (0.37 g, 78%). The crude product was ground into powder in an agate mortar and the powder was repetitively bleached with diethyl ether and dried in vacuum.

Preparation of PEI–RGO

Graphite oxide (GO) was prepared following literature method with modification [50]. While maintaining agitation, expanded graphite (5.0 g) and NaNO_3 (3.75 g) were mixed with sulfuric acid (150 mL, 95%) and then KMnO_4 (20 g) was slowly added. The reaction mixture was further stirred for 20 h at room temperature and then allowed to stand for 5 days before deionized water (500 mL) was slowly added. The reaction

Download English Version:

<https://daneshyari.com/en/article/7709860>

Download Persian Version:

<https://daneshyari.com/article/7709860>

[Daneshyari.com](https://daneshyari.com)