Journal of Molecular Liquids 268 (2018) 343–353

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Facile one-pot synthesis of novel structured IONP@C-HIOP composite as superior electrocatalyst for hydrogen evolution reaction and aqueous waste investigation of bio-imaging applications

Raji Atchudan [a,*,1], Thomas Nesakumar Jebakumar Immanuel Edison [a,1], Suguna Perumal [b,1], Mani Shanmugam [c,1], Yong Rok Lee [a,*]

[a] School of Chemical Engineering, Yeungnam University, Gyeongsan 38541, Republic of Korea
[b] Department of Applied Chemistry, Kyungpook National University, Daegu 41566, Republic of Korea
[c] Department of Chemistry, Institute of Aeronautical Engineering, Dundigal, Hyderabad 500043, India

ARTICLE INFO

Article history:
Received 8 May 2018
Received in revised form 29 June 2018
Accepted 17 July 2018
Available online 19 July 2018

Keywords:
Hydrothermal
Iron oxide nanoparticles
Electrocatalyst
Hydrogen evolution reaction
Hydrogen energy
Bioimaging

ABSTRACT

Hexagon-shaped composite made up of iron oxide nanoparticles@carbon (IONP@C-HIOP) was successfully synthesized at 185 °C by a simple hydrothermal method. All the analytical results confirmed the formation of IONP@C-HIOP with a uniform size without apparent aggregation. The IONP@C-HIOP composite exhibits excellent catalytic activity towards hydrogen evolution reaction (HER) with lowest onset-potential (−25 mV_{RHE}) and Tafel slope (45 mV dec^{-1}) in 0.5 M H_2SO_4 aqueous electrolyte. The high electrocatalytic performance of the composite towards HER attributes to the carbon decorated IONPs, providing a conducting network for fast electron transport from IONPs to electrodes. The composite shows high stability representing a synergistic effect between IONPs and carbon for efficient HER. In addition, the supernatant solution (byproduct) of IONP@C-HIOP showed durable fluorescence activity and was used as a label-free fluorescent probe for live cell imaging applications. This method of synthesis is a simple and economic for multi-diverse applications. Thus, the main product of synthesized IONP@C-HIOP might be an ideal choice for environmental-friendly applications HER and the byproduct for cell imaging.

1. Introduction

In recent years, hydrogen energy has attracted a promising sustainable, secure, and clean alternative fuel in the field of renewable energies [1–3]. Mostly, hydrogens are produced from natural gases, oil, and coke but they emit dangerous gases such as carbon dioxide and other greenhouse gases into the environment. Among them, water electrolysis is quite simple, cost-effective, the eco-friendly pathway for hydrogen production and considered to be the best alternatives of hydrocarbon fuels which could meet the global energy demands [4, 5]. However, precious metal electrocatalysts such as platinum and platinum-based nanomaterials are important for water electrolysis (water splitting), which suffer from shortage and are unaffordable for large-scale hydrogen production [6, 7]. Hence, exploring to find a highly efficient, low-cost and environmental-friendly electrocatalyst for water-splitting systems has attracted challenges in pursuit of researchers. In recent times, the transition metal-based (Fe, Co, Ni and etc.) composites have been widely used as an alternative material instead of platinum and platinum-based nanomaterials due to their abundance, low-cost and high catalytic activity towards hydrogen evolution reaction (HER) [8, 9]. The HER ($2H^+ + 2e^- = H_2$) at the cathode is one of the two half-reactions occur during the water splitting process. The electrode materials with lower overpotential (lower Tafel slope) must be an important factor for enhancing the HER activity. Basic electrocatalytic activity and the active surface area should be significantly high to reach the lower overpotential. In general, Fe, Co, and Ni-based carbon possess good electrocatalytic properties for HER [10]. Among them, Fe-based carbon has been credited numerous attentions due to their unique properties such as good electrical conductivity and etc. Also, it has low-cost and earth abundance [11].

In this work, we report the preparation of IONP@C-HIOP composite using Iron (III) acetylacetonate and benzyl alcohol at 185 °C by a simple hydrothermal method. The synthesized IONP@C-HIOP composite was characterized by various analytical techniques and utilized as a catalyst for HER. IONP@C-HIOP showed enhancement of the electrocatalytic activity, which exemplify the synergic effect between IONP and carbon. This is a simple and economical synthesis of IONP@C-HIOP composite, might be a perfect choice and perspective for many potential energy

* Corresponding authors.
E-mail addresses: atchudanr@yu.ac.kr (R. Atchudan), yrlee@yu.ac.kr (Y.R. Lee).
[1] Authors contributed equally to this work.

https://doi.org/10.1016/j.molliq.2018.07.078
0167-7322/

applications including HER. Also, the supernatant solution, the byproduct was collected by centrifugation of IONP@C-HIOP composite which exhibits blue fluorescence under UV-light irradiation due to the presence of carbon dots (C-dots) in the solution. The obtained C-dots allow potential applications in the biomedical field, especially, live cell imaging with good biocompatibility.

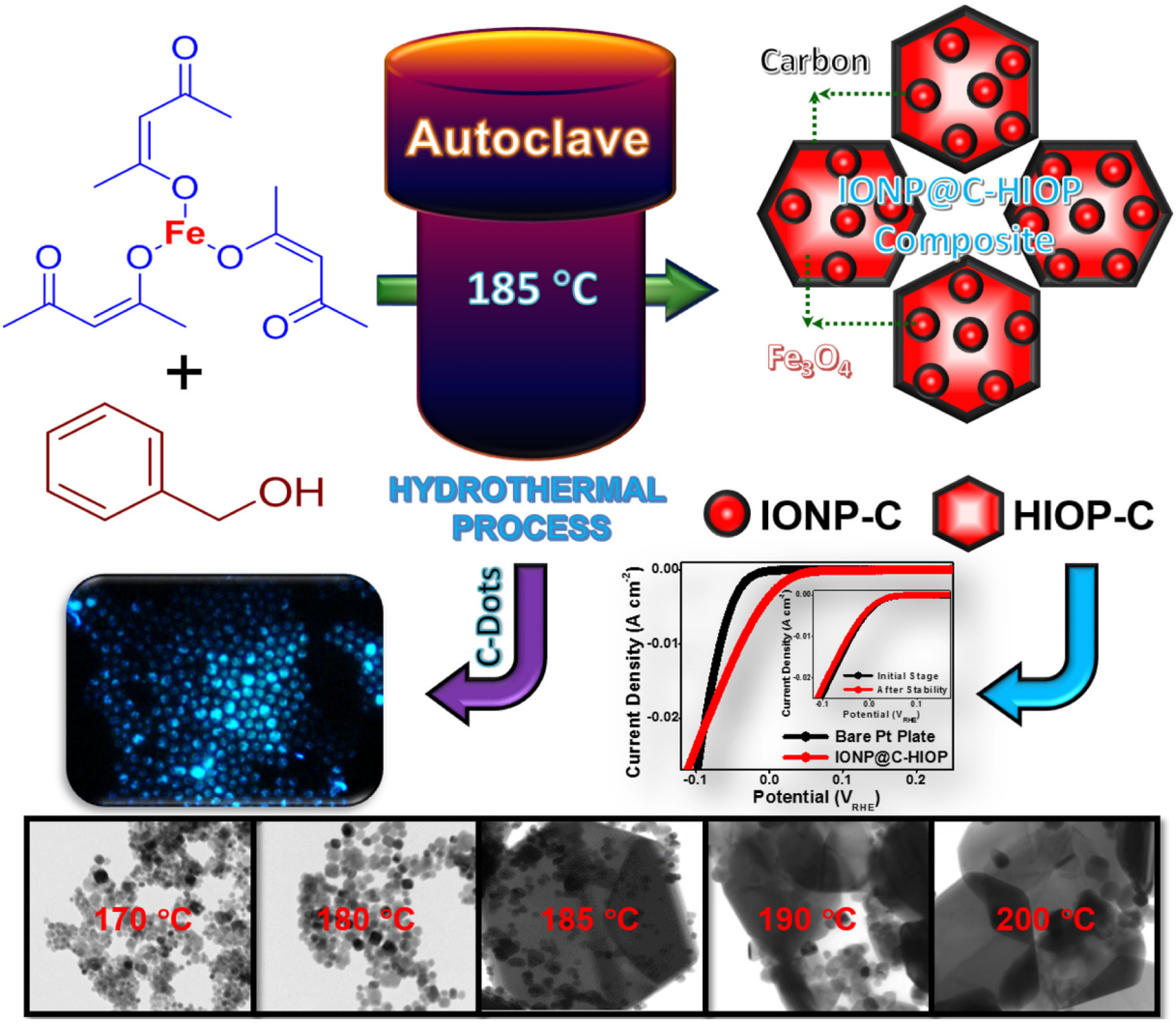
2. Materials and methods

Iron (III) acetylacetonate, polyvinylidene fluoride (PVDF), *N*-methylpyrrolidone (NMP), benzyl alcohol, acetonitrile, ethanol, toluene, dimethyl sulfoxide (DMSO), phosphate buffered saline (PBS), sulfuric acid (H_2SO_4) and dichloromethane (DCM) were purchased from Sigma Aldrich. Carbon cloth (CC) electrode was purchased from FuelCellStore, College Station, Texas, USA. The yeast strains *C. albicans* was obtained from the Korean Cell Type Culture Collection (KCTC), Seoul, Republic of Korea, maintained in 10% v/v glycerol stocks, and stored at −80 °C until further use. Overnight cultures in malt extract (ME) broth were used for the bioimaging experiments. All obtained chemicals were used as received and deionized (DI) water was used throughout this work.

The monodisperse IONP@carbon composites were synthesized by using the procedure described in the earlier reports without any major modifications [12]. 2.0 g of iron (III) acetylacetonate was added to 40 mL of benzyl alcohol inside a glovebox. The reaction mixture was taken into a 100 mL inner volume of Teflon lined autoclave. The autoclave was sealed carefully and then heated to 170–200 °C for 48 h in a hot air oven. After hydrothermal treatment, the final reaction mixture was cooled to room temperature. The final mixture was centrifuged and washed with ethanol and DCM. The resulting solid was dried at 70 °C for 5 h in a hot air oven, and stored under argon until further use. The byproduct will be mention as a supernatant solution throughout this manuscript from this point. The obtained solution was freeze-dried and stored for further use as it contains C-dots. The synthesized C-dots materials were thoroughly characterized by various physicochemical techniques, the detailed instrumentation techniques, and electrochemical measurement procedure are described in the ESI.

3. Results and discussion

The monodisperse IONP@carbon composite and C-dots were synthesized simultaneously by a simple hydrothermal method. Scheme 1 shows the synthesis of novel structured IONP@C-HIOP composite and C-dots, also their suitable biology and environmental-friendly energy applications. The composites were synthesized by varying the reaction temperature from 170 to 200 °C. The composites prepared temperatures from 170 to 180 °C resulted in a spherical shape as shown in Figs. S1 and S2. In addition, size of composites increases with increase in temperature. Whereas irregular plate-like shape composites were obtained for the reaction temperature between 190 and 200 °C. The



Scheme 1. The synthesis route of IONP@C-HIOP composite, C-dots and their suitable applications.