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Microwave Assisted Green Synthesis of Ag/AgO Nanocatalyst as An Efficient OER Catalyst in Neutral Media

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ABSTRACT

The development of robust, stable and abundant materials that are operating under neutral conditions are of great importance for the electrocatalytic conversion of water to hydrogen using sunlight. Here, a robust and highly stable, silver oxide based electrocatalyst composite system for the efficient Oxygen Evolution Reaction (OER) was presented. The developed Ag/AgO composite catalyst with a small (10-15 nm) and homogenous particle size distribution was fabricated using microwave synthesis. In the neutral media, the Ag/AgO electrocatalyst achieved 1 mA cm^{-2} current density at 600 mV overpotential, and exhibited a lower Tafel slope of 80 mV dec^{-1} compared to MnOx-based catalysts in the range of 450–600 mV. These values are comparable to those of the promising catalysts such as Mn, Co, Ni oxide based systems in the neutral media. The results showed that the developed electrocatalyst system based on Ag/AgO composite could be used in multi-layer electrocatalyst system designs.

Keywords:
Silver nanoparticles; Microwave; Catalytic activity; Oxygen evolution reaction.

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INTRODUCTION

In the next 50 years, there is an urgent need for the sustainable and clean alternative energy sources to meet the increasing energy demands. Among the alternative energy sources, hydrogen energy is one of the most promising candidates [1-3]. Water, as an inexpensive and mostly abundant at around the world, is the main source for the generation of the hydrogen; however, obtaining hydrogen from water is thermodynamically unfavorable and requires a high amount of energy [4]. For this reason, economic energy conversion systems are required for the production of hydrogen gas from water [5].In this point, catalysts are considered as one of the most important parts of the energy transformation. Nevertheless, designing new sustainable catalysts, which can achieve energy conversions at low costs and improved in terms of shape, size and chemical composition, is a great criterion. Therefore, there has been a growing interest for the solution of this task [5-7].

In the last decades, nanomaterials have received much attention due to their unique physical, chemical, optical, magnetic, and electrical properties [8, 9]. Among these materials, precious metals such as Pd, Pt, Au and metal oxides; Ru_2O and Ir_2O are the inevitable part of the production of energy from water through its splitting to H_2 and O_2 [10, 11].

However, their high costs and low abundances on the earth make handicap for their easy availability in the sustainable energy system [12, 13]. Regarding these disadvantages, there have been a long-term demand for the development of robust, inexpensive and highly efficient electrocatalyst systems for the energy applications. In this perspective, earth-abundant metals such as Ag, Co, and Ni are considered as more economic alternatives [14, 15]. Nevertheless, a little attention has been devoted to the preparation of electrocatalyst from silver nanocomposites so far [16]. As well as the preparation of the silver nanocomposites, their stabilities in the media where they take a role in the energy applications are of great importance [17, 18]. The nanocomposites may exhibit different characteristics owing to their unique structures and morphologies depending on their synthesis conditions [19]. Therefore, alternative approaches for the synthesis of silver nanocomposites are necessary and important as much as the application field where they take action.

In material synthesis, microwave technology (MT) is a promising alternative to the conventional methods depending on its superiority, especially in terms of spe-

ed, low consumption of chemicals and energy [20]. MT not only keeps the reaction media steady state but also; therefore, promotes uniform product formation [20, 21]. In this way, it also enhances the large-scale production of the advanced materials with the desired quality of interest. Recent studies showed that MT has also a significant role on the reaction kinetics, particle-size and morphology of the resulting products [22]. Due to these advantages, the MT has received an increasing attention in the synthesis of various materials such as metal oxides, carbon and precious metal based catalysts, peroxides and many mores [20-22]. In recent years, MT has also been facilitated in the fabrication of advanced materials, as well [23, 24].

Considering the above-mentioned advantages of MT, herein, we report the rapid, simple and highly reproducible synthesis of Ag/AgO nanoparticles via microwave irradiation. The as synthesized nanoparticles were used as an efficient OER electrocatalyst for water splitting reactions. The prepared Ag/AgO nanocatalysts showed excellent water splitting activity under neutral media conditions.

EXPERIMENTAL SECTION

Materials

Silver nitrate ($AgNO_3$), oleic acid, oleylamine, ethanol and 1-octanol were purchased from Merck and used as receieved

Synthesis of Ag/AgO nanoparticles

In a typical procedure, a mixture of oleic acid (40 ml v/v 1/1), 1-octanol and oleylamine along with 100 mg $AgNO_3$ was added into a 100 mL flask equipped with a stirring bar under nitrogen atmosphere. The as-prepared solution was refluxed under microwave irradiation according to the desired program (100 W, 110 °C, hold for 10 min). Subsequently, ethanol was added to the original reaction solution to precipitate Ag/AgO NPs. Ag/AgO NPs was filtered, washed with deionized water several times, and then dried at 65°C for 24 h.

Instrumentation

Powder X-ray diffraction patterns (XRD) of samples were collected using a Pan Analytical Empyrean instrument with Cu Kα radiation (λ=1.54056 Å) from 3 to 70° (2θ) at a scanning rate of 2° min^{-1}. The morphologies and structure of the samples were examined by scanning electron microscopy (SEM, ZEISS Sigma 300) and Transmission electron microscopy (TEM, Hitachi HT 7700). Microwave-irradiated reactions were carried out with a microwave reactor (Discover SP, CEM, Matthews, NC, USA). The electrochemical measurements were carried on Autolab workstation (PGSTAT204, Metrohm, Switzerland) using three-electrode system.

Electrochemical measurements

The electrocatalytic activitity of Ag NPs was tested in deoxygenated 0.2 M phosphate (at pH 7) buffer solutions by using typical three electrode set-up similar to that reported by Joya et al. [16]. Ag/AgCl electrode (sat. KCl, +204 mV vs. NHE at 25°C) was used as the reference and a Pt plate as the counter electrode (1 cm^2). The potential, measured against an Ag/AgCl electrode, was converted to the potential versus the reversible hydrogen electrode (RHE) according to ($E_{RHE} = E_{Ag/AgCl} + 0.204 + 0.059$ pH). The cyclic voltammogram (CV) and linear sweep voltammogram (LSV) were collected with a scan rate of 20 $mV \cdot s^{-1}$ between 0.2 V - 1.3 V vs. Ag/AgCl. Tafel slope was calculated by using the following equation, η= a+b log (j), where b is the Tafel slope, J is the current density, η is the overpotential value.

Preparation of the electrode

Ag/AgO NPs were obtained in solid form by simple centrifugation from ethanol. A homogeneous suspension for electrode was prepared using the solid Ag/AgO NPs by thoroughly mixing 10 mg of the catalyst with 10 µL of 0.5 wt % Nafion solution, 0.1mL of isopropanol. The electrode was prepared by drop-coating 11 µL of the prepared suspension onto a clean 1 cm^2 Fluorine doped Tin Oxide (FTO). The coated electrode was then dried at 60°C in oven for 30 min.

RESULTS AND DISCUSSION

Characterization of Ag/AgO thin film

The surface of the Ag nanoparticles may be oxidized during the synthesis or film preparation steps (Fig. 1). This change was observed in the XRD results of Ag NPs composed of thin films. The cubic phase of Ag can be indexed to the peaks at 38.1°, 44.3°, 64.4°, and 77.5° corresponding to (111), (200), (220), and (311) of Ag (JCPDS No. 04-0783)

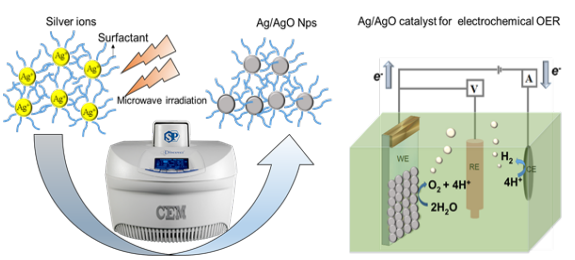

Figure 1. Schematic illustration of Ag/AgO NPs fabrication and its evolution as OER catalyst..

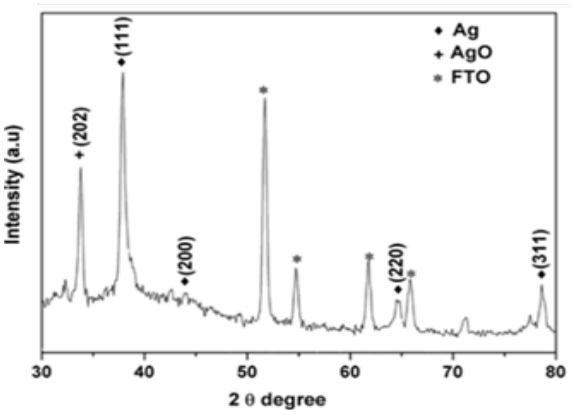

Figure 2. SX-ray diffraction (XRD) pattern for Ag NPs film on FTO glass.

[25], respectively. The peaks of AgO at 32.6° is consistent with the (202) of the standard card of AgO (JCPDS No. 84-1108) [26].

The morphological study was performed using SEM analysis. Fig. 3 shows SEM images of Ag/AgO nanoparticles. SEM image of the electrode surface displays that the coated film consists of Ag-AgO NPs with homogeneous particle size. Film formation on FTO with Ag/AgO catalyst was very smooth and homogeneous. This film preparation demonstrates that the applied procedure and method of application are suitable for the catalyst.

To further observe the morphology of Ag/AgO, the TEM analysis is showed in Fig 4. This image shows the spherical and plate-like morphologies of the NPs. The sizes of sphere-like particles were found to be in the range of 10-15 nm. Although the TEM analysis showed particle size of 10-15 nm, the nanoparticles in the thin film examined by SEM analysis were about 100 nm in size. The difference in particle size in TEM and SEM analysis may be due to agglomeration of Ag/AgO nanoparticles during film preparation.

Water oxidation performance of Ag/AgO NP type electrocatalyst

In recent years, in addition to metal oxides, plasmonic

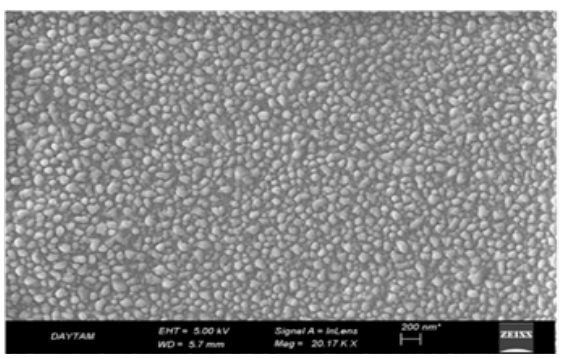

Figure 3. SEM image of Ag/AgO NPs film (top view).

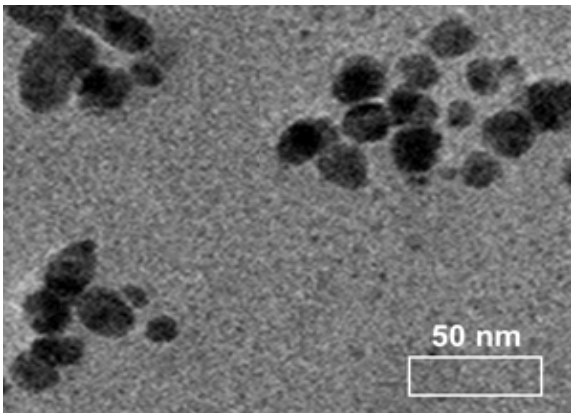

Figure 4. (TEM image of Ag/AgO NPs film.

nanostructures of noble metals (especially Ag and Au) have gained importance in the conversion of solar energy [27, 28]. The particle size, shape and morphology of these nanoparticles can be observed in the SPR band [29]. These physical properties also affect their catalytic activity and stability [28]. Monitoring of physical parameters for the design of electrocatalysts and photocatalysts plays a vital role in the catalyst production process [30]. Therefore, we investigated the electrocatalytic activity of Ag/AgO NPs, as "model"catalyst in water oxidation.

The synthesized Ag/AgO NPs was prepared as a film by 11 µL drop-coating of homogeneous suspension onto FTO coated glass. Electrochemical water oxidation activity of Ag/AgO NPs electrodes was evaluated in deoxygenated 0.2 M phosphate (pH=7) buffer solutions similar to that reported by Joya et al. [16]. Fig. 5a (CV) shows a sharp increase at 1.3 V (E vs NHE) (η ≈ 480 mV), associated with oxygen evolution from the electrode surface. In the neutral medium, Ag/AgO electrocatalyst achieved 1 mA cm^{-2} current density at 600 mV overpotential. At the same time, electrocatalyst exhibited a lower Tafel slope of 80 mV dec^{-1}, compared to MnOx-based catalysts which have operating overpotential in the range of 450–600 mV [31] (Fig. 5a inset). These overpotential value and lower Tafel slope of the Ag/AgO based composite electrocatalyst are comparable to the promising catalyst canditates such as Mn, Co, Ni oxide based systems in neutral medium [32]. In addition, Ag electrocatalysts are quite stable at a neutral pH compared to the loss of activa-

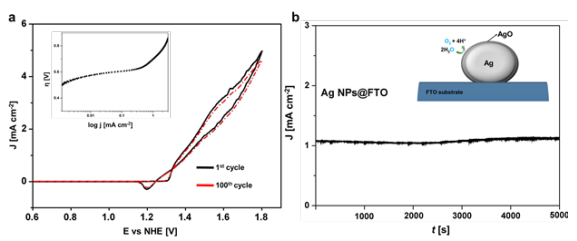

Figure 5. (a) Cyclic voltammetry (CV) (under a scanning rate of 20 mV s-1), (b) Long-term chronoamperometry (LC) (in deoxygenated 0.2 M phosphate buffer) at a constant potential of 1.40 V (E vs NHE).

tion observed in Cyclic voltammetry and Long-term chronoamperometric measurements (Fig. 5a, 5b) in such oxide systems. As a result, electrocatalyst systems based on Ag/AgO composite can be used in multi-layer electrocatalyst system designs.

CONCLUSION

In summary, Ag/AgO based catalysts were prepared as homogenous spherical nanoparticles within 10 minutes using a microwave-assisted protocol. The as-synthesized Ag/AgO nanocomposites were fully characterized by means of X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) methods and their electrocatalytic activities were evaluated for OER in the neutral media. The electrocatalytic activity exhibited by the Ag/AgO composite was found to be comparable to the well-known metal oxide-based catalysts. This catalyst could be one of the promising catalysts in the energy conversion reactions.

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