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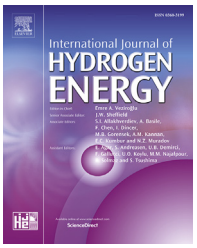

Multifunctional plasmonic Ag-hematite nano-dendrite electro-catalysts for methanol assisted water splitting: Synergism between silver nanoparticles and hematite dendrites

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ABSTRACT

Hydrogen is the most environment friendly fuel and has the largest energy density but still much away from being a viable technology due to the cost associated with its production on-site on-demand. However, hydrogen production via water splitting could become potential commercial technology by designing new catalyst materials with low cost, desired surface structures and properties that govern hydrogen evolution reaction (HER) activity and stability. Here, we report the methanol assisted electrochemical water splitting using silver nanoparticles decorated hematite (Ag-hematite) dendrite nanostructures. Ag-hematite nano-dendrites prepared via two different methods viz. chemical co-precipitation and hydrothermal treatment are analysed and compared for their potential applications towards methanol assisted water splitting. It is found that Ag-hematite nano-dendrites prepared by chemical precipitation method shows much better activity as compared to both the parent materials (i.e. Ag NPs and hematite nano-dendrites) as well as Ag-hematite nano-dendrites synthesized by hydrothermal treatment. A baseline study showing the influence of methanol concentration, catalyst, catalyst support, and operating mode has been established. The analysis of the system was carried out as a function of onset potentials and kinetic parameters, including the Tafel slopes and exchange current densities. The effect of electrochemical promotion was investigated to see if it can increase the efficiency and performance of H_2 production through electrochemical processes. The observed electro-catalytic enhancement could be attributed to the synergistic effect of hematite dendrites, larger surface area of dendrite structure leading to higher loading of Ag NPs on the surface of HDs. Moreover, the endurance study was performed to check the stability of the presented electrocatalyst in acidic medium under both dark and light illumination conditions which shows that the presented composite catalyst is stable for minimum 100 scans even under light illumination with no signs of photo-corrosion.

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Introduction

Hydrogen, due to its largest energy density over any other fuel and no harmful side products after its combustion is considered as an answer to the threat of depleting fossil fuels and the global climate change especially associated with the use of fossil fuels. However, hydrogen is currently expensive than fossil fuels mostly because of the resources and methods used for its production including steam reforming, partial oxidation, plasma reforming and electrolysis [1,2]. Photo-biological and artificial oxygenic photosynthetic approaches of hydrogen production has also attracted significant interest in minimizing the negative impacts of fossil fuels [3,4], particularly manganese compounds have been used as functional models of the water oxidizing complex for hydrogen production via water splitting [5,6]. Among several methods, steam reforming is considered to be the most cost-effective route for large scale hydrogen generation but it has various associated issues; such as carbon monoxide removal, long start-up time, the storage and the transport of hydrogen. Therefore, onsite-on-demand hydrogen production at small scale in eco-friendly manner is under urgent need [7–10].

Hydrogen production from water electrolysis would be the most promising option that can generate most pure hydrogen onsite-on demand [10,11]. However, there are two major concerns associated with this technique which has to be addressed in order to make it a viable technology; (i) The high energy requirement in terms of electrical energy consumption (theoretical; 39.4 kW h/kg & practical; 55 kW h/kg) due to higher voltage (theoretical 1.23 V vs RHE) required for the electrolysis of water [10,11] and (ii) the low efficiency of presently used electro-catalyst materials especially related to their charge shuttling ability and charge carrier separation and collection processes in case of photo-anodes [12,13]. This method can become more promising if low cost electricity generation is followed or electricity from renewable source is used with maximum possible efficiency.

The first issue can be tackled if the water electrolysis is carried out at much lower voltage as compared to 1.23 V vs RHE. In this regard, methanol assisted water electrolysis is a promising method which also serves the onsite-on demand hydrogen production requirement for the portable power supply applications because the theoretical voltage required for methanol-water solution electrolysis is only 0.02 V vs RHE, which is quite lower as compared to water electrolysis without methanol i.e. 1.23 V vs. RHE [10]. Since, the first report on high-efficiency system for electrochemical production of H_2 gas from CH_3OH in aqueous NaOH and KOH media in 2007 by Reichman and William, the methanol assisted hydrogen production technology is looked in a most optimistic way with all potential for commercialization. Narayanan et al. [14] patented H_2 production by electrolysis of organic fuel and water circulating solutions using a wide range of membrane electrode assemblies. Using the preferred configuration which includes Nafion, Toray paper, 1–4 mg/cm^2 supported or unsupported catalyst loadings of Pt–Ru at the anode and Pt at the cathode, un-acidified CH_3OH aqueous solutions from 0.1 to 8 M and temperatures from 5 to 120 °C, it was shown that current densities as high as 800 mA/cm^2 could be sustained at 0.5 V.

Second issue which is related to the electrocatalyst materials can be resolved by boosting the charge shuttling efficiency of the materials for the photo-assisted electrolysis process [13]. This can be achieved by integration of different materials within the same structure so that multiple functionalities may be incorporated in the near proximity for example metal tips grown on semiconductor dendrite structures with quite larger surface area. In case of dendrite nanocomposites, dendritic shape would lend higher surface area which would lead to the better electro-catalyst system. Furthermore, it can not only serve as anchor point for better electrical contact but also improvise the charge separation at the metal–semiconductor interface that may enhance electrocatalytic and photo-electrocatalytic activity [15].

In most of the cases, Pt and Pt-Ru alloys with higher loading (ca. 1–4 mg/cm^2) has been the material of choice for efficient H_2 production using methanol assisted water electrolysis. However, considering the high cost and scarcity of these precious metals, partial or complete substitution and decrease of catalyst loading amount without compromising the electrolysis activity is extremely important. Moreover, CO poisoning of Pt surfaces is widely known challenge for the stability of Pt based electro-catalyst especially for longer usage. Variety of materials, showing high catalytic activity, have been studied as an alternative of Pt. Palladium-based electrocatalysts are shown to be a promising candidate to replace pure Pt, especially for low-temperature fuel cells, due to their lower cost, high activity and better CO tolerance. It has been reported [16] that Pd NPs coated on carbon cloth shows almost fifty times enhancement in activity than Pt as a cathode catalyst for HER. However, there is a concern about the stability of such nanoparticles in hydrogen environment due to structural disorder in the Pd lattice caused by the strong absorption of H_2 [17].

Silver which is one of the most abundantly used noble metals, has high conductivity and promising electro-catalytic activity and could be an impressive replacement to Pt and Pd. In addition to lower cost, Ag NPs are better plasmonic in nature so that if supported on semiconductor substrates can be used as a plasmonic photocatalyst with the possibility of transfer of plasmonic energy directly from the metal to the nearby water molecules in case of water electrolysis [18]. Herein, Ag NPs decorated on dendritic hematite nanostructures are tested for their plausible potential towards methanol assisted water splitting. Dendritic hematite nanostructures were chosen as a support material for decorating Ag NPs because of the larger surface area of dendrite structure that could lead to higher loading of Ag NPs on the surface of HDs. Several kind of methodologies for the synthesis of Ag based composites are reported in the literature. However, the activity of these electro-catalysts are found to be highly specific to the methodology and to the best of our knowledge, no such correlation between the methodology and activity has been studied. Therefore, to further understand the methodology-activity relationship, Ag NPs decorated on dendritic hematite nanostructures obtained via two different methods viz. hydrothermal synthesis and chemical co-precipitation were studied for their comparative electrocatalytic HER activity in presence of methanol. Thus,

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