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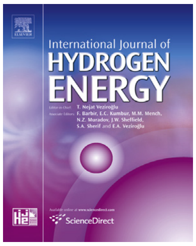

Nano-sized manganese oxide coated sea sand: A new water-oxidizing catalyst

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ABSTRACT

H_2 production by water splitting is a promising fuel to store the intermittent energies. However, water splitting is limited by water oxidation. Herein for the first time we used sea sand for support of nano-sized Mn oxide to obtain a new water-oxidizing catalyst. The compound was synthesized by a simple method and characterized by some methods. The water-oxidizing activities of the compound were also studied under cerium(IV) ammonium nitrate and photochemically produced $Ru(bpy)_3^{3+}$. The results showed that the nano-sized manganese oxide coated sea sand is a good manganese-based water-oxidizing catalyst.

Introduction

Mn oxides are low-cost, environmentally friendly, and stable with polynuclear structures and many redox-active ions [1,2]. In addition, the compounds can appear in a wide diversity of forms with different defects, morphology, porosity and textures, each with a variety of useful and interesting physical and chemical properties [1,2]. Thus, it is not surprising that they are among the most promising compounds for different applications such as using in super capacitors, batteries and water treatment [1,2]. The compounds are also promising as a catalyst or oxidant in different reactions [1,2]. Recently, water splitting to high scale H_2 production has been suggested as a promising route for the conversion of sustainable, but intermittent energies [3]. However, water splitting is limited by water oxidation, therefore, an efficient, stable, cheap and environmentally friendly water-oxidizing compound remains necessary in order to improve water splitting [3].

Among different compounds [4], Mn oxides are very promising for water oxidation [5]. It is interesting to note that Nature uses a Mn cluster to oxidize water to oxygen in the water-oxidizing complex of plants, algae and cyanobacteria [6]. Mn oxides have no easily oxidizable ligands and thus are

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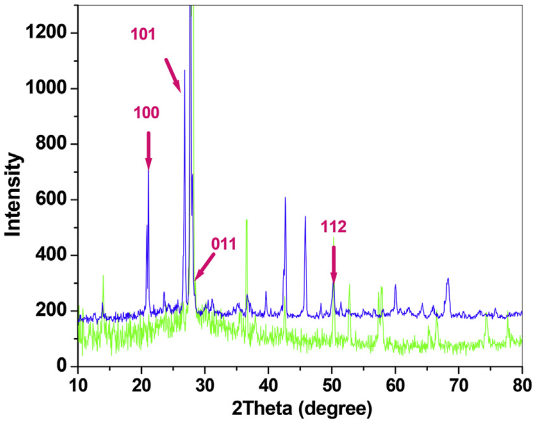

Fig. 1 – XRD patterns of sand (green) and nano-sized Mn oxide coated on sand (blue). In accordance to low amounts and low crystallinity of Mn oxide, the related peaks for the oxide is not observed. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

stable under many conditions [5]. The low number of electrons in antibonding orbitals of Mn oxide, e_g^* and t_{2g}^*, increases the M–O bond order [7]. A few supports have been used for Mn oxides to increase water oxidation. Among different supports, SiO_2-based ones are very promising for different catalysts [8–10]. In 2010, Frei's group reported on nanostructured Mn oxide clusters supported on mesoporous silica in the presence of $Ru(bpy)_3^{3+}$ [8]. The high-surface area silica support can assists in deprotonation during water oxidation [8]. The use of zeolites showed that small particles of Mn oxides are formed in the presence of zeolite or SiO_2-based supports, which are efficient catalysts in water oxidation [9,10]. However, the decomposition reaction in the presence of cerium(IV) ammonium nitrate (Ce(IV)) has also been reported [9]. Additionally, Mn oxide/carbon nanotubes, graphene, graphene oxide, C_{60} and nanodiamond were reported as water-oxidizing catalysts [11–13]. Such catalysts are very important for water splitting systems [13–20]. However, carbon oxidation during water oxidation occurs for these supports.

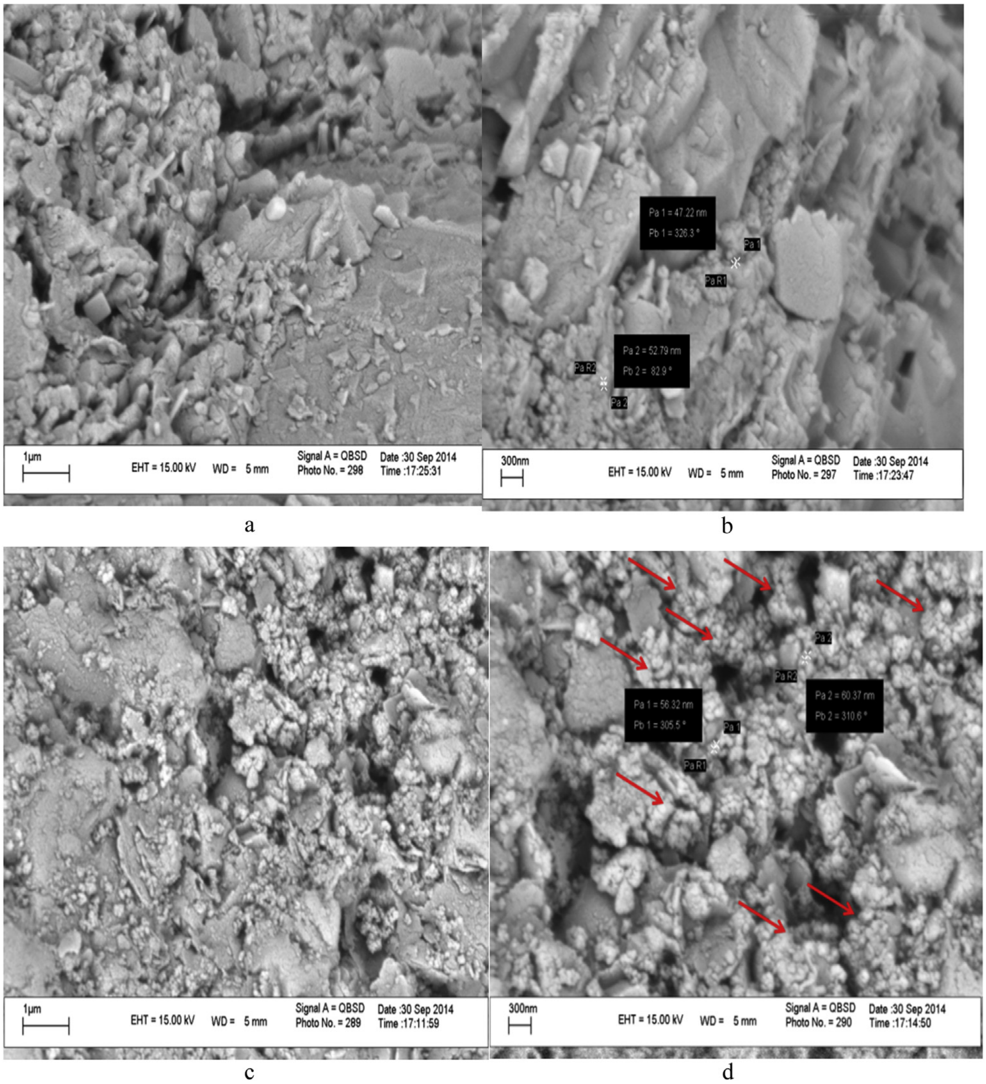

Fig. 2 – SEM images of sand (a,b) and nano-sized Mn oxide coated on sand (c,d). The red arrows show the Mn oxide particles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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