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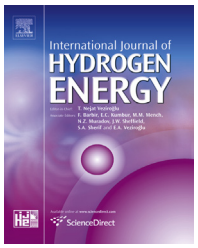

A highly dispersible, magnetically separable and environmentally friendly nano-sized catalyst for water oxidation

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ABSTRACT

The reaction of $KMnO_4$ with cobalt nanoparticles coated with SiO_2 layers forms a highly dispersible, magnetically separable and environmentally friendly catalyst toward water oxidation. The compound was characterized by scanning electron microscopy, energy-dispersive spectroscopy, transmission electron microscopy, X-ray Photoelectron Spectroscopy, X-ray diffraction, electron spectroscopy, Fourier transform infrared spectroscopy and atomic absorption spectroscopy. The nano-sized catalyst shows self-healing in the presence of cerium(IV) ammonium nitrate and under the water-oxidation conditions. The turnover frequencies for the catalyst toward water oxidation in the presence of cerium(IV) ammonium nitrate and $[Ru(bpy)_3]^{3+}$ are 0.15 and 0.25 (mmol O_2/mol Mn·s), respectively.

Introduction

The water splitting to hydrogen and oxygen is an important reaction in artificial photosynthesis to employ sustainable energies. As water oxidation is a bottleneck for water splitting, the finding of an efficient, cheap and environmentally friendly water-oxidizing compound is necessary [1–3]. Among different compounds [4–12], Mn oxides are very promising and interesting because they are not only cheap and

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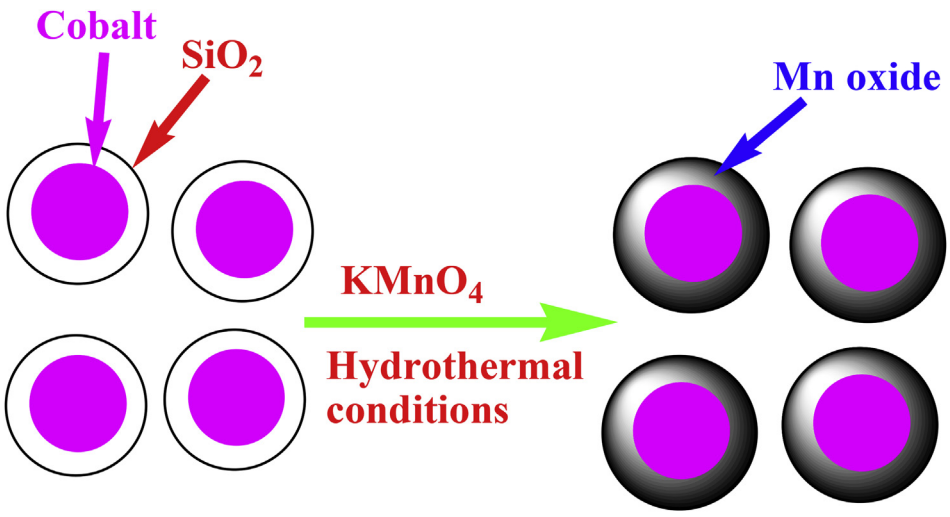

Scheme 1 – Scheme of the synthesis of 1.

environmentally friendly, but also a similar structure is efficiently used by plants, algae and cyanobacteria for the same reaction [13–28].

Oxygen evolution catalyzed by MnO_2 in the presence of cerium(IV) salts as oxidants was reported by Glikman and Shcheglova in 1968 for the first time [29]. Shilov used the catalyst to test water oxidation in the presence of other oxidants [30]. Morita in 1979 considered electrochemical water oxidation catalyzed by Mn oxides and the important role of Mn(III) was reported [31]. Harriman in 1988 extended this work to different metal oxides in the presence of ammonium cerium(IV) nitrate (Ce(IV)) [32].

Nanostructured Mn oxide clusters supported on mesoporous silica were reported as efficient catalysts for water oxidation in the presence of $Ru(bpy)_3^{2+}$ [33]. It is proposed that Si–O groups are important for proton transfer and as stabilizers of Mn oxide [33]. Mn oxides supported on zeolites were reported as efficient catalysts toward water oxidation in the presence of Ce(IV) [34]. However, very small particles are leaking from zeolite in the presence of

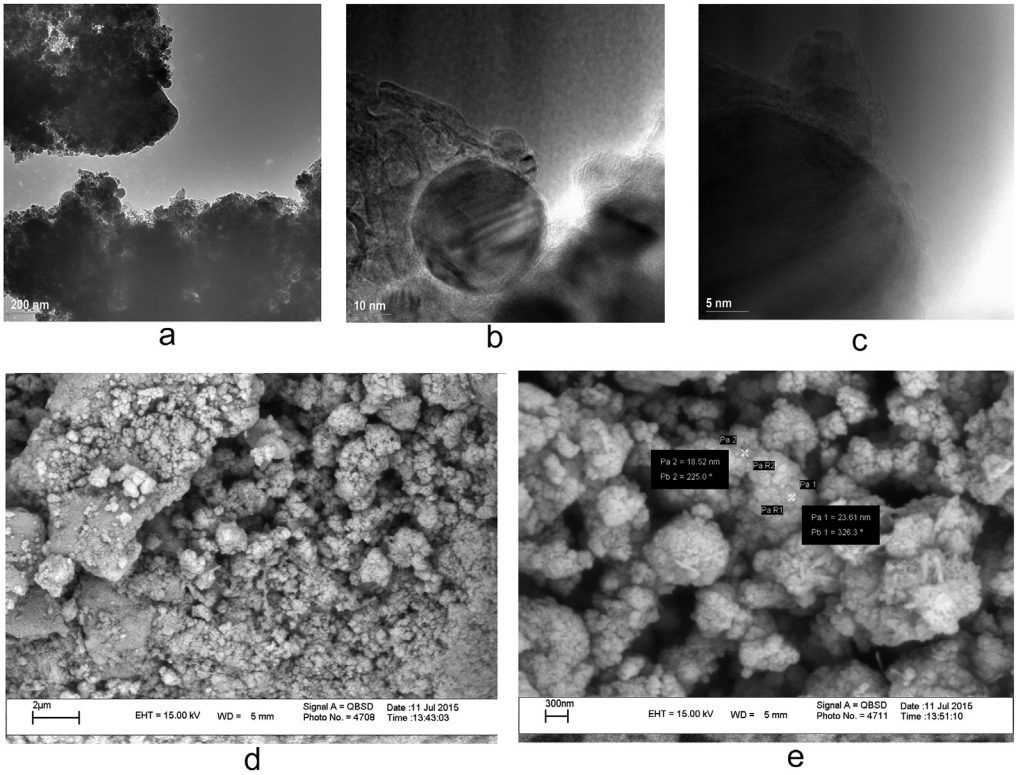

Fig. 1 – TEM (a–c) and SEM (d,e) images for 1.