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Fabrication of nanostructured α-Fe_2O_3 electrodes using ferrocene for solar hydrogen generation

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ABSTRACT

Nanostructured thin films of α-Fe_2O_3 were prepared through atmospheric chemical vapour deposition (APCVD) using ferrocene and iron pentacarbonyl as precursors. Higher optical absorption was observed for hematite films prepared using ferrocene, which was attributed to the higher packing density. Photoelectrochemical (PEC) studies of the films prepared using ferrocene showed superior performance to that of iron pentacarbonyl. Photocurrent density of 540 μA/cm^2 and 1.5 μA/cm^2 at 1.23 V_{RHE} was achieved for hematite films prepared using ferrocene and iron pentacarbonyl, respectively. Our findings suggest that ferrocene can be used as a promising alternative to iron pentacarbonyl to prepare hematite photoelectrodes using APCVD.

1. Introduction

Solar hydrogen generation by water splitting (also known as photoelectrochemical water splitting) has been the focus of intense research activities in the last few years. Hydrogen is believed to be the energy source of the future and PEC water splitting is a promising and environmentally-friendly process for hydrogen generation. Since 1972, when the first work on PEC water splitting was reported by Fujishima and Honda [1], a wide range of materials has been investigated. Hematite (α-Fe_2O_3) is a material of choice to be used as photoanodes in this application. It satisfies most of the requirements such as high stability, close match between the energetics of its band edge positions and redox potentials of water dissociation, band gap, cost effectiveness and ease of fabrication. However, due to the high rate of electron-hole recombination [2] and short hole diffusion length [3] photocurrents achieved for hematite films so far have not met the expectations.

To date, many different processes such as spray pyrolysis [4], sol–gel [5] and APCVD [6] have been used to fabricate hematite photoelectrodes. Recently, Kay et al. [7] reported crystalline Si-doped hematite films prepared by APCVD with efficiencies even higher than that of single crystals [8]. This outstanding performance was attributed to the fine dendritic nanostructure of the films as well as the doping effect of silicon. Although PEC performance of the Si-doped hematite electrodes prepared by APCVD was promising, the performance of un-doped electrodes performance was very poor (ca. photocurrent density <10 μA/cm^2 at 1.23 V_{RHE}) [7].

Due to the specific requirements of APCVD method, i.e. precursor with high vapour pressure, the available iron precursors are limited. Ferrocene is a well-established iron source and has been widely studied in applications such as catalysts [9], gas sensors [10], antiknocking agents [11], ferromagnetism [12] and carbon nanotubes [13]. It is stable at room temperature but becomes highly volatile at higher temperatures (vapour pressure of 30 mmHg at 150 °C [14]). Although its decomposition temperature has been reported above 400 °C [15], Bernhauer et al. [16] observed that the decomposition of ferrocene occurred at temperatures as low as 380 °C . Therefore, it offers a good alternative to iron pentacarbonyl for the deposition of hematite photoelectrodes *via* APCVD. In comparison with iron pentacarbonyl, ferrocene is cheaper, less toxic and easier to handle.

To our knowledge, no work has been reported on the preparation of α-Fe_2O_3 photoelectrodes using ferrocene as the precursor and the investigation of the PEC performance of the electrodes for water splitting applications. In this paper, we report, for the first time, un-doped hematite photoelectrodes prepared by APCVD using ferrocene with photocurrent density of 540 μA/cm^2 at 1.23 V_{RHE} surpassing the

Table 1
Deposition conditions for two different samples

Precursor–sample name	Flow rate		Temperature (°C)	Time (min)	d[a] (mm)	D[b] (mm)
	Ar (ml/min)	Air (l/min)				
Ferrocene	150	2	400	18	20	10
Iron pentacarbonyl	20	2	400	5	20	10

[a] d is the distance between the delivery tube and FTO substrate.
[b] D is the diameter of the delivery tube.

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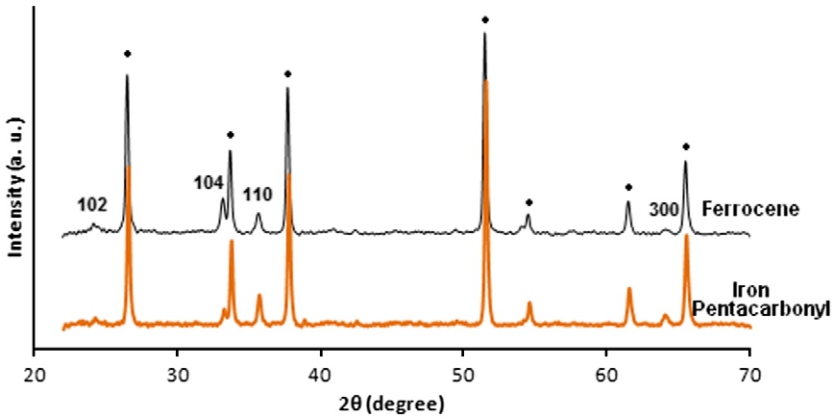

Fig. 1. XRD pattern of the films prepared by ferrocene and iron pentacarbonyl. (102), (104), (110) and (300) reflections correspond to hematite. The peaks labelled with (•) correspond to the SnO_2 in the FTO substrate.

PEC performance of the un-doped hematite photoelectrodes prepared by iron pentacarbonyl.

2. Experimental

α-Fe_2O_3 was deposited on 1×2 cm fluorine-doped tin oxide (FTO) conductive glass substrates (Pilkington TEC8). Prior to deposition, substrates were cleaned ultrasonically using propanol, deionised water, acetone, and absolute ethanol in that order. Ferrocene ($Fe(C_5H_5)_2$, 98%, Lancaster Synthesis) and iron pentacarbonyl ($Fe(CO)_5$, 99.9%, metal purises, Sigma-Aldrich) were used as sources of iron. As ferrocene is in the form of powder at room temperature and its vapour pressure is not high enough to satisfy the requirements of a typical APCVD precursor, it was heated to 160 °C using a hot oil bath. Then, the aerosol was brought into a chamber using argon as the carrier gas and directed towards the heated substrate using air. The delivery tube was positioned 20 mm above the substrate which was heated to 400 °C. The deposition conditions are shown in Table 1.

The phase and crystallinity of deposited films were characterised using a Bruker D8 x-ray diffractometer (XRD) operating with monochromatic

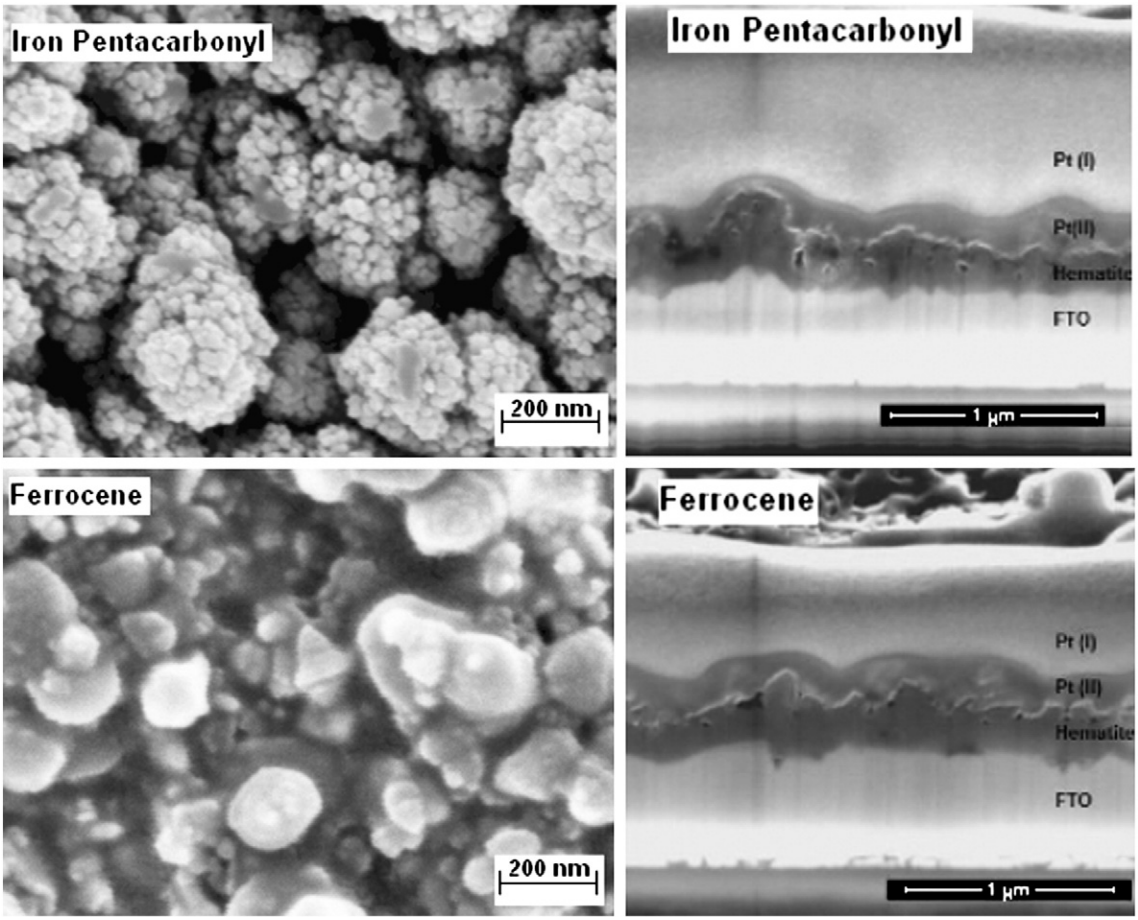

Fig. 2. SEM micrographs of hematite films showing surface morphology and the thickness of the films prepared by iron pentacarbonyl and ferrocene. Pt(I) and Pt(II) are the platinum layers deposited by ion beam and electron beam, respectively. The SEM pictures of the cross section are obtained at a tilt angle of 52°.