Supplementary Information

Synthesis of hydrogen producing nanocrystalline $ZnFe_2O_4$ visible light photocatalyst using rapid microwave irradiation method

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Structural Characterization

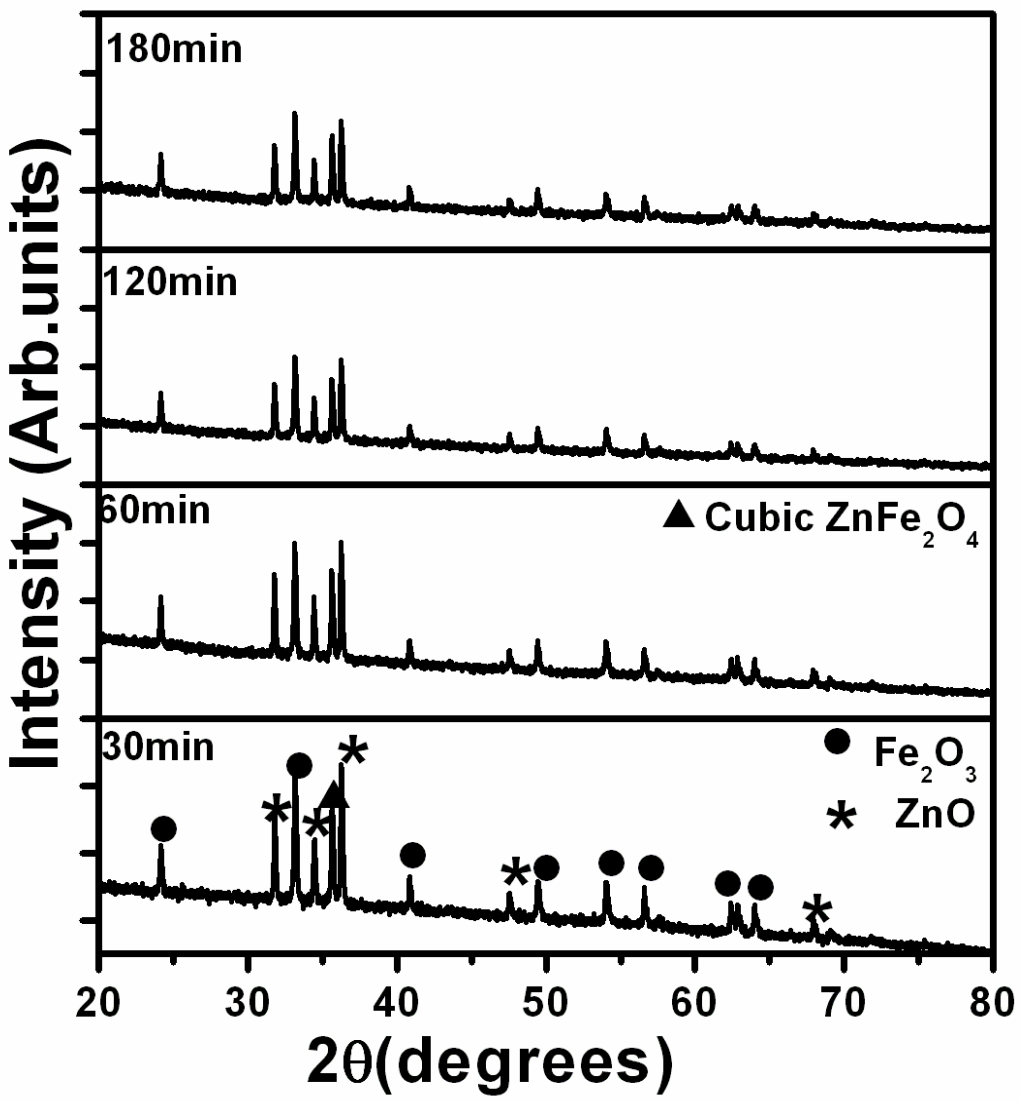

Fig.S.I.1. The XRD spectra of the powder compacts of ZnO+Fe_2O_3 subjected to low microwave power (<1000W *i.e.* kitchen oven) with respect to the time of microwave irradiation. Time of irradiation in range of 30min-180min.

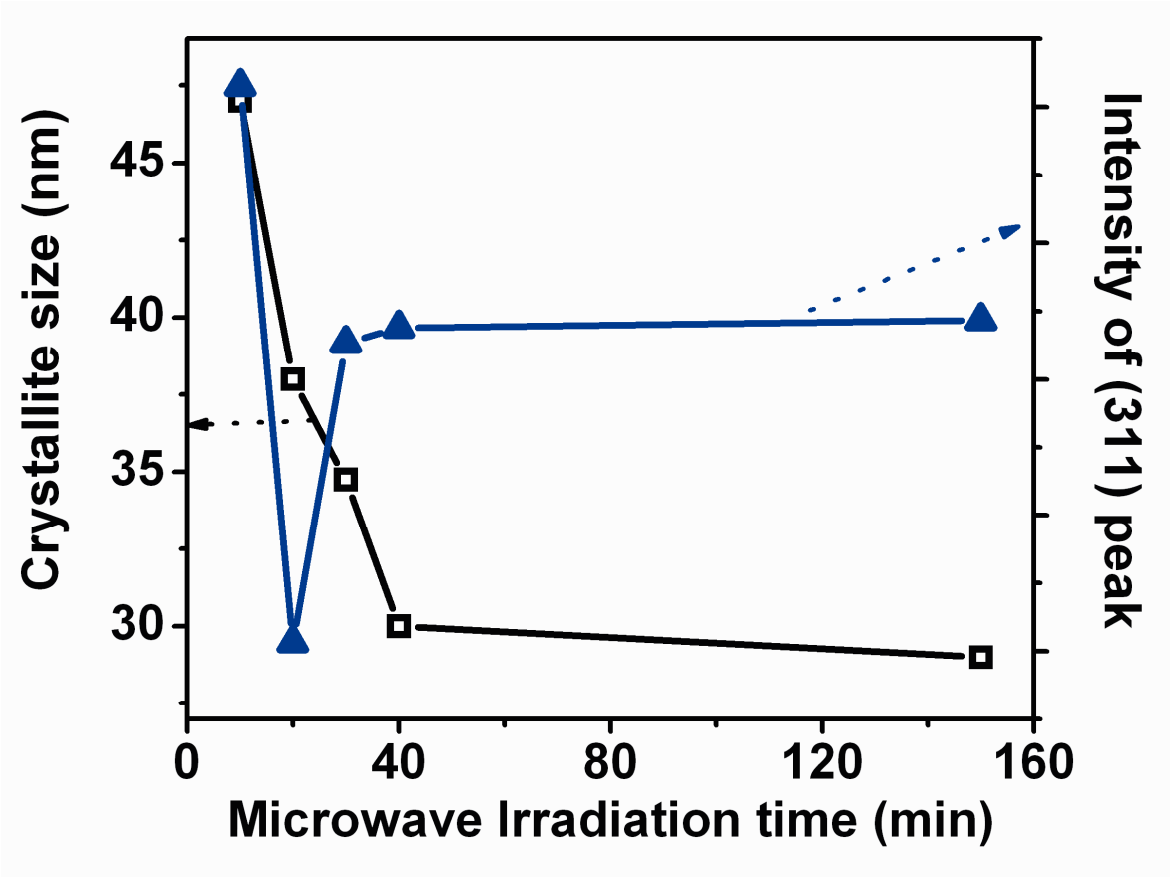

Fig.S.I.2. Crystallite size and intensity of (311) peak of $ZnFe_2O_4$ particles sintered as a function of microwave irradiation time (at 973K).

As seen in Fig.S.I.2, the crystallite size was found to decrease; and (ii) the (311) peak intensity was found to increase - with the increase in irradiation time. The drastic reduction in the crystallite size within first 40min. of irradiation can be correlated with phenomena of de-crystallization known in the microwave sintering methodology.

Photo-catalytic characterization

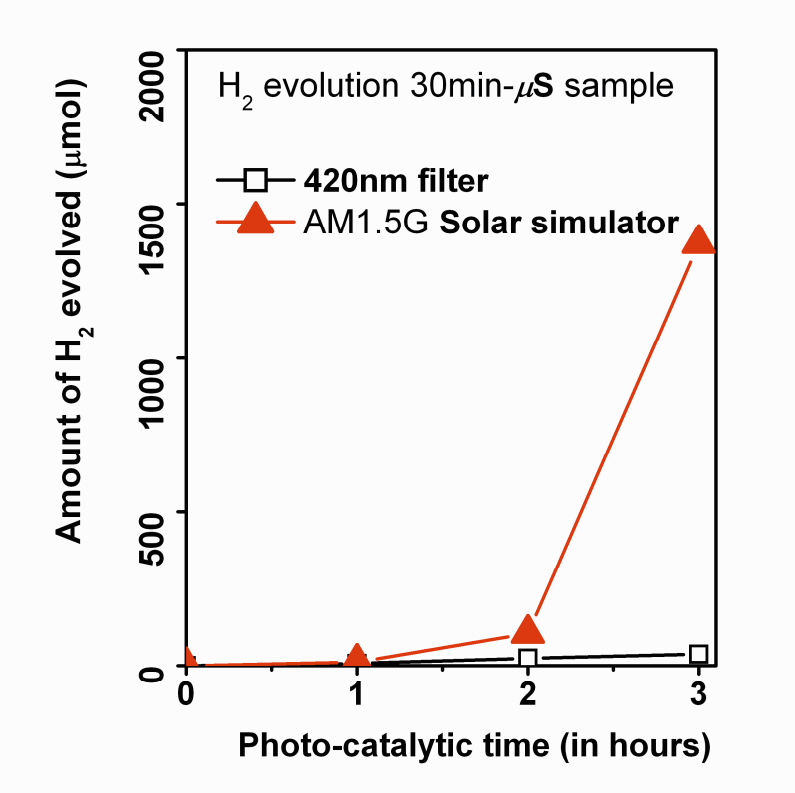

Fig.S.I.3. The amount of H_2 evolved from the microwave sample (30min) during photocatalytic reaction carried out under Visible light (420nm) and Solar radiation.

Electro-chemical Characterization

Inorder to perform measurements shown in Fig.S.I. 4 and 6, the following procedure was followed. $ZnFe_2O_4$ -photocatalyst powders were obtained by microwave and conventional synthesis methods were coated on Flourine-doped Tin oxide (FTO) glass substrates to be used as working electrodes for electrochemical characterization. The FTO substrates were cleaned thoroughly and sonicated in de-ionized water and organic liquids for long time prior to coating. The ZFO powders to be coated were thoroughly mixed with the appropriate binder (PEG) and the paste was coated on the substrates using the Doctor-blade technique (Reference: Suk Joon Hong, Hwichan Jun, Pramod H. Borse, Jae Sung Lee, International journal of hydrogen energy, 2009, **34**, 3234–3242). A small area of the substrate was left uncoated to make contacts for the electrode fabrication. Thus obtained films were dried in air and then calcined in furnace at 450^0C at the rate of 2^0C/min for 1hr. The films were then fabricated into electrodes using Cu wire. High purity Ag paste was used to make contacts with the wire. The electrode was then sealed properly leaving only the portion of deposited area for measurements.

The electrochemical characterization was carried out using a conventional 3-electrode cell, using a Pt plate as counter electrode and Ag/AgCl electrode (3MNaCl) as reference electrode. The electrolyte was 1Molar NaOH aqueous solution at pH~13.6. $ZnFe_2O_4$ powders coated on FTO glass substrates of area 1X1cm^2were used as working electrode. The electrochemical measurements were recorded using electrochemical workstation (PARSTAT –Model 2273) with a built in frequency response detector (Model-1025). The Mott-Schottky plots were recorded in dark at an applied frequency of 10kHz and 10mV Ac voltage. The

electrochemical impedance spectra for different electrodes were recorded at an applied dc voltage of 0.6V(vs.Ag/AgCl) in the frequency range 100mHz-1MHz.

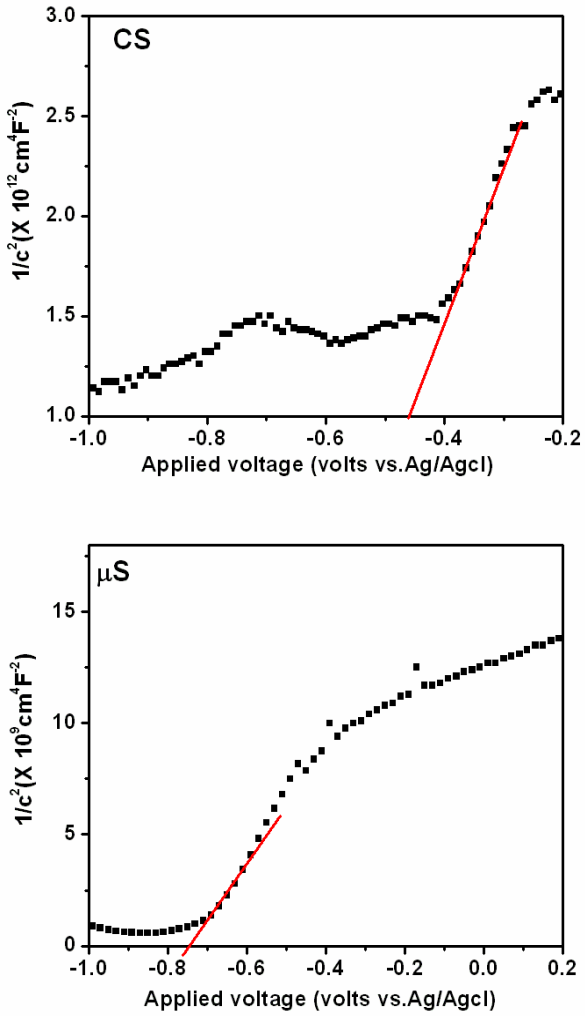

Fig.S.I.4. Mott-Schottky plots of the CS and microwave μS(30min) samples with Ag/AgCl as reference electrode . The AC applied voltage is 10mV at a frequency of 10kHz.

Electronic structure calculation by DFT

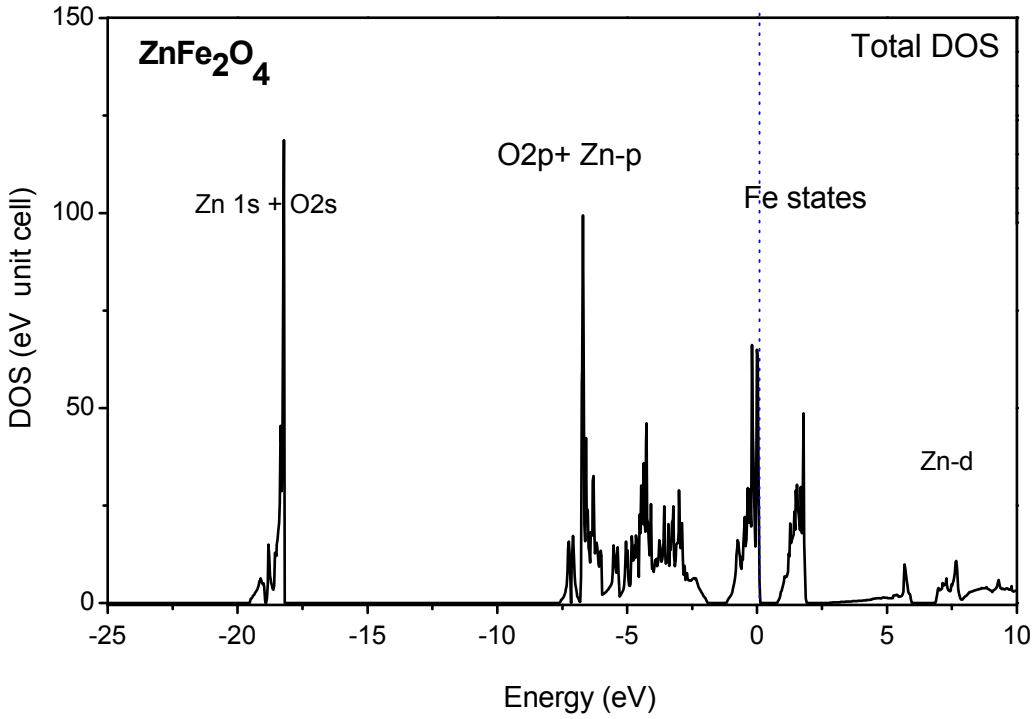

Fig.S.I.5. Electronic band structure calculation using DFT for cubic spinel zinc ferrite structure that was used for the deducing Valence and conduction band to support the experimental observation for Bulk ZFO. Ref: R.Dom, R.Subasri, K.Radha, and P.H.Borse, *Solid State Commun.*, 2011, **151**, 470-473

Electrochemical Impedance spectroscopy

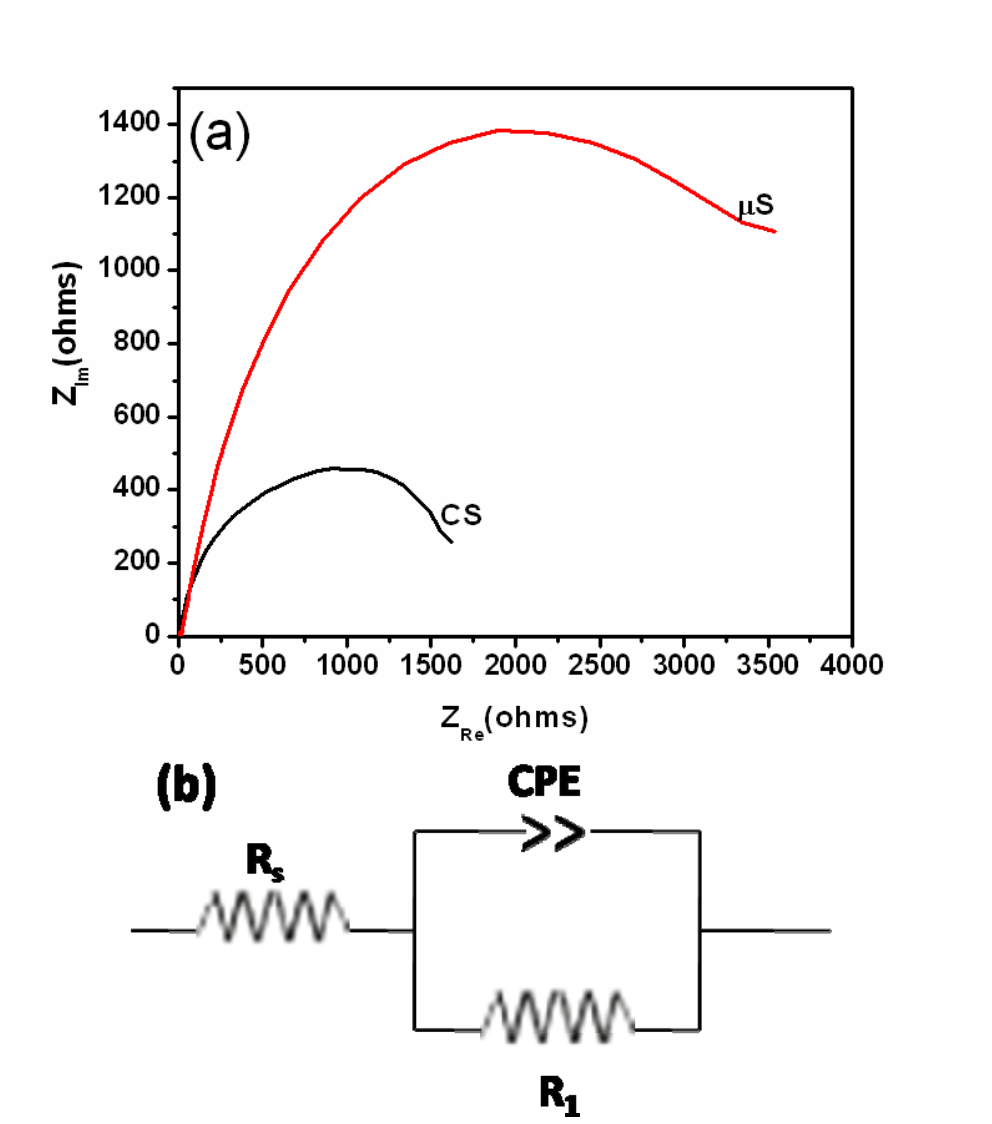

Fig.S.I.6. (a) EIS spectra of the ***C*S** and microwave (***μ*S**-30min) sample recorded at an applied voltage of 0.6V *vs* Ag/AgCl in the frequency range 100mHz-1MHz. (b) The Randells equivalent circuit model fitting the EIS spectra obtained using the Z-View software

Table-S.I.-1: Electrochemical parameters obtained for different powder samples from the EIS results fitted with the ZView software

Sample	$R_s(\Omega)$	$R_1(\Omega)$	CPE1-T Farad	CPE1-P Farad
10min	614.6	62946	$0.45X10^{-6}$	0.60903
30min	14.92	4073	$17.07X10^{-6}$	0.93586
150min	166.6	81028	$6.05X10^{-6}$	0.6155
CS	9.588	74.79	$208.01X10^{-6}$	0.68167