Supplementary Information

Fabrication of $CaFe_2O_4$/$MgFe_2O_4$ Bulk Heterojunction for Enhanced Visible Light Photocatalysis

Hyun Gyu Kim[a], Pramod H. Borse[b], Jum Suk Jang[b], Euh Duck Jeong[a], Ok-Sang Jung[c], Yong Jae Suh[d], and Jae Sung Lee[b*]

[a] *Busan Center, Korea Basic Science Institute (KBSI), Busan 609-735, Korea*

[b] *Eco-friendly Catalysis and Energy Laboratory (NRL), Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), San-31 Hyoja-dong, Pohang 790-784 Korea, Fax: 82-54 279 5528; Tel: 82-54 279 2266; E-mail: jlee@postech.ac.kr*

[c] *Department of Chemistry, Pusan National University, Pusan 609-735, Korea*

[d] Korea Institute of Geoscience and Mineral Resources, Daejeon 305-350, Korea

Experimental Procedure

Preparation of nanocrystalline $CaFe_2O_4$ and $MgFe_2O_4$

The synthesis of $CaFe_2O_4$ was carried out by the PC method. Calcium acetate monohydrate ($Ca(CH_3CO_2)_2$, 99.0%, Aldrich), magnesium carbonate ($MgCO_3$, 99.9%, Aldrich), ethylene glycol ($C_2H_6O_2$, Kanto Chemicals), citric acid ($C_6H_8O_7$, Wako) and iron nitrate nonahydrate ($Fe(NO_3)_3$ $9H_2O$, 99.99%, Aldrich) were used as starting materials. The citric acid (CA) was added into water under constant agitation, at temperature of 60-70°C. Next, the salts of calcium carbonate and iron nitrate hydrate were dissolved in citric acid-water solution to obtain metal-citrate complex. Finally, ethylene glycol (EG) was added to the mixture to yield a mass proportion of 60% CA to 40% EG. The mixture was kept on hot plate (80°C) till it became a transparent colorless solution. The colorless solution was then heated at 130°C for several hours to obtain a polymeric gel. The viscous polymeric product was pyrolyzed at about 300-500°C to form the precursor powders. Thus obtained powder was pressed in the form of pellets, which were calcined at 500-1200°C for 2 h in an electric furnace to obtain nanocrystalline $CaFe_2O_4$ or $MgFe_2O_4$. On the other hand, for the purpose of comparison, $CaFe_2O_4$/$MgFe_2O_4$ was also prepared by the conventional solid-state reaction (SSR) method. A ground mixture of $CaCO_3$ (99%, Aldrich), $MgCO_3$ (99.9%, Aldrich), and Fe_2O_3 (99%, Aldrich) was heated at 1300°C for 2h.

Deposition of Pt and RuO_2 nanoparticles on CFO/MFO

First, RuO_2 was loaded on $CaFe_2O_4$/$MgFe_2O_4$ photocatalyst by an impregnation method. The photocatalyst powder was added in aqueous solution containing a required amount

(1wt% of powder) of $RuCl_3$ and then was dried in an oven at 373 K in air for 2 h. Then the sample was oxidized in air (24 μmol/s) at 473 K for 1 h to obtain RuO_2-loaded CFO/MFO. Next, 1wt% of Pt metals were deposited on $RuO_2/CaFe_2O_4/MgFe_2O_4$ photocatalysts by using a photodeposition method using metal H_2PtCl_6 under a 450-W Xe-arc lamp (Oriel) with UV cut-off filter ($\lambda \geq 420$nm) and then was dried in an oven at 373 K in air for 2 h

XRD and SEM

The $CaFe_2O_4$ samples prepared by the PC and conventional SSR methods were characterized by X-ray Diffractometer (Mac Science Co., M18XHF). The morphology was determined by scanning electron microscopy (SEM, Hitachi, S-2460N) and high-resolution transmission electron microscopy (Philips, CM 200).

Photocatalytic reactions

About 600ppm of gaseous isopropyl alcohol was injected into a 500-mL Pyrex reaction cell filled with air and 0.3 g of catalyst. The concentration of the reaction products (CO_2) was determined by a gas chromatograph equipped with a thermal conductivity detector and a CTR-1 packed column.

The photocatalytic reactions of H_2 or O_2 evolution were carried out at room temperature under atmospheric pressure in a closed circulation system under the visible light irradiation with 450W Hg-arc lamp equipped with cut-off filter ($\lambda \geq 420$nm) and liquid filter to remove IR, after nitrogen-purging for 1 hr for deaeration. The evolved amounts of H_2/O_2 were analyzed by gas chromatography (HP6890) equipped with a thermal conductivity detector (TCD) and molecular sieve 5- column with Ar carrier gas.

Total DOS of CFO and MFO

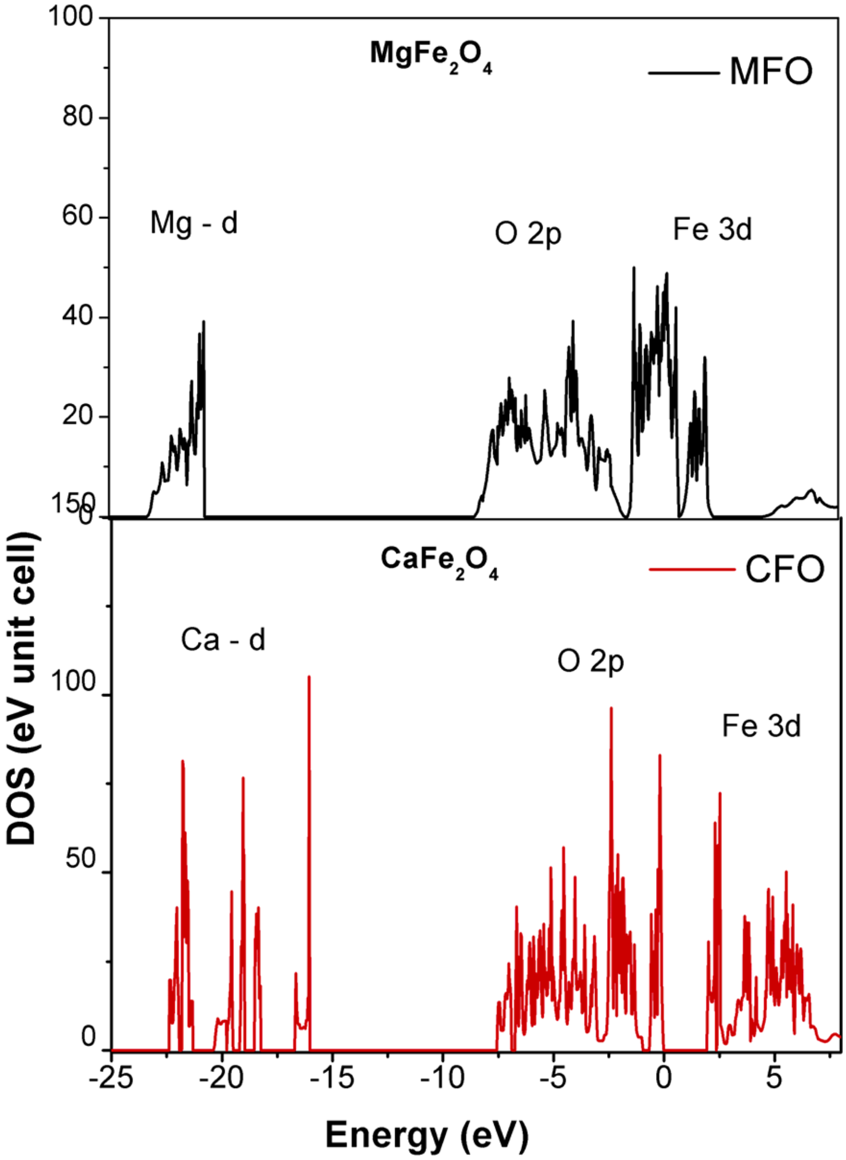

Fig. S1. Theoretically calculated total density of states for $MgFe_2O_4$ and $CaFe_2O_4$. For both ferrites, the top of the valence band is made of O2p orbital, whereas the bottom of conduction band by Fe 3d orbital. Thus the Fe d-orbital play the major role in the optical absorption of visible light photons. The d-orbitals of Ca and Mg are located deep into the core bands.

Elemental Mapping of a bulk heterojunction particle

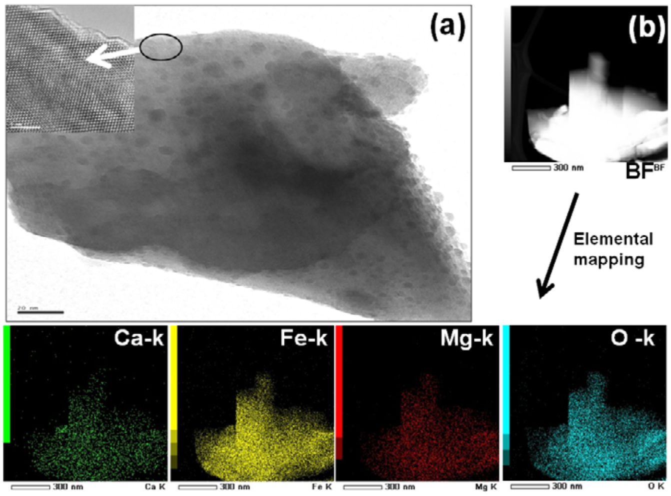

Fig. S2. **(a)** A typical HRTEM of a fabricated CFO/MFO bulk heterojunction particle showing the nano-dimensional entities (RuO_2 or FePt) stacking over the surface. The inset on left top corner clearly reveals the high crystallinity of base material; **(b)** Bight field image of a CFO/MFO particle demonstrating the presence Ca, Fe, Mg and O atoms as observed by elemental mapping during *in-situ* EDAX analysis.

Flat band potential measurements

Slurry method[1,2] was used to determine the positions of the flat band potential (Efb) for each system of photocatalyst ($CaFe_2O_4$, $MgFe_2O_4$). For the photoelectrochemical measurements of each individual system, the mixture of 25mg of photo catalyst and 0.5mM methylviologen dichloride was suspended in 100ml two necked flask in 50mM KNO_3. HNO_3 and NaOH of 100mM were used to adjust the pH value. A Pt flat electrode (1x1 cm2, 0.125mm thickness, both sides exposed to solution), a saturated calomel electrode (SCE), a Pt gauze were immersed in the reactor as working (collector), reference and counter electrodes respectively.

The study was performed by using a 450 W Xe-arc lamp (Oriel) with UV cut-off filter (420nm). The stable photocurrents were recorded about 40 min after adjusting the pH value to desired value. With continuous N_2 purging of suspension, photocurrents were measured (potentiostat EG&G) without applying any potential to Pt electrode. Initially the pH of the suspension was adjusted to pH 3.0-3.5 before measurement. The obtained pH_0 values were converted to E_{fb} at pH 7 by using the equation, [1,2]

$E_{fb} = -0.6865 + (0.059\ pH_0)$

Reproducibility of pH_0 was better than 0.1 pH units. Fig.SI.3 shows the dependence of the photo current on the pH value of electrolyte for (A) p-type CaFe2O4 and (B) n-type $MgFe_2O_4$. From these measurements, their electrochemical potentials (vs. NHE) for band positions at pH=7 (C) are obtained.

[1] J.R. White, A.J. Bard, *J.Phys.Chem.***1985**, *89*, 1947.

[2] A.M. Roy, G.C. De, N. Sasmal, S.S. Bhattacharyya, *Int. J. Hydrogen. Energy* **1995**, *20*, 627.

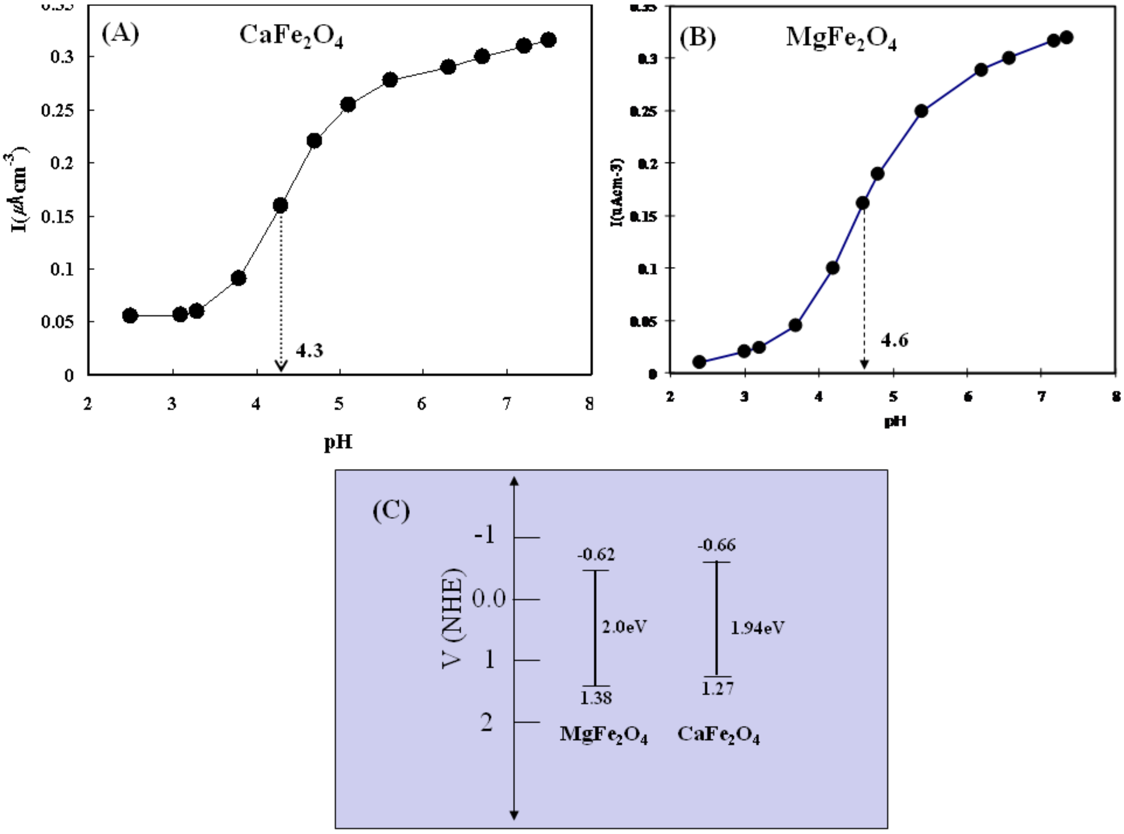

Fig. 3. Dependence of photocurrent on pH value of the electrolyte for (A) $CaFe_2O_4$ and (B) $MgFe_2O_4$; Section (C) shows the flat band potentials that show that band positions can reduce and oxidize water under visible light.

Photocurrent measurements

For photocurrent measurements, 25 mg of photocatalyst was suspended in distilled H_2O (75 mL) containing acetate (0.1m) and Fe^{3+} (0.1 mm) as an electron donor and acceptor, respectively, and the pH value of the suspension was adjusted to 1.4 with $HClO_4$. A Pt plate (1 L 1 cm2, 0.125 mm thick, both sides exposed to solution), a saturated calomel electrode (SCE), and a Pt gauze were immersed in the reactor as working (collector), reference, and counter electrodes, respectively. With continuous N_2 purging of the suspension, photocurrents were measured by applying a potential (+0.6 V vs. SCE) to the Pt electrode using a potentiostat (EG&G).

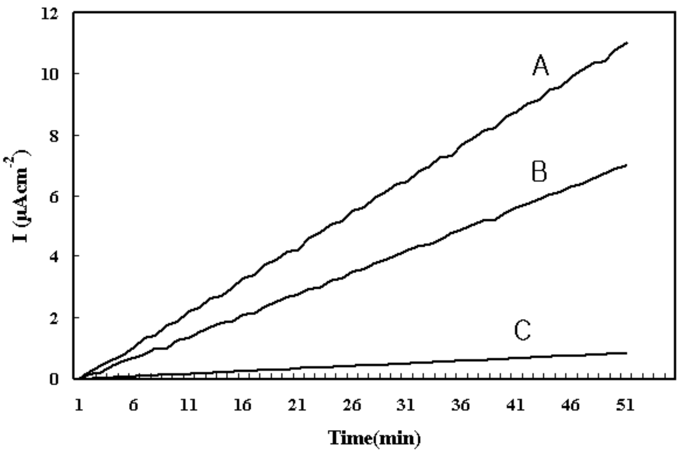

Fig. S4. Comparison of generated photocurrent (accumulated) under visible light irradiation of various materials (25mg) suspended in water containing acetate and Fe^{3+} as an electron donor and acceptor, respectively. A: CFO-MFO (bulk hetreojunction), B: $WO_3/PbBi_2Nb_{1.9}Ti_{0.1}O_9$ and C: N-Doped TiO_2.

Hydrogen evolution

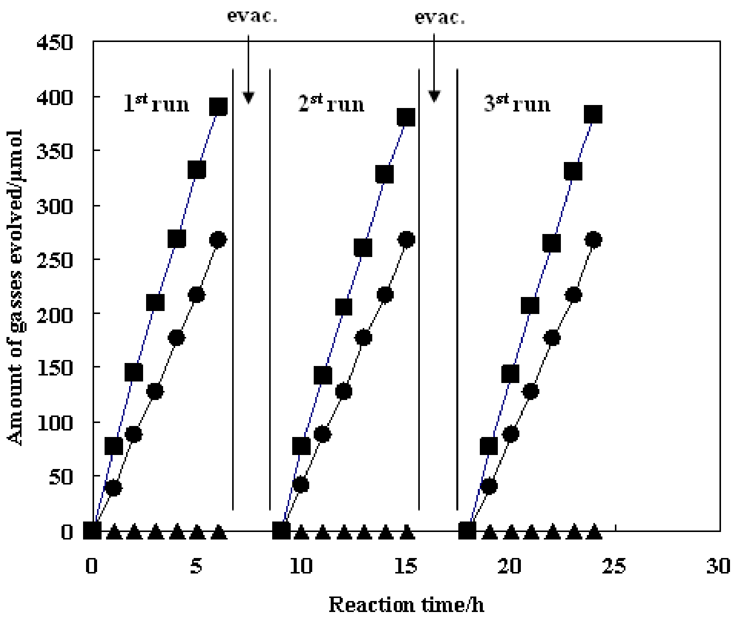

Figure SI. 5. Time course of H_2 gas evolution from ■ CFO-MFO (BH), ● $WO_3/PbBi_2Nb_{1.9}Ti_{0.1}O_9$ and ▲ N-Doped TiO_2 under visible light irradiation in an aqueous solution by stirring 0.1g of catalyst loaded with Pt. The reaction system was evacuated every 5h in order to remove gaseous products from the gas phase.