

# $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> photocatalyst system: synthesis and charge transfer mechanisms

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**Abstract:** Our goal is to provide technology for degradation of persistent organic pollution in drinking water. We are demonstrating aqueous synthesis of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> photocatalyst heterostructure. Materials were obtained in shape of powders and thin film photoanodes. Heterostructures exhibit visible light photocatalytic activity. Powder  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> photocatalyst exhibit Z-scheme charge transfer mechanism and moderate stability, while under applied electric field, when material utilized as photoanode, reverse charge transfer is switched and heterostructure is stable. Powder type materials produce superoxide anions, •O<sup>2-</sup>, but photoanodes not. Materials were tested for dye and persistent organic pollution degradation. Both powders and photoanodes destroy methylene blue but only powders can destroy persistent organic pollutants.

**Keywords:** Hematite, Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, Z-scheme, visible light, photocatalyst.

## 1. Introduction

Oxidation technologies have been effective for water purification. These technologies involve oxidation of water pollutants such as bacteria or organic substances. Oxidation technologies, in our opinion, stand in front of physical methods, such as adsorption or membrane processes, because they are not destroying pollution. Also technologies such as heterogeneous or homogeneous Fenton reactions are not sustainable because they involve applications of chemicals.

Oxidation technologies are ozonation, aeration, TiO<sub>2</sub> photocatalysis, electro-oxidation, UV-photolysis and supercritical water oxidation. Only some of the oxidation technologies could be used for treating drinking water, as well as only some technologies can be used to destroy persistent organic pollution. Most effective technology for destroying persistent organic pollution is supercritical water oxidation, but it is ridiculously expensive. At the same time, persistent pollution is emerging problem, because they are accumulating in nature and can be found in drinking water. These substances cause cancer to people.

Photocatalysis can be used for destroying persistent organic pollution, but as post-treatment technology. In scientific literature many different photocatalytic materials are described, but since now only pristine TiO<sub>2</sub> has been practically applied for wastewater treatment. There are many limitations for various materials to be applied for drinking water. Materials used for photocatalysis can't be toxic, they have to be stable and they must be integrated in thin films to avoid secondary pollution. Pristine TiO<sub>2</sub> is almost the single material occupying 95% from 1 billion market of photocatalysis. Amazing that it is in spite of its inactivity in sunlight. To activate TiO<sub>2</sub>, UV light is used and sunlight contains only 4% UV. Our photocatalyst system provides the same oxidation power as TiO<sub>2</sub> to destroy persistent organic pollution, but our system can be driven by visible light (sunlight). Our materials absorb approximately 40% from sunlight.

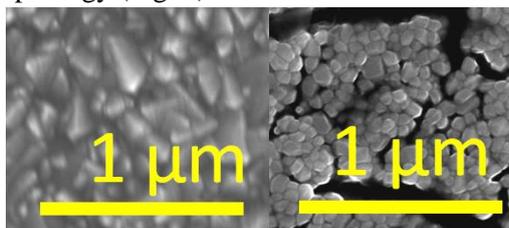
## 2. Experimental

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> photocatalyst heterostructure was obtained by impregnating Fe containing substrate material (amorphous, crystalline hematite and goethite) by Ca<sup>2+</sup>. After impregnation, materials were dried and annealed at 800 °C.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> photocatalyst heterostructures photoanodes were synthesized by amorphous Fe containing layer electrodeposition [1] and Ca<sup>2+</sup> impregnation.

Materials were characterized by XRD, XPS, EDX, HR-SEM, TEM and optical measurements. Photocatalytic activity tests were performed on both powders and tin film photoanodes. The light source used for photocatalytic tests was a 100 W light-emitting diode (LED) (emission band approximately 415–700 nm, i.e., 2.99 eV to 1.77 eV) with an effective power density of  $45\pm 3$  mW/cm<sup>2</sup>.

### 3. Results and discussion

XRD results show that the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> photocatalyst heterostructures forms easily when impregnating amorphous iron-containing nanoparticle substrates with Ca<sup>2+</sup>. Amorphous substrates provide more surface sites and open pores, as well as a higher surface area for precursor spatial infiltration and adsorption with a higher abundance of Fe cations for Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> formation upon heat treatment. Results were confirmed by STEM EDX analysis. Similar results were obtained for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> photoanodes. Calcium impregnation change morphology (Fig. 1).



**Figure 1.** Sem microphotograph showing microstructure of hematite photoanode (left) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> (right).

The samples obtained from the amorphous substrate nanoparticles exhibited two-fold higher methylene blue visible light degradation rate constants for under compared to the other samples. The enhanced photocatalytic performance can be attributed to the tight interface  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> heterostructure formation and improved photogenerated charge-carrier separation over the interface. Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> is a narrow band gap p-type semiconductor with a more-negative CB potential and more-negative VB potential in comparison to hematite [2]. Thus, charge transfer between n-type  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and p-type Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> can be potentially incorporated into a Z-scheme mechanism, where photoinduced electrons on hematite would recombine with photogenerated electron holes on Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub>, leaving electrons on Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> and electron holes on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> for reduction and oxidation reactions, respectively, and consequently providing a high redox potential for the overall system. To verify the Z-scheme charge-transfer mechanism, scavengers were added during the photocatalytic MB degradation tests. Results indicate that  $\bullet\text{O}^{2-}$  has a considerable role in MB degradation. The potential for oxygen reduction from O<sub>2</sub> to  $\bullet\text{O}^{2-}$  is -0.33 eV vs the normal hydrogen electrode (NHE), thus  $\bullet\text{O}^{2-}$  cannot be generated by photoinduced electrons on the CB of hematite, which has a reduction potential of +0.2 eV vs NHE [3]. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> heterostructure powder destroyed also persistent organic substances in wastewater from pharmacy industry (TOC=20 mg/l). At the same time  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> heterostructure powder was not stable and almost inactive already at 4<sup>th</sup> cycle.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> photoanodes also exhibited highest photocurrents and dye degradation efficiency, but wasn't able to treat pharmacy industry wastewater. At the same time they were stable. This can be attributed to charge transfer switching by external bias, thus protecting Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> from photoreduction and decreasing reduction potential of system.

### 4. Conclusions

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> heterostructures were successfully synthesized by aqueous synthesis. Photocatalytic and photoelectrochemical performances and their durability prove Z-scheme charge transfer mechanism for  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Ca<sub>2</sub>Fe<sub>2</sub>O<sub>5</sub> powders.

### References

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