Aqueous synthesis of Z-scheme photocatalyst powders and thin-film photoanodes from earth abundant elements

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ABSTRACT

Solid-state narrow band gap semiconductor heterostructures with a Z-scheme charge-transfer mechanism are the most promising photocatalytic systems for water splitting and environmental remediation under visible light. Herein, we construct all-solid Z-scheme photocatalytic systems from earth abundant elements (Ca and Fe) using an aqueous synthesis procedure. A novel Z-scheme two-component Fe2O3/Ca2Fe2O5 heterostructure is obtained in a straightforward manner by soaking various iron-containing nanoparticles (amorphous and crystalline) with Ca(NO3)2 and performing short (20 min) thermal treatments at 820 °C. The obtained powder materials show high photocatalytic performances for methylene blue dye degradation under visible light (45 mW/cm²), exhibiting a rate constant up to 0.015 min⁻¹. The heterostructure exhibits a five-fold higher activity compared to that of pristine hematite. The experiments show that amorphous iron-containing substrate nanoparticles trigger the Fe2O3/Ca2Fe2O5 heterostructure formation. We extended our study to produce Fe2O3/Ca2Fe2O5 nanostructure photoanodes via the electrochemical deposition of amorphous iron-containing sediment were used. The visible-light (15 mW/cm²) photocurrent increases from 183 μA/cm² to 306 μA/cm² after coupling hematite and Ca2Fe2O5. Notably, the powders and photoanodes exhibit distinct charge-transfer mechanisms evidenced by the different stabilities of the heterostructures under different working conditions.

1. Introduction

Visible-light photocatalysis is a green, reagent-free and zero-energy technology for energy harvesting and environmental remediation [1]. Photocatalysis is based on semiconductor oxides absorbing light with incident photon energy matching or exceeding the semiconductor’s bandgap [2]. Absorbed photons excite electrons to the conduction band (CB) and leave an electron hole in the valence band (VB), thus creating photogenerated electron-hole pairs. In combination with ambient water, the electron-hole pairs trigger the formation of H2 and O2 [3] or reactive oxygen species (ROS) with strong oxidation capacity for the degradation of organic substances [4].

Semiconductor photocatalysis has several disadvantages. First, the most excellent photocatalytic material, TiO2, does not absorb visible light and can only be excited by ultraviolet radiation [5]. Incorporating dopants, such as nitrogen [6], sulfur [7], carbon [8] or transition metals [9], into TiO2 can add visible-light activity, but the utilized synthesis methods generally have low yield, high cost, or high ecological impact. Additionally, the resulting photocatalytic activities may be limited [10].

Narrow band gap visible-light-absorbing semiconductors (WO3, Fe2O3, BiVO4, etc.) have been demonstrated as promising candidates for photocatalysis [11–13], but nevertheless most have limited photo-catalytic efficiency due to the fast recombination of photogenerated charge carriers. Some narrow band gap photocatalysts, for example, Ag2O and Cu2O, are especially active using visible light but are not stable [14,15] and suffer from photocorrosion.

One of the most effective strategies to decrease the overall...
recombination and to improve the photocatalytic efficiency or stability is to increase the spatial separation of photogenerated charge carriers by coupling semiconductor oxides with metal and/or other semiconductors to form two- or three-component systems [16,17]. In the most common system, two semiconductors are coupled with mismatched band edges, generating a potential slope at the interface, which causes electrons to migrate to the component with the more-positive CB edge and causes holes to transfer to the material with the more-negative VB edge. The main drawback of such a system is a de-crease of its (overall) redox potential [18].

The most promising photocatalytic materials are all-solid semi-conductor systems with a Z-scheme photogenerated charge-transfer mechanism [19]. Z-scheme systems have been reported for water splitting [20], dye degradation [21] and CO2 conversion [22]. In Z-scheme systems, semiconductors with mismatched band edges are coupled via ohmic contact to position the CB and VB potentials of one semiconductor more negative than those of the other semiconductor [18]. Ohmic contact in a Z-scheme system triggers the recombination of electrons and electron holes with lower reduction or oxidation potential, thus leaving more reducing electrons and more oxidative holes intact and providing enormously high redox potential for the visible-light-active narrow band gap semiconductor system.

The main obstacles for Z-scheme practical applications are compli-cated (non-industrializable) multistep synthesis methods, small yields and expensive reagents. Moreover, often Z-scheme photocatalyst synthesis are not green, but photocatalysis technology can be fully considered as green if the system is a de-crease of its overall redox potential [18].

2. Experimental section

2.1. Materials

Iron (iii) nitrate nonahydrate (Fe(NO3)3·9H2O, ≥98%), hexam- ethylenetetramine (HMTA, CH2N2·H2O, ≥99%), calcium nitrate tetra-hydrate (Ca(NO3)2·4H2O, ≥99%), sodium hydroxide (NaOH, ≥98%), MB, C12H14ClN3S, ≥95%), BQ (C4H4(O)=O2), certified reference mate-rial), TEA ((HOCH2CH2)2N, ≥99%), and TBA (C4H9O, anhydrous, ≥99.5%) were provided by Sigma-Aldrich and were used as received without performing additional purification steps. Deionized water (Milli-Q, electrical resistivity 18.2 MD cm) was used for the synthesis and photocatalytic tests.

2.2. Synthesis of the nanoparticle substrates, powdered Fe2O3/Ca2Fe2O5 nanoheterostructures and photoanodes

2.2.1. Amorphous Fe-containing nanoparticles

To synthesize the amorphous iron-based substrate nanoparticles, 0.1 M iron(iii) nitrate was dissolved in deionized water. The obtained iron nitrate solution was mixed with a 0.5 M HMTA aqueous solution at an equivolumentary ratio at room temperature. Brown sediment im-mEDIATELY formed after mixing the two solutions. After stirring for 5 min, the sediment was collected by centrifugation and was washed with water until the pH value reached 7. The obtained nanoparticle sediment for the heterostructure synthesis was kept in water without drying.

2.2.2. Goethite (α-FeOOH)

Goethite α-FeOOH nanowires were synthesized by chemical pre-cipitation. In a typical procedure, a 0.1 M iron(iii) nitrate aqueous so-lution was precipitated at room temperature by the dropwise addition of a 0.5 M NaOH aqueous solution. The obtained sediments were stirred for an additional 30 min and aged for 72 h at 60 °C. The obtained yellow goethite nanowires were collected using centrifugation, washed by water until neutral pH value and stored in water without drying.

2.2.3. Hematite (α-Fe2O3)

Crystalline (colloidal) α-Fe2O3 nanoparticles (Fe2O3 (HU)) were synthesized by hydrothermal synthesis. During the synthesis, 40 ml of a 0.1 M iron(iii) nitrate aqueous solution was poured into a 50 ml Teflon-sealed stainless-steel autoclave and hydrothermally treated at 150 °C for 24 h. As for the other nanoparticle substrates for the heterostructure synthesis, the nanoparticles were washed and stored in water without drying to prevent agglomeration.

2.2.4. Fe2O3/Ca2Fe2O5 nanoheterostructure

For the synthesis of the Fe2O3/Ca2Fe2O5 nanoheterostructures, various substrate nanoparticles were dispersed in a Ca(NO3)2 solution, filtered, dried at 60 °C and heat treated at 820 °C for 20 min in the ambient atmosphere. To control amount of Ca2Fe2O5, before filtering and annealing, the substrate nanoparticles were dispersed in 0.1 M, 0.5 M and 1 M aqueous solutions of calcium nitrate.

2.2.5. Fe2O3 and Fe2O3/Ca2Fe2O5 nanoheterostructure photoanodes

The amorphous iron-containing substrate films were prepared by potentiostatic anodic electrodeposition on working electrodes – FTO-coated glass slides (surface resistivity ~ 7Ω/sq, Sigma-Aldrich). Electrodeposition was performed from a 0.02 M FeCl3 aqueous solution using a Pt wire as the counter electrode by applying a potential of 1.2 V. The deposition time and annealing temperature were 35 min and 40 °C, respectively. To obtain the Fe2O3/Ca2Fe2O5 nanoheterostructure photo-anode, amorphous iron-containing substrate films were immersed in a Ca(NO3)2 solution, dried at 60 °C and heat treated at 820 °C for 20 min.

2.3. Structural characterization

The crystalline phases of the synthesized samples were analyzed by powder XRD. A Ultima+ diffractometer (Rigaku, Japan) with Cu-Kα radiation was used for experiments. The SEM morphology studies were performed on a Helios Nanolab, FEI. Electron microscopy at high magnification was performed using TEM (Tecnai G2 F20, FEI) operated at 200 kV. To obtain better phase contrast of the different particles on the nanoheterostructures, STEM was used. EDX was used for sample elemental analysis to verify selected particles on the nanohetero-structures.

The specific surface areas of the synthesized powders were analyzed by recording nitrogen adsorption–desorption isotherms using a NOVA 1200e instrument (Quantachrome, UK). The specific surface areas, S (m2/g), for the synthesized samples were calculated by the BET method. The surface charges (zeta potentials) of aqueous suspensions of hematite (~0.5 mg/mL) were measured using a Zetasizer Nano ZSP (Malvern Instruments).

The optical absorption spectra of the samples in visible range were measured by a UV-NIR spectrophotometer (Agilent, Cary 4000 UV–vis, Germany). XPS was used to investigate the chemical states and ele-mental compositions of the heterostructure powders and photoanodes. The powders for XPS measurements were pressed in indium. A surface station equipped with an electron energy analyzer (SCIENTA SES 100) and a non-monochromatic twin anode X-ray tube (Thermo XRESS2) with a characteristic energy of 1253.6 eV (Mg Ka1,2 FWHM 0.68 eV) were
Fig. 1. XRD patterns (a) of different substrate nanoparticles before and after thermal treatment; SEM images of the as-prepared amorphous iron-containing substrate nanoparticles (b), Fe$_2$O$_3$ obtained by hydrothermal synthesis (c) and goethite nanowires (d).

2.4. Photocatalytic activity studies

Photocatalytic activities and photocorrosion stabilities of the powder samples were estimated by the photocatalytic degradation of MB dye in aqueous solution (dye concentration 10 mg/l, photocatalyst loading 1 mg/mL) under visible-light irradiation. The light source used for experiments 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 ± 3 mW/cm$^2$. The photocatalytic tests were performed at room temperature in closed 20 ml glass vials. Constant stir-ring was provided during the tests.

Before the photocatalytic measurements, the powders were dispersed in glass vials using a Hielscher UP50H Compact Lab Homogenizer at maximum intensity for 3 min. The suspensions were kept in the dark until adsorption-desorption equilibrium was observed.

The photocatalytic degradation rate of MB was monitored by sampling 1.4 ml from each suspension after a certain time interval. After centrifuging, the supernatant was analyzed by the spectrophotometer.

The photocatalytic activity was estimated by calculating the rate constant (k) of MB degradation from a pseudo-first-order kinetic equation, $-\ln(C/C_0) = kt$, where $C_0$ and C are the initial absorption peak intensity of MB and the absorption peak intensity of MB in solution after a period of time (t). The rate constants k were divided by the BET surface area.

To estimate the photocorrosion stabilities, after the photocatalytic tests, the powders were separated by centrifugation, dried at 60 °C and re-dispersed again for the next measurement cycle.

2.5. PEC measurements

PEC measurements were measured in a three-electrode cell containing 1 M NaOH electrolyte (pH = 13), a platinum wire counter electrode, a sample film on an FTO/glass substrate as the working electrode (1 cm$^2$) and SCE as the reference electrode. The open circuit potential was measured after 15 min in the dark. The photocurrent was measured using 5 s light pulses followed by 5 s in the dark with a VoltaLab PGZ 301 potentiostat (Radiometer Analytical) measuring the volt-ampereic (I–V) curves (potential was scanned from −200 mV to +500 mV with a rate of 5 mV/s). The photocurrent was calculated as the difference between currents in the dark and in the light for selected potential increments. After each sample, the electrolyte solution was used for XPS measurements. Ultra-high vacuum with a base-pressure lower than 8 × 10$^{-10}$ mbar was used for the XPS measurements. The binding energy was corrected in XPS experiments by using adventitious C1s, C 1s peak at 284.8 eV.
changed, and the cell was rinsed with deionized water. The light source used for the PEC measurements was a 30 W LED with visible-light ir-radiation (415–700 nm, 15 ± 1 mW/cm²).

2.6. Mott-Schottky analysis

Fixed frequency (10 kHz) impedance measurements using a VoltaLab PGZ 301 (Radiometer Analytical) impedance analyzer were performed to measure the Mott-Schottky curves. The capacitance was measured for each sample in a frequency of 10 kHz at different biases from −500 mV to 300 mV with a step of 50 mV. The measured capacitance was plotted on a Mott-Schottky graph (1/C² versus electrode potential) using the equation:

\[ \frac{1}{C^2} = \frac{2}{e \varepsilon \varepsilon_0 N} \left( V - V_{app} + \frac{dV}{dT} \alpha T \right) \]

where \( C \) is the capacitance of the barrier layer, \( V_{app} \) is the applied bias potential, \( V_{FB} \) is the flat band potential, \( N \) is the concentration of donor charge carriers, and \( T \) is the absolute temperature. The VFB value was determined by extrapolating the linear region in the Mott-Schottky plot to zero.

3. Results and discussion

3.1. Iron-containing (substrate) nanoparticle formation and structural properties

Various iron-containing substrates were used for the preparation of FeO₃/Ca₂Fe₂O₅ nanoheterostructures. Nanosized particle substrates were dispersed in Ca²⁺-containing aqueous solution, filtered and heat treated. Upon heating, Ca²⁺ reacts with the iron species to form the Fe₂O₃/Ca₂Fe₂O₅ nanoheterostructure. A similar strategy was demonstrated by K.J. McDonalds and K.S. Choi, where crystalline α-Fe₂O₃ electrodes were immersed in Zn²⁺-containing solution and heat treated to obtain Fe₂O₃/ZnFe₂O₄ [23]. The tight interface between the semi-conductors in the nanoheterostructure enhances charge transfer and the photocatalytic performances [16,24]. If charge-carrier transfer/mobility is hindered, electron and electron-hole pairs will be more likely to recombine [24]. Here, to achieve effective interfacial charge transfer between Fe₂O₃ and Ca₂Fe₂O₅, various iron-containing nanoparticle substrates, such as amorphous precipitates and two crystalline sub-estrates with different surface chemistry (α-Fe₂O₃ nanoparticles and α-FeOOH nanowires), were tested. The formation of Ca₂Fe₂O₅ should be easier on amorphous substrate nanoparticles. For crystalline materials, solid-state reactions are limited due to ion diffusion, while amorphous substrate nanoparticles serve as a site for the re-precipitation of a crystalline phase [25].

All the nanoparticle substrate materials were synthesized by environmentally friendly, scalable and straightforward aqueous chemistry methods. Amorphous iron-based substrate nanoparticles were obtained by mixing iron nitrate and hexamethylenetetramine (HMTA) water solutions at room temperature. The addition of the HMTA solution in-creases the pH of the ferric aqueous solution from 2.01 to 4.87, and consequently, iron nitrate hydrolysis occurs. As confirmed by X-ray diffraction (XRD) measurements (Fig. 1(a)), amorphous precipitates form after mixing the precursors. The use of amorphous nanoparticle substrates is important for the synthesis of the Fe₂O₃/Ca₂Fe₂O₅ nano-heterostructure immediately after the procedure (sedimentation and washing by water), as storage in water leads to the formation of iron oxide hydroxide, FeO(OH), crystals, as demonstrated by the XRD pattern in the Electronic Supplementary information (ESI), Fig. S1. Ad-ditionally, to obtain amorphous iron-containing nanoparticles, the ferric nitrate and HMTA solutions must be mixed at room temperature. Precipitation at higher temperatures triggers crystallization of α-FeOOH and α-Fe₂O₃. ESI Fig. S2 presents the XRD plot for the sediment obtained upon mixing the ferric nitrate and HMTA solutions in water at 80 °C, where the goethite and hematite phases are clearly distinguished. The microstructure of the sediment was studied by scanning electron microscopy (SEM) (Fig. 1(b)), which revealed the formation of densely packed nanoparticle agglomerates with indeterminable particle size; however, the particle diameter is clearly estimated in the nanometer range. The relatively small particle size can be explained by the overall
tendency to obtain smaller sized particles at lower synthesis temperatures. Heat treatment of the amorphous precipitate at 820 °C for 20 min yields the pure hematite α-Fe₂O₃ (A) (ICDD 00-006-0502) nanoparticles, as demonstrated by the XRD pattern in Fig. 1(a), thus de-monstrating the potential to use the obtained precipitates to construct the hematite-based Fe₂O₃/Ca₂Fe₂O₅ nanoheterostructure.

Crystalline (colloidal) α-Fe₂O₃ (HU) nanoparticles were synthesized by a hydrothermal synthesis approach, where the Fe³⁺ nitrate solution in water was heated at 150 °C for 24 h for homogeneous nucleation, particle growth and α-Fe₂O₃ crystallization [26]. Phase-pure well-crystalline hematite was obtained immediately after the synthesis, as indicated by XRD (Fig. 1(a)), which shows a diffraction pattern with sharp hematite-related peaks (ICDD 00-006-0502) and no adjacent phases. SEM shows hematite particle formation with diameters from 10 nm up to 100 nm during the hydrothermal synthesis, as demon-strated in Fig. 1(c).

Goethite α-FeOOH nanowires were obtained via the precipitation of iron nitrate by NaOH solution in water and aging for 72 h at 60 °C. The precipitation synthesis yielded phase-pure goethite α-FeOOH (ICDD 04-015-2899) with a typical orthorhombic structure, as confirmed by XRD (Fig. 1(a)). The sharp diffraction peaks of the α-FeOOH nanowires in-dicate a well-crystallized material. No peaks arising from impurities were detected by XRD. The formation of one-dimensional α-FeOOH nanowires was confirmed by SEM (Fig. 1(d)). The synthesized nano-wires are up to 500 nm long, and the diameters vary from 20 to 150 nm with an aspect ratio up to 30. Transmission electron microscopy (TEM) images (ESI, Fig. S3) show that most of the goethite nanowires are grouped in bundles, and the actual diameter of a single nanowire is approximately 21 ± 5.5 nm. The α-FeOOH nanowires form during the precipitation synthesis by the olation of tetrameric polycation species to embryos of octahedral double chains, which is a characteristic of the goethite structure [27]. Goethite nanowires transform to phase-pure hematite α-Fe₂O₃ (NW) upon annealing at 820 °C for 20 min, as de-monstrated in Fig. 1(a).

3.2. Formation and structural properties of Fe₂O₃/Ca₂Fe₂O₅ nanoheterostructure powders

Briefly, to obtain the Fe₂O₃/Ca₂Fe₂O₅ nanoheterostructure, sub-strate nanoparticles were dispersed in Ca(NO₃)₂ solution, filtered, dried and thermally treated at 820 °C for 20 min in the ambient atmosphere. The amount of Ca₂Fe₂O₅ can be controlled by molarity of Ca(NO₃)₂. Phases on the XRD pattern (Fig. 2(a) and ESI, Fig. S4) related to he-matite (ICDD 00-033-0664) and brownmillerite CaFe₂O₅ (ICDD 04-002-2559) were observed using the amorphous nanoparticle substrates. Increased peak intensities related to the Ca₂Fe₂O₅ phase were observed upon increasing the molarity of the Ca(NO₃)₂ solution. The observed XRD pattern is in well accordance with the results from scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) spectroscopy analysis on single nanocrystals (Fig. 2(b–d)), which revealed the presence of both calcium and iron within the nanoheterostructure. The XRD peaks related to the Ca₂Fe₂O₅ phase are not as strongly ob-served after the heat treatment of the Ca(NO₃)₂-soaked colloidal α-Fe₂O₃ nanoparticles and goethite α-FeOOH substrates (ESI, Fig. S5). Additionally, the presence of Ca₂Fe₅ in the Ca(NO₃)₂-soaked and thermally treated α-FeOOH is confirmed by the EDX studies presented in ESI, Fig. S6. Moreover, the Ca quantities in the heterostructures derived from the α-FeOOH and amorphous iron-containing nanoparticles are very similar (~5 wt%). The amorphous iron-containing nanoparticle substrates could provide more surface sites and open pores and a higher surface area for precursor spatial infiltration and adsorption with a higher abundance of Fe cations for Ca₂Fe₂O₅ formation upon heat treatment. The surface of the goethite crystals presents a highly dense coating of –OH groups, and heating transforms goethite to Fe₂O₃ by releasing water based on the reaction: 2FeOOH →Fe₂O₃ + H₂O. Water release during the phase transition may prohibit Fe supply for Ca₂Fe₂O₅ formation. The goethite wires also exhibit the lowest surface area among the substrate nanoparticles used for the Fe₂O₃/Ca₂Fe₂O₅ nano-heterostructure synthesis. The multipoint Brunauer-Emmett-Teller (BET) specific area values for amorphous iron-containing sub-strates, crystalline α-Fe₂O₃ and α-FeOOH were 115.7 m²/g, 109.40 m²/g and 60.23 m²/g, respectively.
3.4. Photocatalytic dye degradation by hematite and Fe2O3/Ca2Fe2O5 nanoheterostructure powders

The photocatalytic activities of the synthesized materials were estimated by the degradation of methylene blue (MB) under visible-light irradiation (45 ± 3 mW/cm²). The change of the most intense absorption peak of MB centered at 665 nm was evaluated to study MB degradation. The blank experiments show that only a 1% decrease of MB occurs in the absence of a photocatalyst during a 5 h irradiation. α-Fe2O3 was obtained by thermal phase transition/treatment at 820 °C for 20 min from: (i) amorphous Fe-containing precipitates (α-Fe2O3 (A)), (ii) α-FeOOH nanowires (α-Fe2O3 (NW)) and (iii) hydrothermal synthesis derived α-Fe2O3 (α-Fe2O3 (HU)). The photocatalytic activities of α-Fe2O3 were studied to estimate the enhancement in performance after coupling with Ca2Fe2O5 (Fig. 4). The pseudo-first-order rate constant (k) for MB degradation for the various hematite samples are very similar and decrease in the following order: α-Fe2O3 (A) (2.97·10⁻³ min⁻¹) → α-Fe2O3 (NW) (1.73·10⁻³ min⁻¹) → α-Fe2O3 (HU) (1.45·10⁻³ min⁻¹). The observed rate constants are almost the same as those previously reported for MB degradation under visible-light irradiation by flower-like hierarchical nanosized α-Fe2O3 [32].

Multipoint BET surface area measurements revealed the following specific surface area values of the hematite samples: α-Fe2O3 (A) (2.16 m²/g), α-Fe2O3 (NW) (28.84 m²/g) and α-Fe2O3 (HU) (12.55 m²/g). To exclude the effect of the specific surface area, the k values were divided by the surface areas. The specific rate constants for the various samples decrease in the following order: α-Fe2O3 (A) (1.38·10⁻³ min⁻¹ g⁻¹ m⁻²) → α-Fe2O3 (HU) (0.11·10⁻³ min⁻¹ g⁻¹ m⁻²) → Fe2O3 (NW) (0.08·10⁻² min⁻¹ g⁻¹ m⁻²). The results show that α-Fe2O3 (A) exhibits considerably higher photocatalytic activity, which is related to various surface properties. The measured Z-potential values for the various samples were: α-Fe2O3 (A) (+23.9 eV) → α-Fe2O3 (HU) (+17.6 eV) → Fe2O3 (NW) (~37.9 eV).

The k value increased 5 times for α-Fe2O3 (A) (k = 0.015 min⁻¹) and 4.8 times for α-Fe2O3 (HU) (k = 0.007 min⁻¹) when the samples (before thermal treatment) were soaked in 1 M aqueous Ca(NO3)2 solution. No enhancement was observed for the materials obtained from the FeOOH substrate nanoparticles. The samples obtained from the amorphous substrate nanoparticles exhibited two-fold higher rate constants compared to the other samples. We also studied the specific surface areas to normalize the rate constants and exclude the effect of a larger surface area. The specific surface areas were 12.4 m²/g and 6.3 m²/g for Fe2O3/Ca2Fe2O5 obtained from α-Fe2O3 (A) and α-Fe2O3 (HU), respectively. The specific rate constant for Fe2O7/Ca2Fe2O5 obtained from α-Fe2O3 (A) (1.21·10⁻³ min⁻¹ g⁻¹ m⁻²) is still higher than those observed for the other samples but is similar to the samples obtained from crystalline α-Fe2O3 (1.12·10⁻³ min⁻¹ g⁻¹ m⁻²). The results show that both amorphous iron-containing nanoparticles can be used for substrate materials to obtain an efficient Fe2O7/Ca2Fe2O5 photo-catalyst nanoheterostructure. The sample obtained from the FeOOH substrate nanoparticles showed a considerably lower rate constant (0.034·10⁻³ min⁻¹ g⁻¹ m⁻²), which could be attributed to hindered Ca2Fe2O5 formation, as discussed in the section above about the formation and structural properties of the Fe2O7/Ca2Fe2O5 nanoheterostructure powders.
tight interface Fe$_2$O$_3$/Ca$_2$Fe$_2$O$_5$ nanoheterostructure formation and improved photogenerated charge-carrier separation over the interface. Ca$_2$Fe$_2$O$_5$ is a narrow band gap p-type semiconductor with a more-negative CB potential and more-negative VB potential in comparison to hematite [33]. Thus, charge transfer between n-type α-Fe$_2$O$_3$ and p-type Ca$_2$Fe$_2$O$_5$ can be potentially incorporated into a Z-scheme mechanism, where photoinduced electrons on hematite would recombine with photogenerated electron holes on Ca$_2$Fe$_2$O$_5$, leaving electrons on Ca$_2$Fe$_2$O$_5$ and electron holes on α-Fe$_2$O$_3$ for reduction and oxidation reactions, respectively, and consequently providing a high redox potential for the overall system. Z-scheme photocatalytic systems have been considered the most effective photocatalytic systems due to their excellent charge separation (reduced recombination) and high redox potentials compared to classical heterojunction-type photocatalytic systems, where electrons are transferred to the CB with a lower reductive potential, and electron holes are transferred to the VB with a lower oxidation potential [18]. In a Z-scheme, two semiconductor compounds are primarily coupled via ohmic contact (conductor) with low contact resistance [34]. The first reported all-solid Z-scheme was the three-component semiconductor-conductor-semiconductor system (TiO$_2$-Au-CdS) published in 2006 by Tada et al. [35]. Other two-component solid-state Z-scheme systems, where low contact resistance was provided by conductive contact interface [18] or a p-n junction [36,37], have also been reported. Here, our Z-scheme may be formed through a p-n junction between p-type Ca$_2$Fe$_2$O$_5$ and n-type α-Fe$_2$O$_3$. P-type conductivity in brownmillerite Ca$_2$Fe$_2$O$_5$ is provided by oxygen interstitials, which are charge compensated by holes associated with Fe cations due to variable oxidation states [38].

To verify the Z-scheme charge-transfer mechanism, various scavengers were added during the photocatalytic MB degradation tests. First, benzoquinone (BQ) was added to scavenge superoxide anions, %O$_{2^-}$, the k value for MB degradation by Fe$_2$O$_3$ (A)/Ca$_2$Fe$_2$O$_5$ decreased by an order of magnitude from 0.015 (min$^{-1}$) to 0.0015 (min$^{-1}$), indicating that %O$_{2^-}$ has a considerable role in MB degradation. However, we did not observe a decrease in photocatalytic activity for bare Fe$_2$O$_3$ after BQ addition. The potential for oxygen reduction from O$_2$ to %O$_{2^-}$ is −0.33 eV vs the normal hydrogen electrode (NHE), thus %O$_{2^-}$ cannot be generated by photoinduced electrons on the CB of hematite, which has a reduction potential of +0.2 eV vs NHE [39], while the CB of Ca$_2$Fe$_2$O$_5$ has a more-negative reduction potential than that of oxygen reduction to produce %O$_{2^-}$, Therefore, %O$_{2^-}$ release was ex-perimentally observed [33]. We also studied the influence of triethanolamine (TEA) to quench holes and tert-butyl alcohol (TBA) for scavenging hydroxyl radicals, %OH. Both scavengers displayed an almost equal effect on MB degradation by the photocatalytic process. The rate constants for MB degradation over Fe$_2$O$_3$ (A)/Ca$_2$Fe$_2$O$_5$ decreased from 0.015 to 0.004 and 0.006 (min$^{-1}$) with added TEA and TBA, respectively. The VB oxidation potential of α-Fe$_2$O$_3$ is sufficiently positive to oxidize H$_2$O to %OH and H$^+$ (H$_2$O + h$^+$ → %OH + H$^+$), where re-leased H$^+$ can generate ROS H$_2$O$_2$ and %OH.

3.5. Fe$_2$O$_3$ and Fe$_2$O$_3$/Ca$_2$Fe$_2$O$_5$ photoanodes and their PEC performances

Photoelectrochemical (PEC) measurements were performed on the α-Fe$_2$O$_3$ and Fe$_2$O$_3$/Ca$_2$Fe$_2$O$_5$ photoanodes to gain better understanding of the photoinduced charge-carrier separation and transport over the nanoheterostructure. The photoanodes were obtained in a similar way as the Z-scheme Fe$_2$O$_3$/Ca$_2$Fe$_2$O$_5$ nanoheterostructure powders – by
soaking iron-containing sediment in a Ca(NO$_3$)$_2$ solution and subsequently drying and heating at 820 °C for 20 min. Iron-containing substrate films were prepared by potentiostatic anodic electrodeposition on F-doped SnO$_2$ (FTO) transparent conduction oxide substrates. The utilized anodic deposition conditions favor the oxidation of Fe$^{2+}$ to Fe$^{3+}$ and precipitation of the amorphous oxyhydroxide [40]. To obtain the Fe$_2$O$_3$/Ca$_2$Fe$_5$O$_9$ nanoheterostructure, iron-containing substrate films were immersed in a Ca(NO$_3$)$_2$ solution, dried and heat treated.

The XRD patterns confirm the formation of the hematite phase. The optical band gaps of the obtained Fe$_2$O$_3$ and Fe$_2$O$_3$/Ca$_2$Fe$_5$O$_9$ photoanodes were 1.94 eV and 1.96 eV, respectively. Similar to the powders (see Section 3.3), a small blue shift was observed upon adding Ca$_2$Fe$_5$O$_9$ to Fe$_2$O$_3$.

The SEM images show very different morphologies for Fe$_2$O$_3$ and the Fe$_2$O$_3$/Ca$_2$Fe$_5$O$_9$ heterostructure. The hematite photoanode formed from tetragonal-like single crystals with edges up to 500 nm. The het-erostructure photoanode reveals a microstructure composed of relatively small (70–150 nm) irregularly shaped nanocrystals and cracks. The cross-sections of both films reveal very similar thicknesses of approximately 500 nm and, again, different morphologies along the entire cross-sections, indicating that calcium nitrate was impregnated deep in the electrochemically deposited iron-containing amorphous substrate layer. The presence of Ca$_2$Fe$_5$O$_9$ in the films was confirmed by X-ray photoelectron spectroscopy (XPS) (ESI, Fig. S7). The locations and shapes of the photoinduced charge separation is improved [16,17]. Our electron microscopy observa-tions reveal a remarkable decrease in grain size for the samples im-mersed in calcium nitrate before annealing, while charge-carrier se-paration is improved in the heterostructure because both the CB and VB edges of hematite lie energetically lower than the CB and VB of brownmillerite. Thus, photoinduced electrons are transferred from Ca$_2$Fe$_5$O$_9$ to Fe$_2$O$_3$ under applied bias and anodic conditions. Moreover, photoinduced electron holes are expected to be transferred from hematite to brownmillerite for oxidation reactions.

The observed results correlate with the Mott-Schottky analysis based on electrochemical impedance measurements in the dark on bare Fe$_2$O$_3$ and Fe$_2$O$_3$/Ca$_2$Fe$_5$O$_9$. The flat band potential (VFB) position was 346.6 eV, and the Fe 2p3/2 maximum is located at 710.5 eV, with a satellite signal associated with Fe$^{3+}$ also present at higher binding energies.

The PEC measurements were measured under visible light (15 ± 1 mW/cm$^2$) in a three-electrode cell containing 1 M NaOH electrolyte (pH = 13), a platinum wire counter electrode, the sample film on an FTO/glass substrate as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. J-V curves for the hematite Fe$_2$O$_3$ and Fe$_2$O$_3$/Ca$_2$Fe$_5$O$_9$ photoanodes are demonstrated in Fig. 6(b). A photocurrent of 183 μA/cm$^2$ was observed at 0.5 V for bare hematite, and this photocurrent increased to 306 μA/cm$^2$ for Fe$_2$O$_3$/ Ca$_2$Fe$_5$O$_9$. The photocurrent indicates the number of photogenerated holes that reach the semiconductor/liquid interface. The higher p-ho-tocurrent can be due to the increased relative volume of the space charge layer and enhanced photogenerated charge-carrier separation. Nanostructuring is an effective strategy to increase the relative volume of the space charge layer [42], while heterostructuring enhances charge-carrier separation [16,17]. Our electron microscopy observa-tions reveal a remarkable decrease in grain size for the samples im-mersed in calcium nitrate before annealing, while charge-carrier se-paration is improved in the heterostructure because both the CB and VB edges of hematite lie energetically lower than the CB and VB of brownmillerite. Thus, photoinduced electrons are transferred from Ca$_2$Fe$_5$O$_9$ to Fe$_2$O$_3$ under applied bias and anodic conditions. Moreover, photogenerated electron holes are expected to be transferred from hematite to brownmillerite for oxidation reactions.

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mechanism of Ca$_2$Fe$_2$O$_5$ in the Z-scheme regime is different from that of bare brownmillerite, which transforms to carbonates during the pho-todegradation process of methylene orange [45].

However, the Fe$_2$O$_3$/Ca$_2$Fe$_2$O$_5$ system is stable under PEC measurements, indicating a different charge-transfer mechanism. A similar p-n junction photoanode, where hematite was coupled with CaFe$_2$O$_4$, was demonstrated by M.G. Ahmed et al. [44]. Under illumination, photogenerated holes were transferred to CaFe$_2$O$_4$, while photo-generated electrons transferred from the CaFe$_2$O$_4$ CB to the Fe$_2$O$_3$ CB and further to the contact electrode. Here, under the proposed mechanism, Ca$_2$Fe$_2$O$_5$ in the Fe$_2$O$_3$/Ca$_2$Fe$_2$O$_5$ system is protected from photocorrosion and thus exhibits stable photocurrent, as demonstrated in Fig. 7(b).

4. Conclusions

An all-solid-state Z-scheme nanoheterostructure was successfully constructed from an earth abundant, environmentally friendly element based on n- and p-type narrow band gap semiconductors, hematite α-Fe$_2$O$_3$ and brownmillerite Ca$_2$Fe$_2$O$_5$, by soaking Fe-containing nano-particle substrates (free standing particles in suspensions or thin films) with Ca$_2^+$ aqueous solutions. The heterostructure formation was more pronounced on amorphous Fe nanoparticle substrates than on crystal-line hematite, while the formation of Ca$_2$Fe$_2$O$_5$ was not observed on goethite α-FeOOH. In comparison with hematite, the Fe$_2$O$_3$/Ca$_2$Fe$_2$O$_5$ nanoheterostructure exhibited a five-fold higher photocatalytic dye degradation rate and two-fold enhanced photocurrent. The Z-scheme photoinduced charge-carrier transfer mechanism in the Fe$_2$O$_3$/Ca$_2$Fe$_2$O$_5$ powders was confirmed by chemical methods, where the photocatalytic activity was strongly influenced by %O$_2^-$ scavengers. However, the degradation ability of Fe$_2$O$_3$ was not influenced by these scavengers. Long-term photocurrent measurements revealed the stable performance of Fe$_2$O$_3$/Ca$_2$Fe$_2$O$_5$ while Ca$_2$Fe$_2$O$_5$ was less stable under the Z-scheme regime due to a lower tolerance against photoreduction.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jece.2018.04.003.

References

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