Recycling Rusty Iron with Natural Zeolite Heulandite to Create a Unique Nanocatalyst for Green Hydrogen Production

Mohamed Shaban 1,2,*, Mohammad BinSabt 3, Ashour M. Ahmed 2,† and Fatma Mohamed 2,4

1 Department of Physics, Faculty of Science, Islamic University in Madinah, Al-Madinah Al-Munawarah 42351, Saudi Arabia
2 Nanophotonics and Applications (NPA) Lab, Physics Department, Faculty of Science, Beni-Suef University, Beni-Suef 62514, Egypt; ashour.elshemey@gmail.com (A.M.A.); fchem2010@yahoo.com (F.M.)
3 Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Safat 13060, Kuwait; Mohammad.binsabt@ku.edu.kw
4 Polymer Research Laboratory, Chemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef 62514, Egypt
* Correspondence: mssfadel@aucegypt.edu

Abstract: Corrosion-induced iron rust causes severe danger, pollution, and economic problems. In this work, nanopowders of $\text{Fe}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$/zeolite are synthesized for the first time using rusted iron waste and natural zeolite heulandite by chemical precipitation. The chemical composition, nanomorphologies, structural parameters, and optical behaviors are investigated using different techniques. The $\text{Fe}_2\text{O}_3$/zeolite nanocomposite showed smaller sizes and greater light absorption capability in visible light than $\text{Fe}_2\text{O}_3$ nanopowder. The XRD pattern shows crystalline hematite ($\alpha$-$\text{Fe}_2\text{O}_3$) with a rhombohedral structure. The crystallite sizes for the plane (104) of the $\text{Fe}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$/zeolite are 64.84 and 56.53 nm, respectively. The $\text{Fe}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$/zeolite have indirect bandgap values of 1.87 and 1.91 eV and direct bandgap values of 2.04 and 2.07 eV, respectively. $\text{Fe}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$/zeolite nanophotocatalysts are used for solar photoelectrochemical (PEC) hydrogen production. The $\text{Fe}_2\text{O}_3$/zeolite exhibits a PEC catalytic hydrogen production rate of 154.45 mmol/g.h @ 1 V in 0.9 M KOH solution, which is the highest value yet for $\text{Fe}_2\text{O}_3$-based photocatalysts. The photocurrent density of $\text{Fe}_2\text{O}_3$/zeolite is almost two times that of $\text{Fe}_2\text{O}_3$ catalyst, and the IPCE (incident photon-to-current conversion efficiency) reached 62.34%@307 nm and 1 V. The electrochemical surface area (ECSA) values for $\text{Fe}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$/zeolite photocatalysts were 7.414 and 21.236 m$^2$/g, respectively. The rate of hydrogen production for $\text{Fe}_2\text{O}_3$/zeolite was 154.44 mmol h$^{-1}$/g. This nanophotocatalyst has a very low PEC corrosion rate of 7.6 pm/year; it can retain ~97% of its initial performance. Therefore, the present research can be applied industrially as a cost-effective technique to address two issues at once by producing solar hydrogen fuel and recycling the rusted iron wires.

Keywords: rusted iron; $\text{Fe}_2\text{O}_3$/zeolite nanocomposite; water splitting; hydrogen production; photocatalyst

1. Introduction

Fossil fuel burning is the major source of CO$_2$ emissions (CO$_2$ and CO) in atmospheric air, which causes global warming. The resulting air pollution can have catastrophic effects on humans and animals alike [1,2]. Hydrogen fuel is a carbon-free, renewable, and environmentally friendly source of energy that can be used as an ideal alternative to fossil fuels.

Therefore, the developments of effective techniques for large hydrogen fuel production at reasonable cost are important research areas. The photoelectrochemical (PEC) hydrogen production utilizing semiconductor-based catalysts is a promising technique to meet these requirements. In the PEC process, the photocatalyst produces an electron/hole pair after absorbing a photon, which is then isolated, transported, and contributed to the cathodic hydrogen evolution/anodic oxygen evolution reactions at applied voltage [3,4].
Under incident light with a suitable wavelength, electron/hole pairs are created in the semiconductor. The holes reacted with H$_2$O to generate hydroxyl radical (OH). The electrons can react with O$_2$ to produce superoxide radicals (O$_2^-$). These reactive species are primarily responsible for the water splitting and hydrogen production [5]. There are several semiconductor materials such as WO$_3$, ZrO$_2$, Ir$_2$O$_3$, SnO$_2$, Fe$_2$O$_3$, TiO$_2$, ZnO, CuO, and CdS that were applied to upgrade the PEC performance. Among them, Fe$_2$O$_3$ is used as a photocatalyst for the PEC due to its hard solubility, high chemical stability, low cost, and massive abundance [6,7]. Additionally, it is a non-toxic and ecologically benign substance, all of which are required for large-scale solar energy conversion at a reasonable cost. Fe$_2$O$_3$ has semiconducting properties with a narrow bandgap (~2.1 eV). This low bandgap enables it to be a good photocatalyst in the visible region. However, this material has many drawbacks that limit its application in practical photocatalytic such as low diffusion lengths of holes, poor conductivity, fast electron–hole recombination, poor adsorption property, agglomeration, and difficulty in being recovered [8]. Several studies immobilized the Fe$_2$O$_3$ nanoparticles on different supports, such as activated carbon, silica, alumina, clay, and zeolite to overcome these disadvantages. Among them, zeolite is of particular interest because, besides its semiconducting nature, it has a high adsorption capacity against organic contaminants. Zeolite possesses ionic exchange properties that are idyllic for the adsorption/degradation of organic dyes [9,10]. It also has enormous unique areas, adjustable hydrophobicity/hydrophilicity, and photochemical stability [11,12]. In addition, zeolite is low-cost, abundant, and bio-compatible. Zeolite is a monocrytal mineral composed of Si and Al atoms in a tetrahedral arrangement (TO$_4$; T = Si, Al) [13]. It can be used in many applications such as cement, porcelain, electronics, and water splitting for the production of hydrogen. When a semiconductor is supported on a suitable support, such as zeolites, the semiconductor particles are evenly dispersed, preventing them from aggregating. In the past few years, zeolite was used as a support for semiconductor-based PEC catalysts to enhance the hydrogen production rate. The ZnCo/CdS/zeolite heterostructure was prepared and optimized by Jia-Hui et al. to achieve photocatalytic hydrogen activity 59 times greater than that of pristine CdS, which is ascribed to zeolite’s role in improving the separation and transportation capacity of photo-generated charge carriers [14]. Yue and Khan reported the formation of vacant sites on the zeolite surface due to the exchange of ions in titano-zeolites, which assists the hydrogen photoproduction [15]. Additionally, Pt/zeolite and Cu/zeolite were prepared and applied for the hydrogen [16,17]. Owing to its large use in many applications such as cement, porcelain, electronics, and water splitting for the production of hydrogen. When a semiconductor is supported on a suitable support, such as zeolites, the semiconductor particles are evenly dispersed, preventing them from aggregating. Hence, the Fe$_2$O$_3$ nanoparticles production from rusted iron wastes can thus be considered in many fields as a viable alternative to synthetic and natural iron supplies. Previously, different techniques have been used to prepare Fe$_2$O$_3$ nanostructures such as sol-gel, spray pyrolysis, hydrothermal, chemical vapor deposition, and thermal evaporation [18,19]. Most of these methods require complicated reactions, high energy intakes, and poor product yield. Since no special additives or equipment are needed, chemical precipitation is considered the most effective and low-cost technique for the production of Fe$_2$O$_3$.

The objective of this work is to replace the iron precursors with rust wastes as a source of iron for the synthesis of Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite nanopowder by chemical precipitation. The prepared Fe$_2$O$_3$/zeolite nanocomposite is applied for the PEC production of solar hydrogen fuel. The photon-to-electron and photon-to-hydrogen conversion efficiencies are calculated for Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite.
2. Materials and Experimental Procedures

2.1. Materials

Natural zeolite was delivered from a zeolite mine located southwest of Taiz (Al-Ahyuq region, Taiz City, Yemen). HCl and KOH were received from El-Nasr Company (Cairo, Egypt). All chemicals were at least 99 percent pure, and they were utilized just as they were bought, with no further purification. Rusted iron wires were collected from construction sites.

2.2. Preparation of the Zeolite, Fe$_2$O$_3$ and Fe$_2$O$_3$/Zeolite

Rusted iron wire fragments were collected from construction sites in Egypt’s Beni-Suef City. The average length of wires is about 30 cm with a diameter of about 1 cm. The color of the wires is dark red. Upon cutting to small fragments, the rusted wires were washed using deionized (DI) water. A total of 10 g of these pieces was dissolved in 80 mL of HCl (37%) and 170 mL DI water under magnetic stirring at 85 °C. The solution was filtered, and 20 mL of H$_2$O$_2$ (30%) was added to the obtained pale green-colored solution. Under intense 60 min-stirring, the ammonia solution was dropped to the iron solution. In a glass beaker with a volume of 200 mL, the iron was precipitated. Varying volumes of ammonium hydroxide solution (10, 15, and 20 mL) were used to prepare Fe$_2$O$_3$ powders with different crystallite sizes. The samples were labeled as Fe$_2$O$_3$ (I), Fe$_2$O$_3$ (II), and Fe$_2$O$_3$ (III), where I, II, and III refer to the 10, 15, and 20 mL of ammonia supplied to the reaction, respectively. Then, the resulting precipitated iron powder was filtered before washing and drying. Then, the resulting precipitated iron powder was heated for 3 h at 500 °C. A total of 15 g of raw zeolite mine was washed with DI water and dried in the air. Then, it was triggered mechanically by ball milling. Table 1 shows the conditions for ball milling parameters.

| Condition                  | Description      |
|----------------------------|------------------|
| Vessel size                | 15 cm            |
| Diameter balls             | from 1.11 to 1.75 cm |
| Materials of vessels       | stainless steel  |
| Materials of balls         | porcelain        |
| Ball/precipitate mass ratio| 8:1 mass ratio   |
| Speed                      | 5000 rpm         |
| Time                       | 5 h              |

For preparing Fe$_2$O$_3$/zeolite nanocomposite with optimized composition, different weight ratios of activated zeolite and iron powder (Fe$_2$O$_3$ (III)) were added to 100 mL of DI water under ultrasonication for 3 h. The total weight of Fe$_2$O$_3$/zeolite nanocomposite is kept at 2 g. The weight ratios were 0.2/1.8, 0.6/1.4, 0.8/1.2, 1.0/1.0, 1.2/0.8, 1.4/0.6, and 1.8/0.2. The resulting mixtures were dried at 80 °C for 12 h. Finally, the Fe$_2$O$_3$/zeolite nanocomposites were calcinated at 550 °C for 240 min. The nanopowders were recorded as xFe$_2$O$_3$/yzeolite, where x and y were denoted to the adding weight of Fe$_2$O$_3$ and zeolite, respectively. The synthesis steps of Fe$_2$O$_3$/zeolite nanocomposite are illustrated by a schematic in Figure 1.

2.3. Characterizations

A Philips X’Pert Pro MRD diffractometer (XRD, λ = 0.154 nm, Philips X’Pert Pro MRD, Royston, UK) was utilized to obtain the X-ray diffraction (XRD) patterns of the samples with an operating voltage of 40 kV in the range from 5° to 80°. The samples nanomorphologies were examined using a JEOL JSM-5400LV scanning electron microscope (SEM, JEOL, Tokyo, Japan). The chemical compositions were investigated by Energy Dispersive X-ray spectrometry (EDX, JEOL JED-2300 SEM, Tokyo, Japan). FT-IR (Fourier
Figure 1. Schematic of the synthesis steps of Fe$_2$O$_3$/zeolite.

2.4. PEC Water Splitting Measurements

The PEC behaviors in 0.9 M KOH (100 mL, pH 13.5) were measured at room temperature (20 °C) utilizing a Keithly measuring-source unit (Tektronix Company, model: 2400, Beaverton, OR, USA) with LabTracer software and a 400 W metal-halide lamp (Newport, 66926-500HX-R07, Newport, UK) with a set of linear optical filters (307–636 nm). The sweeping scan rate was 1 mV/s. Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite doses of 1 g were used. The PEC current density–voltage (J–V) curves were quantified in darkness, monochromatic, and white light exposure conditions. In addition, the Fe$_2$O$_3$/zeolite stability was investigated using current density–time (J–t) measurements. All PEC measurements were carried out in a quartz cell of volume 150 mL.

3. Results and Discussion

3.1. Photocatalysts Characterization

3.1.1. Structural of Fe$_2$O$_3$ and Fe$_2$O$_3$/Zeolite

The crystallinity and phase of the Fe$_2$O$_3$, zeolite, and Fe$_2$O$_3$/zeolite nanocomposite were identified using XRD analysis as seen in Figure 2A. Zeolite’s distinctive XRD peaks, in Figure 2A, are noted at 20 ~9.68°, 11.00°, 17.16°, 18.87°, 22.24°, 26.01°, 27.97, 29.84°, 31.83°, 35.88°, 47.58°, 61.76°, and 67.31°. Such peaks correspond to the crystallographic plane (020), (200), (111), (−131), (−222), (−351), (−530), (−202), (005), (311), and (223), based on PDF card No. 00-053-1176, respectively. Based on the XRD card, the type of zeolite is heulandite.

For iron oxide, the XRD pattern in Figure 2A suggests that crystalline hematite (α-Fe$_2$O$_3$) with rhombohedral structure (space group: R-3c) was formed according to the standard card No. 01-089-0597. This agrees with the previously reported data for Fe$_2$O$_3$ [20]. The pattern of Fe$_2$O$_3$ nanoparticles displays the core α-Fe$_2$O$_3$ feature peaks. These peaks are found at 33.00°, 35.39°, 49.32°, 53.84°, and 63.74° and correspond to the planes (104), (110), (024), (116), and (300). The sharp and intensive peaks indicate the high purity and crystallinity of the synthesized hematite nanoparticles using bulk Fe-based rust. These XRD data are similar to previously synthesized iron oxide in many works using synthetic precursors [21–23]. From the estimated FWHM of the strongest (104) and (110), the crystallite sizes of the Fe$_2$O$_3$ nanoparticles were estimated based on the Debye–Scherrer relation to be ~64.84 and 50.46 nm, respectively.
Figure 2. (A) XRD patterns of zeolite, Fe$_2$O$_3$, and Fe$_2$O$_3$/zeolite nanocomposite; and (B) XRD (104) and (110) peaks of Fe$_2$O$_3$ (I), Fe$_2$O$_3$ (II), and Fe$_2$O$_3$ (III).

For zeolite, many distinct peaks are observed at 22.72° (101), 41.05° (210), and 54.24° (221), corresponding to tetragonal zeolite (Al$_{0.05}$Si$_{0.95}$O$_2$) according to card No. 04-002-8520. As illustrated in Figure 2A, the main core features of XRD patterns of Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite are very close, indicating that the introduction of zeolite did not affect the structural properties of the Fe$_2$O$_3$ photocatalyst. However, the coupling of Fe$_2$O$_3$ with zeolite leads to an increase in the FWHM and a slight shift in the plane position of the Fe$_2$O$_3$ toward higher angles after coupling. Hence, the crystallites sizes of (104) and (110) peaks for Fe$_2$O$_3$ nanoparticles were decreased to 56.53 and 47.85 nm for Fe$_2$O$_3$/zeolite nanocomposite. Similar behavior was reported for hydrothermally prepared 4A-zeolite supported alpha-Fe$_2$O$_3$ [24]. In addition, the relative intensities of the diffraction peaks of Fe$_2$O$_3$/zeolite nanocomposite became weaker than the peaks of Fe$_2$O$_3$, indicating a change in the crystallinity of the Fe$_2$O$_3$ photocatalyst due to the distribution of Fe$_2$O$_3$ on the surface of the zeolite [25]. The structural parameters such as crystallite size (D), interplanar distance (d), dislocation density (δ), and microstrain (ε) are calculated for the highest two peaks, (104) and (110), utilizing the XRD patterns of Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite nanopowders. Besides peak position, peak height, and relative intensity, the obtained values are displayed in Table 2. For the two planes (104) and (110), the value of microstrain increases while d-spacing decreases after loading the zeolite with Fe$_2$O$_3$. The strongest peak corresponds to the plane (104), which indicates the preferred growth orientation of hematite. This growth orientation is beneficial to carrier transport [26]. The number of lattice defects was estimated depending on the dislocation density, δ, which refers to the dislocation lines length per unit volume of the crystal. The δ value is estimated using the relation; δ = 1/D$^2$. The values of δ for the Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite at the preferred orientation (104) are 2.378 × 10$^{-4}$ and 3.129 × 10$^{-4}$ dislocation/mm$^2$, respectively. The increase in dislocation density proposes the decrease of Fe$_2$O$_3$/zeolite crystallinity [27], which strongly influences the photocatalytic properties of the fabricated nanomaterials. This is also confirmed by the decreasing of the XRD peaks intensities after loading Fe$_2$O$_3$ on zeolite, as seen in Table 2. The existence of a high density of the defects in the Fe$_2$O$_3$/zeolite nanocrystallites can contribute positively to the photocatalytic properties as a result of the active surface area increase and the formation of a high density of the active centers [28]. These active centers may result from the formation of static charge fields about the dislocation lines [29].
Table 2. Values of the crystallographic parameters of Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite nanohybrid.

| Parameter       | Planes (hkl) | Position (° 2θ) (degree) | Height (cts) | d-Spacing (Å) | Relative Intensity (%) | Crystallite Size (nm) | Microstrain (Å) | Dislocation (δ) (10$^{-4}$ nm$^{-2}$) |
|-----------------|--------------|--------------------------|--------------|---------------|------------------------|-----------------------|-----------------|--------------------------------------|
| Fe$_2$O$_3$     | (110)        | 35.39                    | 83.37        | 2.536         | 89.78                  | 50.46                 | 0.251           | 3.927                                |
|                 | (104)        | 33                       | 92.86        | 2.714         | 100                    | 64.84                 | 0.209           | 2.378                                |
| Fe$_2$O$_3$/zeolite | (110)     | 35.77                    | 27.45        | 2.51          | 67.22                  | 47.85                 | 0.262           | 4.367                                |
|                 | (104)        | 33.32                    | 40.83        | 2.689         | 100                    | 56.53                 | 0.238           | 3.129                                |

Figure 2B shows the XRD (104) and (110) peaks of Fe$_2$O$_3$ (I), Fe$_2$O$_3$ (II), and Fe$_2$O$_3$ (III) that were prepared using different amounts of ammonium hydroxide solution (10, 15, and 20 mL). From Figure 2B, the average crystallite size (D) for the highest two planes (104) and (110) were calculated by the Debye–Scherer equation at different amounts of ammonia solution. The average values of D for Fe$_2$O$_3$ (I), Fe$_2$O$_3$ (II), and Fe$_2$O$_3$ (III) are found to be 57.65, 44.12, and 36.42 nm respectively. Then, the average crystallite size of Fe$_2$O$_3$ depends on the volume of used ammonium hydroxide. According to the effective mass model, when particle size is reduced at the nanoscale, quantum confinement has an influence on electrons in nanoparticles. Changing the quantum (crystallite) size can alter the optical characteristics. As a result, the crystallite size is critical to the generation of hydrogen.

3.1.2. Surface Morphology

It is well-known that the photocatalytic activity of the photocatalyst is strongly related to its surface morphology. The morphologies of natural zeolite, Fe$_2$O$_3$, and Fe$_2$O$_3$/zeolite nanopowders are examined utilizing the SEM technique as shown in Figure 3.

The SEM images of natural zeolite, Figure 3A, show micro/nano-stones in nonuniform shapes of various sizes. The sizes of stones for zeolite are changed from 21.6 to 3.2 µm, as seen in the corresponding particle size distribution (left of Figure 4A) of the particle size distribution. The mean particle size is 10.951 ± 0.820 µm with a standard deviation of 6.027 ± 1.647 µm. A close look at the image reveals the existence of many small nanoprotrusions/nanograins over zeolite particle surfaces with an average size of ~115 nm. Additionally, there are many small nanopores with a diameter of ~71 nm on the surface of zeolite with irregular shapes as seen in high magnification Figure 3A. The high surface area due to the porous framework provides a chance to incorporate iron oxide nanoclusters inside the pore cavity of zeolite [30]. Additionally, these pores can adsorb organic pollutants, which can increase photodegradation efficiency.

The Fe$_2$O$_3$ nanopowder was composed of many nanoparticles with semi-spherical shapes. The SEM image of Fe$_2$O$_3$ nanoparticles shows that the nanoparticles are small in size, seen in Figure 3B. The corresponding particle size distribution is shown on the left of Figure 3B. Based on Gaussian fitting; the mean size of Fe$_2$O$_3$ nanoparticle is 113.65 ± 4.67 nm with a standard deviation of 14.92 ± 5.95 nm. These nanoparticles are self-assembled and aggregated to form nanopores of average diameter ~20.99 nm with a standard deviation of ±6.02 nm, as shown from the inset pore-diameter distribution of Figure 3B.

Fine spherical Fe$_2$O$_3$ nanoparticles coated the zeolite surface and appeared as homogeneous distributions that produced a nano-sized Fe$_2$O$_3$ coating surface over zeolite stones after loading zeolite with the intended Fe$_2$O$_3$ photo-catalyst, Figure 3C. It is also possible that the Fe$_2$O$_3$ coating was quite homogeneous, with no obvious uncoated zeolite sites. The size of the Fe$_2$O$_3$ nanoparticles seems to be decreased after loading on zeolite compared to the free-standing Fe$_2$O$_3$ nanopowder. The size distribution of the supported Fe$_2$O$_3$ nanoparticles on the surface of zeolite, left of Figure 3C, indicates an average value of 88.94 ± 1.67 nm. Additionally, the high magnification SEM image, inset of Figure 3C, shows a more homogeneous pore-diameter distribution with a mean value of 35.50 ± 2.25 nm.
Figure 3. SEM micrographs and the corresponding particle size distribution for (A) natural zeolite, (B) Fe$_2$O$_3$, and (C) Fe$_2$O$_3$/zeolite. The inset of (B) shows the pore diameter distribution.

The interlock between Fe$_2$O$_3$ nanoparticles and their precipitation over the zeolite is expected to be beneficial for PEC activity. Haileyesus et al. reported that similar interlock structures can offer a rapid migration of the induced electrons and holes to the catalyst surface, which leads to a low probability of recombination [31]. Additionally, the decrease of the particle size to the nanoscale and the widening of the pores can offer a huge effective surface area of Fe$_2$O$_3$ nanocatalyst. This can offer intensive absorption of the incident light.

3.1.3. Chemical Compositions of the Photocatalysts

To identify the chemical compositions of the designed photocatalysts and atomic ratios of the elements, the EDX spectra of zeolite, Fe$_2$O$_3$, and Fe$_2$O$_3$/zeolite nanocomposite were measured and presented in Figure 4. The chemical composition for the zeolite shows the main three elements (O, Al, and Si) as revealed by EDX analysis. Additionally, small signals for K, Ca, and Fe are observed, in addition to a small trace from Cu. These signals are similar to previously reported signals for the zeolite [32].
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The EDX analysis of Fe$_2$O$_3$, Figure 4B, indicated the presence of O (37.62%) and Fe (62.38%) signals as the main components at around 0.525 and 6.398 keV. The atomic ratios of Fe to O suit the stoichiometry ratios of Fe$_2$O$_3$ well. This confirms the high purity of the prepared Fe$_2$O$_3$ nanopowder, which coincides with the XRD results. After loading Fe$_2$O$_3$ onto zeolite, there are main four characteristic peaks for O, Al, Si, and Fe with atomic ratios of 53.12%, 6.30%, 26.63%, and 9.01%, respectively. This indicates the successive loading of Fe$_2$O$_3$ onto the surface of the zeolite.

3.1.4. The Photocatalysts’ Optical Properties

Nanomaterials’ optical properties are important characteristics that influence their uses [33,34]. The absorption (A) and transmittance (T) spectra from 250 to 850 nm of zeolite, Fe$_2$O$_3$, and Fe$_2$O$_3$/zeolite are shown in Figure 5. The zeolite sample has a sharp peak corresponding to a strong absorption band at the UV region (below $\lambda$ = 300 nm), as seen in Figure 5A. Then, the absorbance decreases sharply with increasing the wavelength from 280 up to 850 nm. Therefore, the zeolite sample displayed a very low spectral response in the visible region.

![EDX spectrum of (A) zeolite, (B) Fe$_2$O$_3$, and (C) Fe$_2$O$_3$/zeolite nanocomposite.](image-url)
The absorbance spectra for Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite show similar optical behaviors, as seen in Figure 5B,C. The Fe$_2$O$_3$ has strong photoabsorption in the UV and visible spectral regions [35]. Fe$_2$O$_3$ shows an absorption band edges up to 580 nm. The wide absorption band of Fe$_2$O$_3$ in the visible region is due to the direct transition (O$^2−$-2p→Fe$^{3+}$3d) and the spin-forbidden-excitations (Fe$^{3+}$3d→3d), which rises the indirect transitions [36–38].

For the Fe$_2$O$_3$/zeolite, Figure 5C, the right edge of the photons uptake band shifts to a longer $\lambda$ compared with that of Fe$_2$O$_3$, Figure 5B. This is correlated with the size of the nanoparticles of the Fe$_2$O$_3$ formed in the zeolite matrix. Hence, a broad and intense visible absorption range was observed for the Fe$_2$O$_3$/zeolite in Figure 5B. This would be better to achieve a massive electron–hole pair generation through electron transportation between the valence and conduction bands.

The absorbance values at $\lambda$ = 500 nm are 0.185, 0.765 and 1.219 for zeolite, Fe$_2$O$_3$, and Fe$_2$O$_3$/zeolite, respectively, as seen in Figure 5D. This means more photons in the visible region, the concentrated portion of the solar light, can be absorbed by Fe$_2$O$_3$/zeolite than Fe$_2$O$_3$. This high absorbance refers to the dispersion of the Fe$_2$O$_3$ aggregates within the zeolite mesoporous structure and the modification of the electronic structure of Fe$_2$O$_3$/zeolite. Hence, zeolite has effectively enhanced the visible light absorption capability of the loaded Fe$_2$O$_3$ nanostructures. From Figure 5D, the general behavior of the transmittance spectrum of zeolite is the increase of transmittance% with the wavelength from UV to the visible region. The low transmittance for zeolite in the UV region is due to the existence of a strong absorption band in this region. The transmittance spectra for Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite (Figure 5D) can be divided into two regions. At wavelengths from 250 to 550 nm, the transmittance is nearly constant below 12%. Above 550 nm, the transmittance of Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite varies linearly with wavelength. The transmission of Fe$_2$O$_3$/zeolite is higher than that of Fe$_2$O$_3$ in the whole range of wavelengths.

The diffuse reflectance spectra (DRS) of the photocatalysts were measured to estimate the bandgap energies of the Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite. For this purpose, the Kubelka–Munk (K–M) model was used. Based on the following equation, this approach allows
the absorption coefficient to be calculated by measuring diffuse light reflectance from a powdered mixture comprising absorbing and scattering components [39].

\[
F(R) = \frac{(1 - R)^2}{2R} = \frac{\alpha}{S}
\]

where \(F(R), R, S, \text{ and } \alpha\) indicate the K–M function, diffuse reflectance of the sample, the scattering coefficient, and the absorption coefficient, respectively. The K–M function is directly proportional to the absorption coefficient. Therefore, the direct and/or indirect band gaps of \(\text{Fe}_2\text{O}_3\) and \(\text{Fe}_2\text{O}_3/\text{zeolite}\) were estimated by the following equation

\[
(\alpha E_p)^n = G (h\nu - E_g)
\]

where \(E_p, E_g\), and \(G\) refer to the photon energy, bandgap energy, and independent constant. For indirect bandgaps, \(n = 1/2\), while for direct bandgaps, \(n = 2\) [40]. The absorption bandgaps energies (direct or indirect) can be calculated from the straight-line portions of \((\alpha E_p)^n\) versus \(E_p\) curve that intersects the energy axis, as shown in Figure 6.

![Figure 6](image-url)

**Figure 6.** Indirect energy gap (A,B) for \(\text{Fe}_2\text{O}_3\), and \(\text{Fe}_2\text{O}_3/\text{zeolite}\) and direct energy gap (C,D) for \(\text{Fe}_2\text{O}_3\), and \(\text{Fe}_2\text{O}_3/\text{zeolite}\), respectively.

The \(\text{Fe}_2\text{O}_3\) and \(\text{Fe}_2\text{O}_3/\text{zeolite}\) have indirect bandgap values of 1.87 and 1.91 eV and direct bandgap values of 2.04 and 2.07 eV, respectively (Figure 6), which demonstrates the formation and incorporation of \(\text{Fe}_2\text{O}_3\) nanoparticles in the zeolite. These values are consistent with the reported values for \(\text{Fe}_2\text{O}_3\) prepared by different techniques in the [22,41]. Based on the quantization effect, the bandgap is proportional inversely to the crystallite size due to the confinement of the movement of electrons. Therefore, the increase in the bandgap of \(\text{Fe}_2\text{O}_3/\text{zeolite}\) compared to \(\text{Fe}_2\text{O}_3\) can be understood based on the decrease in the crystallite size as seen in XRD data. This behavior is similar to that reported for many nanomaterials such as \(\text{ZnO}\) and \(\text{ITO}\) [42,43]. The studied optical properties suggest that the produced \(\text{Fe}_2\text{O}_3\) from the rusted iron and its loading on zeolite as a host can greatly
improve its semiconducting performance toward the massive absorption of the visible light. This suggests that the prepared Fe$_2$O$_3$/zeolite can be used for solar energy applications.

3.1.5. FT-IR Study

FT-IR data of Fe$_2$O$_3$, zeolite and Fe$_2$O$_3$/zeolite nanocomposite are shown in Figure S1 (Supplementary Materials). The FT-IR spectrum of Fe$_2$O$_3$ nanoparticles was observed in the 4000–400 cm$^{-1}$ wavenumber range, Figure S1. The bands of Fe$_2$O$_3$ appear at 1641 and 3415 cm$^{-1}$, owing to the bending vibrations of the absorbed H$_2$O and surface hydroxyl, and O–H stretch modes [20]. The appeared absorption modes at 2920 and 2850 cm$^{-1}$ are assigned to the symmetric and asymmetric $\text{–CH}_2$ groups stretch modes. A strong Fe–O asymmetric stretching mode was detected around 1040 cm$^{-1}$ [44]. The located bands at 461, 537, and 790 cm$^{-1}$ were attributed to the Fe–O stretch mode of Fe$_2$O$_3$ as confirmed in the literature [45]. A strong Fe–O asymmetric stretching mode was detected around 1040 cm$^{-1}$ [44]. The located bands at 461, 537, and 790 cm$^{-1}$ were attributed to the Fe–O stretch mode of Fe$_2$O$_3$ [45]. For zeolite, the bands at 3620 and 3446 cm$^{-1}$ were attributable to Si–OH groups with H-bonding. The absorption mode at 1640 cm$^{-1}$ was attributed to the OH bending mode [46]. The strong 1040, 790, and 600 cm$^{-1}$ modes were significant to the internal asymmetric stretch and external symmetric stretch of X–O–X (X = Al or Si), and the internal X–O bending mode of AlO$_4$/SiO$_4$ tetrahedral [46]. The modes at 600 and 470 cm$^{-1}$ authorize the existence of double five-membered rings of the pentasil zeolite [46]. For Fe$_2$O$_3$/zeolite, there are mixed bands between Fe$_2$O$_3$ and zeolite. The presence of broadband at 3429 cm$^{-1}$ can be certified the O–H stretch mode, while the mode at 1650 cm$^{-1}$ can be referred to as the O–H bending [47]. Bands of the zeolite appear at 461, 537, and 790 cm$^{-1}$ in the nanocomposite, and the shift of these bands relative to that of zeolite refers to the break of H-bonds as a result of the existence of Fe on zeolite SiO$_2$ [44]. The located bands at 461, 537, and 790 cm$^{-1}$ were attributed to the Fe–O stretch mode of Fe$_2$O$_3$/zeolite weight ratios [45]. The located bands at 461, 537, and 790 cm$^{-1}$ were attributed to the Fe–O stretch mode of Fe$_2$O$_3$/zeolite [45]. The bands of the zeolite appear at 1000 cm$^{-1}$ in the nanocomposite, and the shift of these bands relative to that of zeolite refers to the break of H-bonds as a result of the existence of Fe on zeolite SiO$_2$/AlO$_4$ surfaces. Strong bands at 720, 598, 530, and 460 cm$^{-1}$ were attributed to the symmetric vibration of (Al or Si)–O due to the internal vibration of zeolite.

3.2. Photoelectrocatalytic (PEC) H$_2$ Generation

3.2.1. PEC Characteristics and Conversion Efficiencies

PEC technology for converting solar energy to hydrogen via the water-splitting cycle was aided by the catalysts Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite. When Fe$_2$O$_3$ is subjected to light, the electron (e$^-$) can be excited from the valence band, leaving a hole (h$^+$) to the conduction band. The rate of hydrogen production depends on the lifetime of the carrier charge. The limitations of bare Fe$_2$O$_3$ faces in use as a PEC photoanode arise from the electronic structure of the material. The Fe$_2$O$_3$ suffers from a high density of mid bandgap trap states arising from closely spaced d levels that result in closely spaced optical transitions spanning the visible and into the near-ultraviolet regions. This leads to low carriers’ mobility and short lifetimes. In the Fe$_2$O$_3$/zeolite nanocomposite, the electrons can be trapped on the surface of the mesoporous zeolite. The zeolitic network can inhibit recombination of e/h pairs due to strong electric field strength through the distribution of photogenerated electrons inside zeolite [48]. Hence, the effective e$^-$/h$^+$ separation occur over robust interfacial interactions in Fe$_2$O$_3$/zeolite. This causes a decrease in e$^-$/h$^+$ recombination rates, which results in an efficient photoelectrocatalytic performance of Fe$_2$O$_3$-zeolite. Additionally, the Fe$_2$O$_3$/zeolite has a large effective surface area due to the porous framework of zeolite, which can increase PEC efficiency and allow for more intense absorption of incident light.

The optimized content of Fe$_2$O$_3$ and zeolite is highly desirable to reach high PEC performance. The photocurrent density is measured for Fe$_2$O$_3$ (III), Fe$_2$O$_3$ (II), and Fe$_2$O$_3$ (I) at an applied voltage of 1 V in 0.9 M KOH under light illumination, as seen in Figure S2 (Supplementary Materials). The photocurrent density is found to be 57.5, 48.82, and 42.64 mA/cm$^2$ Fe$_2$O$_3$ (III), Fe$_2$O$_3$ (II), and Fe$_2$O$_3$ (I), respectively. Therefore, Fe$_2$O$_3$ (III) photoelectrode produces the highest photocurrent, which considers the optimized PEC photocathode. Additionally, nanocomposites of varied Fe$_2$O$_3$ (III)/zeolite weight ratios (0.2/1.8, 0.6/1.4, 0.8/1.2, 1.0/1.0, 1.2/0.8, 1.4/0.6, and 1.8/0.2) are utilized to manufacture
Fe$_2$O$_3$/zeolite photoelectrodes for hydrogen production in order to optimize the nanocomposite composition. The photocurrent densities for all electrodes are measured under light illumination and at 1 V, as seen in Figure S3 (Supplementary Materials). The highest photocurrent density is found to be 57.93 mA/cm$^2$ for Fe$_2$O$_3$/zeolite with a weight ratio of 1:1.

Figure 7 shows the PEC performance of the optimized electrode. The variation of the current density (J) in darkness and white lighting from a metal-halide lamp versus the applied voltage (E) is presented in Figure 7A at 25 °C with a sweep rate of 0.1 mV/s. Using the Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite photo-electrocatalysts and in white lighting, the value of J is greatly enhanced vs. the positive applied voltage. By switching from the dark status to white light illumination status, the current density of Fe$_2$O$_3$ is increased from 1.14 to 29.1 mA/cm$^2$ at +1 V, which refers to the PEC effect of Fe$_2$O$_3$. As shown in Figure 7A, J is increased by loading Fe$_2$O$_3$ on zeolite from 29.1 to 57.6 mA/cm$^2$ at +1 V. This is due to the extending of the bandgap to the Vis/NIR range, which speeds up the redox reactions and then facilitates the PEC reaction. This also suggests a ~2-fold enhancement of the J-value relative to the Fe$_2$O$_3$ photocatalyst, which agrees with the increase of the surface charge, the extension of $E_g$, and the strong absorptions in the Vis/NIR because of the loading of Fe$_2$O$_3$. In addition, it is very well-associated with the size variation of the Fe$_2$O$_3$ nanoparticles. Reduction in the size of Fe$_2$O$_3$ nanoparticles after loading on zeolite compared to Fe$_2$O$_3$ nanopowder, Figure 3, leads to greater surface areas and enhanced active surface spots that improve hydrogen generation activity. Additionally, Fe$_2$O$_3$/zeolite’s quantum confinement raises the reduction potentials to transfer the bound protons to H$_2$ molecules. The quantum containment of Fe$_2$O$_3$/zeolite allows for further effective absorption in the Vis/NIR region (Figure 5). Note that Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite photoelectrocatalysts exhibit light-harvesting with J-values of 0.58 and 1.01 mA/cm$^2$ at 0 V, and photocurrent onset at $-0.098$ and $-0.056$ V, correspondingly. It shows that, after loading Fe$_2$O$_3$ on the zeolite matrix, the interfacial transport resistances decrease, emphasizing the importance of the loading process in improving PEC efficiency. As a result of ions’ exchange ability, vacant sites in the zeolite surface also photoassisted hydrogen production [49]. Simultaneously, zeolite’s aluminosilicate frame is contributing to delayed charge carriers’ separations [50]. Since the control processes of electron/hole transfer are very important in photocatalytic reactions, zeolite can play an active role in electron transfer processes as an electron acceptor or electron donor [51,52]. The Z-scheme mechanism for the nanocomposite can maintain photogenerated charge carriers with strong redox ability. The spatial isolation of charge carriers is providing a large driving force for the photocatalytic water reduction reaction [53]. To assess the photoelectrocatalysts’ performances as a tiny outer voltage is introduced between the electrodes of the PEC cell, the electrical energies introduced to the cell have to be deducted. This may be accomplished using the applied bias photon to current conversion efficiency (ABPE). The following Equation (3) is used to compute ABPE [54]:

$$\text{ABPE(%) } = \frac{J \times (1.23 - E_{\text{app}})}{p} \times 100 (3)$$

where $E_{\text{app}}$ is the externally applied bias and p refers to the illuminating light power density (75 mW/cm$^2$). Figure 7B demonstrates how ABPE varies with applied voltage at various wavelengths. The two highest ABPE% values are de-convoluted under white light illumination; (3.37% at 0.464 V and at 8.78% at 0.997 V) for Fe$_2$O$_3$ and (12.05% at 0.430 V and 20.01% at 0.882 V) for Fe$_2$O$_3$/zeolite. This indicates a ~3-fold improvement along with a decrease of the applied voltage, which can be beneficial for PEC cell operation. Additionally, Fe$_2$O$_3$/zeolite photocatalyst displays ABPE% of 1.64% at 0 V. This demonstrates that interfacial transport resistances have been reduced and photocatalytic performance has improved [54].
Here, \( n \), \( C \), and \( T \) stand for the number of electrons in a redox reaction \( (n = 1) \), analyte concentration, and temperature, correspondingly, while \( F \), \( R \), and \( D \) stand for Faraday, gas-molar, and analyte diffusion constants \([26]\). Utilizing Figure 7A, the ECSAs of the photocatalysts were found using \( \text{ECSA} = Q \cdot \frac{m}{C} \), whereas \( Q \), \( m \), and \( C \) indicate the negative-scan hydrogen-adsorption charges after double-layer charge modification, photocatalyst mass, and complete monolayer charge of the electrode-cover H-atoms, respectively \([26]\). The \( Q \) value was estimated by integrating the curve of the photocatalyst, Figure 7A, divided by the scan rate. The values of \( \text{ECSA} \) for the photocatalysts are determined and presented in Table 3. For \( \text{Fe}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3/\text{zeolite} \), the values were 7.414 and 21.236 m\(^2\)/g, respectively. The 3-fold improvement in the \( \text{ECSA} \) explains the improved PEC performance, Figure 7A, of \( \text{Fe}_2\text{O}_3/\text{zeolite} \) versus the \( \text{Fe}_2\text{O}_3 \). Then, the estimated STH value was 12.74\% for the \( \text{Fe}_2\text{O}_3/\text{zeolite} \) photocatalyst.

The enhanced solar absorption of the \( \text{Fe}_2\text{O}_3/\text{zeolite} \) photocatalyst is verified by estimating the photon-to-current incident efficiency (IPCE) at various wavelengths \( (\lambda) \) of the incident photons and constant potential (+1 V). The IPCE is calculated using the following Equation (4) \([40]\):

\[
\text{IPCE\%} = 1240 \cdot \frac{J}{\lambda \cdot P} \cdot 100
\]

where \( \lambda \) is in nm. The variation of IPCE\% with the wavelength of the monochromatic light for \( \text{Fe}_2\text{O}_3/\text{zeolite} \) photocatalyst is represented in Figure 7C. The highest IPCE\% is \( \sim 27.34\% \) @307 nm, in addition to another peak of 20.37\% centered at \( \sim 440 \) nm corresponding to the highest absorption seen in Figure 5.

![Graphs showing current density, IPCE%, and H2 moles over time for different conditions.](attachment:graphs.png)
In the IPCE calculations, optical losses including transmittance (T) or reflectance (R) of incident photons were neglected. To compensate the optical losses, the absorbed photon to current conversion efficiency (APCE) is measured. APCE represents the number of photogenerated carriers that participate per absorbed photon in the generated photocurrent. The APCE is computed using the following Equation (5) [55]:

$$APCE(\lambda) = \frac{IPCE(\lambda)}{A(\lambda)} = \frac{IPCE(\lambda)}{1 - R - T}$$ (5)

Here, A represents the optical absorbance. Figure 7D displays the behavior of APCE% as a function of the wavelength. As noted, APCE% is 19.1%@307 nm; then, it decreases to reach 13.8%@490 nm, followed by a successive increase to reach a maximum value of 33.0%@636 nm.

The stability of the Fe$_2$O$_3$/zeolite photocatalyst, for H$_2$ generation, is studied for a prolonged time in 0.9 M KOH under white light and an applied voltage of +1 V Figure 7E shows the evolution of the J throughout time. The J-value dropped dramatically within the first 16 s, reaching roughly 6.9 mA/g. Then, limited photocorrosion processes occur between the PEC catalyst and the redox electrolyte, which account for the dramatic fall in the J-value [3]. For time > 16 s, before achieving a steady value of roughly 4.63 mA/g for 60 s, there is a slight reduction in J-value. This demonstrates that, in spite of the early decline in J-value, the Fe$_2$O$_3$/zeolite photocatalyst has high photochemical stability and a long lifespan as an active photocatalyst for the PEC H$_2$ generation.

The full amount of hydrogen energy generated to the overall input sunlight energy (AM 1.5 G, 100 mW/cm$^2$) is the solar-to-hydrogen conversion efficiency (STH). It can be used to calculate the total efficiency of the PEC cell [56]:

$$STH = \frac{[(mmol \, H_2/s) \times (237 \, KJ/mol)]}{P_{total} \times ECSA}$$ (6)

where $P_{total}$, ECSA, and H$_2$/S refer to the total light power density in mW cm$^{-2}$, the electrochemical surface area in cm$^2$, and the rate of hydrogen generation/s, respectively. Applying Faraday’s law, the number of generated H$_2$ moles by the PEC cell can be calculated using Equation (7).

$$H_2(\text{moles}) = \int_0^t \frac{\text{J} \, dt}{F}$$ (7)

Here, F refers to the Faraday constant ($9.65 \times 10^4$ C/mol), and t is the period of generation. Figure 7F shows the variation of H$_2$ (moles) versus the production time. The creation rate of H$_2$ is 154.44 mmol h$^{-1}$ g$^{-1}$. Zeolite plays an effective role in the rapid spread of hydrogen bubbles which escape from the photocatalyst. This paves the way for higher current and additional H$_2$ creation over the same period [57].

The ECSA of Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite photocatalysts were obtained utilizing the Randles–Sevcik equation,

$$ECSA = \frac{I(RT)^{0.5} (C \, n \, F)^{-1.5} (v \, D)^{-0.5}}{0.4463}$$ (8)

Here, n, C, and T stand for the number of electrons in a redox reaction (n = 1), analyte concentration, and temperature, correspondingly, while F, R, and D stand for Faraday, gas-molar, and analyte diffusion constants [26]. Utilizing Figure 7A, the ECSAs of the photocatalysts were found using ECSA = Q·m$^{-1}$/C, whereas Q, m, and C indicate the negative-scan hydrogen-adsorption charges after double-layer charge modification, photocatalyst mass, and complete monolayer charges of the electrode-cover H-atoms, respectively [26]. The Q value was estimated by integrating the curve of the photocatalyst, Figure 7A, divided by the scan rate. The values of ECSA for the photocatalysts are determined and presented in Table 3. For Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite, the values were 7.414 and 21.236 m$^2$/g, respectively. The 3-fold improvement in the ECSA explains the improved PEC performance, Figure 7A,
of Fe$_2$O$_3$/zeolite photocatalyst versus the Fe$_2$O$_3$. Then, the estimated STH value was 12.74% for the Fe$_2$O$_3$/zeolite photocatalyst.

Table 3. ECSA values and corrosion and Tafel parameters for Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite photocatalysts.

| Sample          | ECSA (m$^2$/g) | $E_{corr}$ (mV) | $I_{corr}$ (µA cm$^{-2}$) | $\beta_a$ (mV dec$^{-1}$) | $R^2$ | $\beta_c$ (mV dec$^{-1}$) | $R^2$ | $R_p$ (Ω cm$^2$) | Corr Rate (nm year$^{-1}$) |
|-----------------|----------------|-----------------|---------------------------|---------------------------|-------|--------------------------|-------|-----------------|-----------------------------|
| Fe$_2$O$_3$     | 7.414          | 478.28          | 3.15                      | 63.4 ± 0.9                | 0.996 | 6.8 ± 0.2                 | 0.988 | 847.66          | 0.01502                     |
| Fe$_2$O$_3$/zeolite | 21.236        | 376.72          | 2.66                      | 139.9 ± 2.8               | 0.992 | 5.5 ± 0.1                 | 0.989 | 864.98          | 0.00761                     |

3.2.2. Corrosion and Tafel Parameters of Fe$_2$O$_3$ and Fe$_2$O$_3$/Zeolite Photocatalysts

The Tafel relationship, $V = \beta \log(J) + C$, was used to quantify combined anodic and cathodic Tafel or polarization parameters to determine the mechanism of the H$_2$ generation reaction (HGR) and the rate-limiting phase [58]. Low Tafel slopes, high current exchange rates, and good HGR performances are all characteristics of the ideal photocatalyst. Figure 8A shows the Tafel plots for Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite. Figure 8B,C displays the main characteristics: corrosion potential and current ($E_{corr}$ and $I_{corr}$) and anodic ($\beta_a$) and cathodic ($\beta_c$) Tafel slopes for the Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite. The values of $\beta_a$ and $\beta_c$ for Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite are found using the slopes of the curves’ linear segments, as shown in Figure 8D,E [26,59]. The obtained values of $E_{corr}$, $I_{corr}$, $\beta_a$, and $\beta_c$ were presented in Table 3 for Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite. For Fe$_2$O$_3$/zeolite, the $\beta_a$ and $\beta_c$ values are 139.9 and 5.5 mV dec$^{-1}$, respectively, and 63.4 and 6.8 mV dec$^{-1}$ for Fe$_2$O$_3$. The PEC HGR mechanism and rate-limiting phases are indicated by the Tafel slopes. The Volmer–Heyrovsky mechanism is predominant when the recombination phase is a rate limit and the Tafel slope is 30 mV dec$^{-1}$. The Volmer–Heyrovsky H$_2$ generation process could be presumed to be dominant when PEC desorption is a rate limit and the Tafel slope is 40 mV dec$^{-1}$. The reaction pathways are dependent on the surfaces covered with adsorbed hydrogen if the Tafel slope is 120 mV dec$^{-1}$. The $\beta_a$-value denotes the needed over-potential to enhance the HGR rate by a factor of ten [26,59]. The low values of $\beta_a$ refer to the low optical band gaps of the designed Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite photocatalysts. This means that small amounts of energy (low overpotentials) are needed to achieve efficient HGR.

The corrosion rate is directly dependent on $I_{corr}$, where $E_{corr}$ offers aspects about the solution’s corrosion propensity. From Figure 8A–C, the Fe$_2$O$_3$/zeolite presents nobler behavior. The Fe$_2$O$_3$/zeolite has a smaller $E_{corr}$ (376.7 mV) than Fe$_2$O$_3$ (478.3 mV). Generally, the $E_{corr}$ values revealed in this work are greater than any earlier stated values for Fe$_2$O$_3$-based photocatalysts and are moved to more noble behaviors when compared to commercial Fe$_2$O$_3$ [60].

To verify the relative ability of the electrode to resist corrosions; the values of $I_{corr}$, polarization resistance ($R_p$), and corrosion rate (CR) could be determined. The CR is related to the kinetic value $I_{corr}$ directly, while $R_p$ is inversely proportional. From Table 2, the loading of Fe$_2$O$_3$ on the zeolite host reduces $I_{corr}$ from 3.15 to 2.66 µA cm$^{-2}$, which is much smaller than any previously reported Fe$_2$O$_3$ photocathode’s corrosion current. For example, Kim et al. reported 5.31 µA/cm$^2$ for Fe$_2$O$_3$ and 8.69 µA/cm$^2$ for Fe$_3$O$_4$ [60]. The values of $R_p$ are determined by the Stern–Geary equation, $R_p = \beta_a \beta_c /[2.303 I_{corr} (\beta_a + \beta_c)]$, utilizing the straight segments near to $E_{corr}$ of the curves. The values of CR (n year$^{-1}$) are determined by $CR = \sqrt{3272} [I_{corr} \times W/(ECSA \times d)]$, whereas $E$ and $d$ represent the equivalent weight (g eq$^{-1}$) and density (g cm$^{-3}$). For Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite, the values of $R_p$ and CR are reported in Table 3. The $R_p$ values are increased from 847.66 to 864.98 Ω cm$^2$, whereas CR is decreased from 15.02 to 7.61 pm Year$^{-1}$ by loading Fe$_2$O$_3$ on zeolite host. Therefore, photocorrosion is suppressed by the loading of the Fe$_2$O$_3$ photocatalyst into zeolite [61]. This is because zeolite can provide specific photophysical properties such as preventing the Fe$_2$O$_3$ nanoparticles from aggregating and improving their stability against sinterisation. The above-mentioned corrosion metrics show a significant improvement.
of the Fe$_2$O$_3$ photocatalyst’s stability through the use of zeolite as catalyst support. The obtained CR values outperform any prior Fe$_2$O$_3$-based PEC electrode results [62,63].

![Graphs](image-url)

**Figure 8.** Combined anodic and cathodic polarization of Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite (A), $E_{corr}$ and $J_{corr}$ of (B) Fe$_2$O$_3$ and (C) Fe$_2$O$_3$/zeolite; calculation of (D) anodic ($\beta_a$) and (E) cathodic ($\beta_c$) Tafel slopes.

## 4. Conclusions

A highly effective recycling technique for rusted iron wastes and a scalable method for the preparation of Fe$_2$O$_3$ and Fe$_2$O$_3$/zeolite nanocomposite have been reported. The Fe$_2$O$_3$/zeolite nanocomposite showed smaller sizes, more homogeneous nanopore diameter distribution, greater Vis/NIR light absorption capability, and a wider bandgap than Fe$_2$O$_3$ nanopowder. Fe$_2$O$_3$/zeolite nanocomposite was applied successfully as a low-cost nanophotocatalyst. The application of Fe$_2$O$_3$/zeolite for photoelectrolytic hydrogen production showed a production rate of 154.45 mmol g$^{-1}$ h$^{-1}$ at 1 V in 0.9 M KOH solution, which is the highest value yet for Fe$_2$O$_3$-based photocatalysts. The photocurrent density of Fe$_2$O$_3$/zeolite is almost 2-fold that of the Fe$_2$O$_3$ catalyst, and the IPCE% reached ~27.34%@307 nm and 1 V nm. This nanophotocatalyst has also shown remarkable stability with a very low PEC corrosion rate of 7.6 pm/year. Additionally, it can retain ~97% of its initial performance.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/nano11123445/s1, Figure S1: FT-IR spectra of Fe$_2$O$_3$, zeolite, and Fe$_2$O$_3$/zeolite nanocomposite. Figure S2: Variation of current density ($J$) for Fe$_2$O$_3$ (I), (II), and (III) under white light illumination and at 1 V. Figure S3: Variation of current density ($J$) for Fe$_2$O$_3$ (III)/zeolite photoelectrodes with different Fe$_2$O$_3$ (III)/zeolite weight ratios at 1 V under white light illumination.

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