Efficient hydrogen generation by ZnAl$_2$O$_4$ nanoparticles embedded on a flexible graphene composite

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This work reports the hydrogen generation properties of ZnAl$_2$O$_4$ (ZAO) powders synthesized by a combustion method, which produced carbon dots (C-dots) on the ZAO surface. These ZAO nanoparticles decorated with C-dots were incorporated into a polycrylate matrix to form a photocatalytic membrane (named PAZO), which was subsequently attached to a flexible graphene composite (FGC) to form a FGC/PAZO (GAZO) composite. The morphological analysis by scanning electron microscopy shows embedded ZAO nanoparticles with sizes of 20–90 nm into the polymeric matrix. In addition, hydrogen generation rates of 260, 4640 and 1580 mol g$^{-1}$ h$^{-1}$ were obtained for different ZAO powders annealed at 600, 700, and 800 °C, respectively. Moreover, the PAZO membrane and the GAZO composite produced hydrogen generation rates of 560 and 2860 mol g$^{-1}$ h$^{-1}$, respectively. Although the GAZO composite had a lower hydrogen generation rate ($\approx$ 38% less) than the best ZAO powder (annealed at 700 °C), the GAZO composite could be attached easily in the inner wall of photocatalytic reactors which facilitates its removal after hydrogen production, this advantage is not possible by using photocatalytic powders. Therefore, the GAZO composites, presented here, could be a feasible option for hydrogen generation when attached to the inner walls of photoreactors.

1. Introduction

The interest for developing clean sources of energy has increased due to the continuous contamination of the environment, which is produced by the consumption of fossil fuels. For this reason, the photocatalytic hydrogen production (under solar or UV light) using semiconductor oxides has emerged as a suitable process to produce clean energy from water splitting [1]. Since Fujishima et al. [2] demonstrated that the TiO$_2$ semiconductor can be used as electrocatalyst for hydrogen generation, several semiconductors have received much attention for hydrogen production, such as ZnO, Co$_3$O$_4$, Fe$_3$O$_4$, BiVO$_4$, and WO$_3$ [3,4]. In most of these photocatalytic materials, the band gap energy limitation is a key issue that results in low hydrogen production. To solve this issue, some photocatalysts have been modified via noble metal doping, being the most efficient the Pt element but it is expensive [4]. The photocatalytic activity of the oxides for hydrogen production is low due to the high recombination rate of the photogenerated electron-hole pairs [5]. Hence, the development of materials with high photocatalytic activity, low cost and made with abundant elements is highly important in order to use water splitting as commercial source of energy.

The AB$_2$O$_4$ spinel-type oxides (where B$^{3+}$ and A$^{2+}$ could be metallic ions) are alternative materials for hydrogen generation due to their narrow band gap, high chemical stability, high surface area, high melting point (2135 °C), high mechanical resistance (at high temperatures) and low thermal expansion coefficient. These characteristics promote the light absorption, improve the separation of...
photogenerated electron-hole pairs and increase the interfacial charge transfer [6,7]. In fact, some composites based on spinels have been reported for photocatalytic applications: The NiFe$_2$O$_4$–g-C$_3$N$_4$ composite produces degradation of methylene orange dye under visible light irradiation because its component g-C$_3$N$_4$ inhibits the electron-hole recombination and enhances the light absorption [8]. The FeCu$_2$O$_4$ spinel decorated with TiO$_2$ nanoparticles enhances 3 times the photocatalytic reduction from CO$_2$ to methanol under visible light irradiation [9]. Moreover, the presence of titania increases the lifetime of the photogenerated electron and facilitates the reactions of CO$_2$ to methanol [9]. Other spinels such as magnetic NiFe$_2$O$_4$ and Mn$_3$-xCo$_x$O$_4$ have been used for hydrogen generation, reaching a maximum production of 15 µmol h$^{-1}$ [10,11]. Moreover, the spinels CuFe$_2$O$_4$, MgFe$_2$O$_4$ and ZnFe$_2$O$_4$ have presented water splitting activity by electro-photocatalytic processes [12]. Another spinel composite such as CuFe$_2$O$_4$–g-C$_3$N$_4$ is able to produce H$_2$ under visible light at a maximum rate of 76 µmol h$^{-1}$ [13]. Particularly, the ZnAl$_2$O$_4$ (ZAO) spinel semiconductor offers several advantages such as high thermal stability, low surface acidity, high mechanical resistance and high surface area (70–300 m$^2$/g) [14,15]. The ZAO spinel can be prepared at low temperatures by simple methods such as sol–gel, solid state, co-precipitation and microwave-hydrothermal among others [14–17]. This spinel is currently considered as a photocatalyst material or as catalyst support material for the degradation of contaminant dyes and catalytic conversion of gases [16,18]. According to previous reports, ZAO has been used for total degradation of reactive red 141 (RR141) dye (after 180 min under solar irradiation) [19] and Eosin dye (after 40 min under UV irradiation) [20]. Other publications demonstrated a degradation above 98.5% for rhodamine B and methyl orange dyes after only 60 min using ZAO, which overcomes the performance of the commercial titania Degusa P25 [21,22]. ZAO has been also added to commercial ZnO to form the ZnO/ZnAl$_2$O$_4$ composite, which produces higher degradation percentage (> 50% more) for methylene blue dye than ZnO [23]. In all these reports, the authors demonstrated that an increase on mesoporosity and surface area in ZAO enhances the degradation of dye pollutants [20]. There are also few articles where the ZAO material has been modified with CeO$_2$ or ZrO$_2$ oxides to produce H$_2$ at high temperatures of 650 °C [24]. ZAO has been also decorated with ZnO to produce a maximum hydrogen generation rate of 0.3 mol h$^{-1}$ g$^{-1}$ at 460 °C [25]. Although the ZAO has been effectively used for photocatalytic degradation of dyes as mentioned above, there are not reports about the use of this material for H$_2$ generation at low temperatures to the best of our knowledge. For this reason, a systematic study to understand the capacity of ZAO powders to produce H$_2$ under UV light (at room temperature) is proposed. Here, the ZAO powder was incorporated into a polymeric matrix to form a polymeric membrane with ZAO (PAZO), which is attached on a flexible graphene composite (FGC) in order to obtain a flexible composite with photocatalytic properties for hydrogen production. This work also demonstrates that the flexible composite PAZO + FGC (GAZO) is a hybrid composite with strong mechanical properties, which could be employed as a coating/lining material into reactors for hydrogen generation.

2. Experimental section

2.1. Fabrication of the flexible graphene composite (FGC), polymer membrane with ZnAl$_2$O$_4$ nanoparticles (PAZO) and PAZO + FGC composite (GAZO)

The ZAO nanoparticles were synthesized using the procedure previously reported in Ref. [26], followed by an annealing treatment in air at 600, 700, 800, and 900 °C. The FGC (used as support of the ZAO nanoparticles) with 0.9 ± 0.1 mm thickness was fabricated using a methodology published by Oliva et al. [27]. Once the ZAO nanoparticles (ZAO600, ZAO700, and ZAO800) are synthesized, the powder is poured into a beaker which contains a mixture of acetone (AC), ethanol (ETHO), distilled water (W), a photoinitiator (PI), and acrylic monomer (AM) with weight ratios of 0.3:1:1.1:1:0.1:0.5, for ZAO:AC:ETHO:W:PI:AM, respectively. After this, the mixture of monomer + solvents + ZAO powder was stirred at 90 °C for 60 min until a viscous white liquid is observed. Next, 0.4 ml of this mixture is taken using a micropipette and dropped on a Corning glass. Subsequently, the formed membrane is dried at 80 °C and cured with UV light for 30 min. Consequently, the obtained solid membrane is peeled off from the Corning glass. The polymeric membrane with ZAO powder is named PAZO and its average thickness is ≈ 125 µm. The GAZO composite is fabricated by putting the PAZO membrane on the FGC with a pressure loading machine at 1 ton.

2.2. Structural and morphological characterization

The structural characterization of the samples was carried out by X-ray diffraction (XRD) using a Brucker diffractometer with CuK$\alpha$ radiation (\(\lambda = 1.5418\) Å). The X-ray diffraction patterns were recorded in the 20 range from 10° to 70° with a scan rate of 0.05°/s. The morphology of samples was analyzed by scanning electron microscopy (JEOL JSM 64900V equipment). The analysis by energy dispersion spectroscopy (EDS) was achieved with an Oxford Instruments detector.

2.3. Optical characterization

The absorbance spectra of the powder samples were measured from 200 to 1200 nm, using a UV–Vis Cary-5000 Agilent spectrophotometer equipped with an integrating sphere. The Fourier transform infrared (FTIR) spectra were obtained for all the samples using the ATR technique and a Cary 670 FTIR spectrophotometer. Photoluminescence spectra of the PAZO and GAZO samples were collected with a modular Acton Spectra Pro Fluorometer (Princeton Instruments), which is equipped with a SP-2300i excitation monochromator aligned to a 75 W xenon lamp (Newport Oriel), and a SP-2500i emission monochromator attached to a R955 photomultiplier (Hamamatsu). Both monochromators were controlled by the Spectra Sense software from Princeton Instruments. The photoluminescence (PL) measurements were performed under air conditions at room temperature (28 °C).

2.4. XPS analysis and mechanical measurements

The x-ray photoelectron spectroscopy (XPS) analysis was performed using an equipment (Model K-Alpha) from Thermo Scientific Instruments, which employed a monochromatic AlKa radiation (E = 1486.68 eV) with 0.1 eV of resolution. The deconvolution of the XPS spectra were achieved using a SDP v4.1 software. For the mechanical tests, the samples were prepared according to the ASTM D-FGC638 standard. The tensile properties were measured by utilizing a home-made universal testing machine [28] controlled with a LabView software and a cross-head speed of 7 × 10$^{-4}$ mm/s.

2.5. Photocatalysis tests for hydrogen generation and reuse experiments

The water splitting reaction was performed by photocatalytic tests using a quartz reactor (250 ml) coupled to gas chromatography equipment. 50 mg of photocatalyst (ZAO powder, PAZO
membrane or GAZO composite) was dispersed (for powders) or suspended (for PAZO or GAZO) in 100 mL of deionized water into the reactor. Before the photocatalytic reaction, the mixture was deoxygenated by bubbling nitrogen gas. The photocatalytic reaction started when the UV-lamp ($\lambda = 254$ nm) was turned on. The hydrogen gas generated was monitored with a chromatograph of gases which has a column equipped with a thermal conductivity detector (Thermo Scientific 3 GC Ultra). The production of hydrogen was monitored every 30 min during 3 h during the photocatalytic reaction.

2.6. Detection of generated protons with scavenger

Ciprofloxacin (CPX) was used as scavenger for detecting reactive protons $H^+$. CPX is an antibiotic molecule commonly used to treat bacterial infections but was used as scavenger to demonstrate that the superoxide anion $O_2^-$ and the $H_2O_2$ are involved in the hydrogen generation reactions [29]. The procedure for the detection of protons $H^+$ was as follows: 5 mL of a CPX solution (20 ppm) and 0.05 g of the composite catalyst (PAZO or GAZO) were added to 100 mL of deionized water. Subsequently, the mixture was stirred and aliquots of 1 mL were extracted at regular intervals of time (from 0 to 60 min) under UV irradiation and their fluorescence was measured immediately in the range of 350–550 nm under excitation with 315 nm wavelength. The fluorescence spectra were collected by using an Ocean Optics spectrophotometer QE6500 coupled with an optical fiber.

3. Results and discussion

3.1. Structural and morphological analysis of FGC, PAZO and GAZO

The FGC (graphene support) is formed by coalesced graphene nanoplates whose edges are protruding from its surface, see Fig. 1a (top view). A closer inspection of the FGC composite surface also shows coalesced graphene nanoplates in the in-plane direction, see inset in Fig. 1a. For this composite, the pore size is in the range of 50–12000 nm, which is lower than that previously reported in FGCs for hydrogen production [27]. We tried to have a smooth surface on the FGC in order to facilitate the deposition of the PAZO membrane (made with ZAO700) on it. Fig. 1b shows a cross-section image where both, the FGC and the PAZO membrane are visualized at the same time. The dotted yellow line marks the edge between the FGC and the PAZO membrane. The cross-section view of the PAZO membrane shows a smooth and flat surface. On the contrary, the cross-section view of the FGC shows a very porous surface with pore size in the range of 15–120 μm. Fig. 1c shows an image of the PAZO membrane deposited on the FGC (top view of its surface). As observed, ZAO nanoparticles are embeded on the polymeric membrane and their sizes are in the range of 20–200 nm, which is in agreement with the size of ZAO700 nanoparticles previously reported [26]. Further, Fig. 1c demonstrates that the ZAO nanoparticles are partially exposed, which is important for the hydrogen production. If the ZAO nanoparticles are completely covered by the polymeric matrix, they could not react with the water (during the irradiation with UV light) to generate hydrogen. According to the mechanical characterization, the elastic modulus ($E$) for the FGC, PAZO membrane and GAZO (PAZO + FGC) composite were 17.53, 28.53 and 45.01 ± 0.02 MPa, respectively. These values indicate that the $E$ value for the GAZO composite is approximately equal to that obtained by the sum of the individual $E$ values for the FGC and PAZO membrane. The presence of the ZAO particles embedded in the polycrylate matrix of the PAZO membrane was confirmed by the EDS mapping of the GAZO composite, see Fig. 2. As observed, the EDS maps showed with different colors the presence of Zn, Al, C and O elements, thus, the ZAO nanoparticles are deposited on the surface of the photocatalytic flexible composite.

The structural quality of the composites was studied by XRD measurements. Fig. 3a shows two diffraction peaks at 25.5° and at 54.5° which correspond to graphene [27] while Fig. 3b shows the diffraction peaks of the PAZO membrane that are associated to the

![Fig. 1. SEM images of: a) FGC, b) cross-section of GAZO composites and c) PAZO membrane. The inset in Fig. 1a shows the FGC at higher magnification.](image-url)
(200), (311), (422), (511) and (400) planes of the cubic spinel structure [26] of the ZAO particles embedded in the polymeric matrix. Further, the GAZO composite showed a combination of peaks related with the ZAO powders and graphene, see Fig. 3c. This is expected because the GAZO composite was formed by attaching the PAZO membrane to the FGC. It is worthy to mention that a broad band is observed at about 21° in all the XRD patterns of Fig. 3, that band is attributed to the presence of the polyacrylate polymer [27].

### 3.2. Surface analysis of the PAZO and GAZO composites

The FTIR analysis can be useful to determine whether the ZAO nanoparticles and graphene are exposed in the FGC, PAZO and GAZO composites. Fig. 4a shows the FTIR spectra of the FGC, where the bands at 1090 cm⁻¹ and 1527 cm⁻¹ are associated to C=O and C–O vibrations, respectively. These bonds correspond to the acrylic polymer used to fabricate the FGC. The broad band at 1694 cm⁻¹ can be attributed to the C=C and C(CH₃) vibrations [27,30,31]. Additionally, the bands at 2855 and 3300 cm⁻¹ are attributed to OH and CH₂ groups [27,30,31]. In the case of the PAZO composite, its FTIR spectra clearly shows several peaks in the region 1000-1800 cm⁻¹ which correspond to the polyacrylate polymer where the ZAO nanoparticles are embedded [32], see Fig. 4b. This spectra also shows the bands at bands at 2941 and 3331 cm⁻¹ which are attributed to OH and CH₂ groups. The dotted lines at 440 cm⁻¹ and the peaks centered at 764 cm⁻¹ indicates the presence of Zn–O and Al–O bonds [26], respectively. The presence of the C–C, Al–O and Zn–O bonds in the PAZO membrane indicates that the graphene nanoplates and ZAO nanoparticles are exposed. If the ZAO material is completely covered by the polymer matrix, only the bonds related with the polymer matrix would appear in the FTIR spectra, which is not our case.

Although the exposure of the AZO and graphene materials was demonstrated by FTIR measurements, it is important to elucidate if the PAZO membrane is chemically attached to the FGC. For this, the XPS spectra would be a useful tool. Fig. 5a shows the XPS spectrum of the C1s orbital with deconvoluted bands for the GAZO sample. There are bands centered at 288.7, 286, 284.8, 284.3 and 283.4 eV which are attributed to the O–C=O/C=O, C–O, C–H, C–C and C=C bonds [33–36], respectively. After the incorporation of the PAZO membrane on the FGC to form the GAZO composite, the overall intensity of the deconvoluted bands increased as illustrated in Fig. 5b (this XPS spectra was measured on the side in the GAZO composite where the PAZO membrane is found). Interestingly, an increase of the shoulders at 288.7 and 286 eV, which are associated to the O–C=O/C=O and C–O bonds occurred. Such increase means that the new carbon-oxygen bonds are formed, probably between the oxygen groups in the PAZO membrane with the carbon groups located in the FGC. This result confirms that the PAZO membrane is chemically linked to the FGC.

### 3.3. Photocatalytic hydrogen generation by ZAO powders, PAZO membrane and GAZO composite

The photocatalytic hydrogen generation of ZAO powders annealed at different temperatures (600, 700 and 800 °C) as well as for the PAZO membrane and GAZO composite was evaluated under UV irradiation. Fig. 6a shows that the hydrogen generation rates for
the ZAO600, ZAO700 and ZAO800 are 13, 232 and 79 μmol h⁻¹, respectively. According to our previous report, the ZAO powders presented a decrease of their photoluminescent (PL) emission intensity (in the range of 400–700 nm) by following the order: ZAO700> ZAO800> ZAO600 [26]. This means that the ZAO700 and ZAO600 samples presented the highest and the lowest emission intensity, respectively. The ZAO700 and ZAO600 samples also had the highest and the lowest hydrogen generation rates, respectively. Therefore, we infer that the ZAO powders with a higher PL emission should also have a higher hydrogen generation rate. The PL emission of ZAO powders is produced by the carbon dots grown on their surface, which contain defects [26]. The carbon dots (C-dots) act as electron trapping centers, thus, more holes are available to quickly react with water, this in turn, favors the H⁺ formation as indicated by equation (1):

\[
2H_2O + 4h^+ \rightarrow 4H^+ + O_2
\]  

(1)

After this, the produced protons can react with free electrons for the generation of hydrogen gas according to equation (2):

\[
4H^+ + 4e^- \rightarrow 2H_2
\]  

(2)
Thus, the C-dots delay the electron-hole recombination, which promote the hydrogen generation. Fig. 6b shows the positions for the conduction (CB) and valence (VB) bands calculated theoretically for ZAO700 using Eqs. (1S) and (2S) in the Supporting Information. These equations were taken from Ref. [37] while the energy level for C-dots (-1.2 eV) was taken from Refs. [38,39]. The energy level diagram in Fig. 6b shows that the CB of the ZAO powders and C-dots are above the potential for the Hydrogen reduction reaction and the CB for ZAO700 is above the CB for C-dots, this means that the electrons photogenerated by ZAO700 can jump toward the CB of C-dots and this favors the reduction of $H_2$. Regarding the flexible composites: FGC, PAZO and GAZO samples had generation rates of 0.23, 28 and 143 $\mu$mol h$^{-1}$ (see Fig. 6a), respectively. The GAZO sample was made using the ZAO700 powder because this presented the highest hydrogen generation rate. The curve of Hydrogen generation for the FGC is showed in Fig. S1 of supporting information, as observed, the contribution of the FGC is very low. The hydrogen generation rate for PAZO membrane is about 4 times lower than that for the GAZO composite (which contains both, the PAZO membrane and the FGC). The lower performance of the PAZO membrane could be due to the diminution of the surface defects in the carbon dots attached to the ZAO surface after covering it with the polycrylate. These defects are considered the electron trapping centers that benefit the performance of ZAO for hydrogen generation, thus, if their presence is decreased, it is expected a lower hydrogen production [26]. However, the value of $H_2$ generation rate of the GAZO composite is about 38% lower in comparison with the ZAO700 powder, see Fig. 6a. The literature indicates that graphene would help to delay the recombination of the photogenerated electron-hole pairs by trapping electrons, which makes more holes available for the photocatalytic hydrogen generation [40]. Eventually, the trapped electrons are transported across the graphene nanoplates toward the reactive sites for H$_2$ formation due to the high electrical conductivity of graphene [41]. Thus, the presence of graphene is useful to enhance the hydrogen production (2–4 times) as observed in CdMoO$_4$/graphene and TiO$_2$/MoS$_2$/graphene composites [40,42]. When the PAZO membrane is put on the FGC, the graphene makes a heterojunction contact with the ZAO particles and this helps to transfer the electrons on graphene, enhancing the efficiency as explained above. The proof for this heterojunction could be the fact that the PAZO and FGC components had much lower hydrogen generation rates individually in comparison with that obtained when both components are together (GAZO composite). The CB and VB for GAZO composite were also estimated theoretically (see supporting information) and the energy level for graphene around -0.27 eV was taken from Ref. [43]. Furthermore, the GAZO composite had a higher hydrogen production than the PAZO membrane. Some reasons for this could be the following: 1) the fact that the absorbance is broader in the VIS region for GAZO in comparison with PAZO (compare black and red curves in Fig. 6c), which benefits the photogeneration of the electron-hole pairs and 2) the fact that the optical band gap is lower for the GAZO composite (a lower band gap indicates that the sample is electrically more conductive, which is suitable to provide quickly electrons to water for $H^+$ reduction), see Fig. 6d. These band gaps were calculated from the Tauc plots [44,45], see Eq. (3S) in the Supporting Information.

In order to determine which photocatalyst (ZAO700, PAZO or GAZO) generated more $H^+$ protons, photoluminescence (PL) measurements of aqueous solutions that contained the scavenger CPX were achieved. When the CPX is added in water with the...
photocatalysts material and subjected to UV irradiation, the H⁺ protons generated by the photocatalyst tend to protonate the CPX molecules (the H⁺ can be chemically linked to the F element or O element found in the extremities of the CPX molecule, see inset of Fig. 6d). After protonation of the CPX molecule, its PL emission intensity decreases. Therefore, it is expected a diminution of the PL intensity for the CPX molecule as the amount of H⁺ increases in the aqueous solution. Fig. 7a–c shows the PL spectra as a function of time for the ZAO700 powder, GAZO composite and PAZO membrane, respectively. In all the cases, there is a diminution of the PL intensity as a function of time, which suggests that the H⁺ protons are continuously protonating the scavenger molecule CPX (the H⁺ protons are generated by the photocatalyst due to its continuous exposure with UV light). A comparison of the PL spectra (at t = 60 min, see blue dark curves) obtained from the aqueous solutions with the three different photocatalysts indicates that the PL emission decreases in the order: ZAO700 > GAZO > PAZO. This means that the highest amount of protons was generated by ZAO700 and the lowest by the PAZO membrane. This trend is in accordance with the hydrogen production rate showed in Fig. 6a (ZAO700 had the highest H₂ production rate while the PAZO membrane had the lowest).

Since the main goal of this work is designing a photocatalytic flexible material able to be adapted on the wall of a chemical reactor for hydrogen generation, it is suitable to evaluate the performance of the GAZO composite after several cycles of use. Fig. 7d shows the total amount of hydrogen generated after 4 cycles of use of the GAZO composite (each cycle lasted 3 h). The generation of H₂ was reduced by 10%, 19% and 27% after the second, third and fourth cycles of use, respectively. Similarly, the ZAO700 sample (which presented the highest hydrogen production rate) was tested for 4 cycles of use, see Fig. S2 in the Supporting Information. In this case, the hydrogen generation was reduced ≈ 24% after the fourth cycle of use. This reduction percentage is comparable to that for the GAZO membrane for the same cycles of use (≈ 27%). Hence, the GAZO composite is potentially useful to be reused several times and can be removed easily from the inner wall of reactors in comparison with the photocatalytic powders. In addition, the method of deposition of the photocatalyst (PAZO membrane) on the FGC was easier than that used in a previous work where the FGC was decorated with Ni(OH)₂ nanoparticles using chemical methods [27]. In this case, the ZAO photocatalyst was incorporated into a polyacrylate membrane and subsequently deposited on the FGC using a press machine. The advantages of this last method are the fact that the time for the incorporation of the photocatalyst is reduced from approximately from 17 to only 1 h and the fact that the mechanical resistance of the flexible photocatalyst increased from 17.5 to 45 MPa due to the coupling of the FGC and PAZO membrane to form GAZO.

Considering that the mass used for the photocatalytic experiments was 50 mg, we can calculate the hydrogen generation rates of ZAO powders and composites per gram of photocatalyst. As result, the hydrogen generation rates were 260, 4640 and 1580 μmol g⁻¹ h⁻¹ for the ZAO powders annealed at 600, 700, and 800 °C, respectively. Moreover, the PAZO membrane and the GAZO composite produced hydrogen generation rates of 560 and 2860 μmol g⁻¹ h⁻¹, respectively. The hydrogen generation rate obtained with the GAZO composite (2860 μmol h⁻¹) is higher than the obtained with other binary graphene composite powders such as: Ni/RGO, NiO/RGO, TiO₂/RGO, RGO/CdS, Cu₂O/RGO or ternary...
composites: CdS/ZnO/RGO, and TiO2/MoS2/RGO with H2 production rates of 30–750 μmol h⁻¹ [41]. Moreover, the hydrogen production of GAZO composite is higher than that for Ru[dcbpy]32–RGO (2533 μmol h⁻¹), CTAB/TPPH-RGO (2250 μmol h⁻¹) and ZnCdS/RGO (1824 μmol h⁻¹) systems, but a little lower than that for [Ru(bipy)3]2+@RGO (3290 μmol h⁻¹) systems [41]. The last composites mentioned a high H2 generation rates but employs toxic materials such as Cd or expensive materials such as Ru as co-catalyst. Other disadvantages of these materials are: 1) they are binary or ternary composites prepared with complex chemical procedures, and 2) the wt% of each component for these composites is difficult to reproduce during their synthesis procedure. Moreover, all these materials are nanocomposite powders and their removal after hydrogen generation from any reactor is more difficult in comparison with the flexible GAZO composite that can be adhered on the walls of the photocatalytic reactor. Table 1 summarizes the hydrogen production rates for other graphene systems used for hydrogen generation. A comparison with the results presented in this table indicates that the hydrogen produced by the ZAO700 powder (4640 μmol g⁻¹ h⁻¹) is higher than that obtained for composites of Ag3PO4–TiO2–graphene oxide [46], RuO2/TiS2/RGO [47] or (S,N-GQD/TiO2) [48]. Those last composites use the whole content of other efficient materials for hydrogen generation and these are made of expensive materials such as Ag or Ru or. In contrast, ZAO700 is an inexpensive powder that needs only the UV component to produce hydrogen gas. On the other hand, the GAZO composite had a lower H2 generation rate (2860 μmol g⁻¹ h⁻¹) than the CdMoO4/graphene (3624 μmol g⁻¹ h⁻¹) and Pt–Graphene/TiO2 (6580 μmol g⁻¹ h⁻¹) composites [41,49], see Table 1. However, the GAZO composite was made without toxic elements such as Cd or precious metals such as Pt to produce hydrogen, that composite only employed low cost graphene, ZAO and polyacrylate for its fabrication. Table 1 also indicates that the rGO/CuFe2O4–TiO2 composite has a high generation rate of 35981 μmol g⁻¹ h⁻¹ [50], but it is a ternary composite difficult to synthesize. It is worthy to mention that the graphene based composites presented in Table 1 could be good candidates to be deposited on the FGC (support) instead of ZAO powder, this would increase even more the hydrogen generation of the flexible composite. Studies about the incorporation of other efficient materials for hydrogen generation into the flexible composite presented here will be reported elsewhere in near future.

4. Conclusions

This work proposed a simple method to fabricate flexible photocatalytic composites capable to produce hydrogen gas under UV irradiation. X-ray diffraction analysis confirmed the formation of the FGC (PAZO (GAZO) composite due to the simultaneous presence of diffraction peaks associated to graphene and ZAO nanoparticles. The ZAO powders produced hydrogen because the C-dots on their surface acted as electron trapping centers, which in turn, favored the formation of H⁺ protons required for the hydrogen production. The ZAO700 sample presented the highest hydrogen production because it had the highest concentration of C-dots on its surface (this was confirmed by PL measurements).

On the other hand, FGCs were used as support for the ZAO nanoparticles and had two main roles: i) to increase the overall mechanical strength of the flexible photocatalytic composite, and ii) to produce a heterojunction between the ZAO powder and the graphene nanopolates, which enhanced the hydrogen generation rates. The flexible photocatalytic material (GAZO composite) can be easily removed from any reactor where a photocatalytic hydrogen reaction is achieved. Contrarily, the removal of photocatalytic powders is more difficult because they require complicated centrifugation or precipitation processes to be separated from the liquid solution. Additionally, the fabrication process of the flexible GAZO composite avoids the use of complicated chemical methods to grow photocatalyst nanoparticles on the FGCs as was previously reported.

The hydrogen generation rates were 260, 4640 and 1580 μmol g⁻¹ h⁻¹ for the ZAO powders annealed at 600, 700, and 800 °C, respectively. In addition, the PAZO membrane and the GAZO composite produced hydrogen generation rates of 580 and 2860 μmol g⁻¹ h⁻¹, respectively. According to these values, the hydrogen reduction was reducing ≈38% after the incorporation of the ZAO powders on the flexible graphene composite. Thus, the results presented here open new opportunities for developing flexible photocatalyst materials that can be easily used on the inner surface of industrial reactors for hydrogen production.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement


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<table>
<thead>
<tr>
<th>System</th>
<th>Material type</th>
<th>Light Source</th>
<th>Hydrogen production rate (μmol·g⁻¹·h⁻¹)</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Ag3PO4–TiO2–graphene oxide</td>
<td>Powder</td>
<td>Solar simulator</td>
<td>218.7</td>
<td>[46]</td>
</tr>
<tr>
<td>CdMoO4/graphene</td>
<td>Powder</td>
<td>Sunlight</td>
<td>3624</td>
<td>[40]</td>
</tr>
<tr>
<td>RuO2/TiS2/RGO</td>
<td>Powder</td>
<td>Solar simulator</td>
<td>97.5</td>
<td>[47]</td>
</tr>
<tr>
<td>(S,N-GQD/TiO2)</td>
<td>Powder</td>
<td>Solar simulator Simulator</td>
<td>141</td>
<td>[48]</td>
</tr>
<tr>
<td>TiO2–CdS–Cdy,S</td>
<td>Powder</td>
<td>Solar simulator</td>
<td>1824</td>
<td>[41]</td>
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<tr>
<td>Pt–Graphene/TiO2</td>
<td>Powder</td>
<td>UV lamp + solar simulator</td>
<td>6580</td>
<td>[49]</td>
</tr>
<tr>
<td>rGO/CuFe2O4–TiO2</td>
<td>Powder</td>
<td>UV lamp</td>
<td>35981</td>
<td>[50]</td>
</tr>
</tbody>
</table>

Table 1 Summary of hydrogen production rates reported in graphene-based systems.


