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Photocatalytic performance of Au/ZnO nanocatalysts for hydrogen

production from ethanol

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Graphical Abstract

Highlights

 H_2 was photocatalytically produced at a constant rate, from a water-ethanol mixture, using ZnO and Au/ZnO catalysts Loading ZnO materials with gold increased the photoefficiency towards H_2 production. Au/ZnO materials with variable morphology are obtained by a double impregnation method for gold loading.

Gold nanoparticles size plays a major role in the photoefficiency of Au/ZnO materials.

Abstract

Gold was loaded on several ZnO samples with different morphologies: needle-like (ZnO-n), flower-like (ZnO-f), rods (ZnO-r), and prepared by a thermal calcination process (ZnO-t). A commercial ZnO sample (ZnO-c) was also used for comparison. Bare ZnO and Au/ZnO materials were used for the photocatalytic production of H₂ from a water-ethanol solution under UV-visible irradiation ($\lambda > 300$ nm). During the photocatalytic runs, hydrogen was generated at a constant rate for all samples, as well as CH₄ and CO. The obtained results show that bare ZnO materials were able to promote H₂ photogeneration, being ZnO-f the most efficient in terms of H₂ generation. Loading with Au, in general, increased the photoefficiency for all materials. The most active gold loaded photocatalysts were the ones with the lowest gold nanoparticle sizes: Au/ZnO-f (427 μ mol h⁻¹ g_{cat}⁻¹; 5.4 nm) and Au/ZnO-n (280 μ mol h⁻¹ g_{cat}⁻¹; 5.8 nm). The samples with largest size (Au/ZnO-r and Au/ZnO-t with 6.2 nm, and Au/ZnO-c with 12.5 nm) were not so efficient (values below 230 μ mol h⁻¹ g_{cat}⁻¹). Au/ZnO-f seems to be the most promising photocatalyst, generating the highest amount of H₂ and the lowest quantities of CH₄ and CO. It is also possible that the intricate morphology of ZnO-f may scatter the incoming light, enhancing light absorption efficiency and increasing the photoefficiency of this material.

Keywords: Photocatalysis; Hydrogen production; Zinc oxide; Gold catalysts; Photoreforming

1. Introduction

Hydrogen energy and hydrogen economy are at the forefront of any nation's commitment and intentions when addressing the clean energy agenda. Hydrogen gas promises a redly available source, without harmful emissions, non-toxic (a rarity among the most used fuel sources), more powerful (it takes less to accomplish more), more efficient (more energy per mass of fuel) and potentially inexhaustible. Like always, every silver lining has a cloud. Hydrogen, although abundant and present pretty much everywhere, is never alone and needs to be separated from other elements or substances. Then unlike oil and gas that are easy to store and transport, hydrogen requires an all new set of economic and technical challenges – even a new infrastructure to distribution and commercial use. Finally, most of the industrial processes for isolating hydrogen still require the use of fossil fuels – it is but ironic that for reducing our dependency on the non-renewable sources we must rely on them.

Reforming (partial oxidation of hydrocarbons) is a well know of such processes [1], but it produces CO_2 and needs large amounts of energy. A very simple way to obtain H_2 is through electrolysis of water [2]. It consists in exposing water to an electrical current, which will separate it into hydrogen and oxygen. The visible drawback is the need for an intensive supply of energy. Hydrogen can also be obtained from the gasification of biomass [3-6], but the application is limited by the economical viability of the process.

Applying photon induced processes to the already available procedures can be a noteworthy improvement, leading to the production of hydrogen from sustainable and renewable natural sources. Naturally this requires the use of solar energy to become really independent of non-renewable sources. Thus, photocatalytic water splitting [7, 8] and photocatalytic reforming of biomass [9-11] are promising alternatives to generate hydrogen. The later has advantages since hydrogen is produced with concomitant (photocatalytic) degradation of organic molecules present in water at mild conditions, also contributing to the treatment of industrial

waters. If other natural renewable resources (like solar energy, widely abundant in south European and south American countries) are used, then process becomes even more attractive.

Titanium dioxide (TiO₂) has been extensively used in photo-related processes [12, 13]. The enormous consumption of this material has prompted the search for alternative catalysts with improved characteristics [14]. Zinc oxide (ZnO) is a promising alternative, since it has a bandgap similar to that of TiO₂, and has low cost and morphological versatility [15]. ZnO materials with several shapes can be obtained, like nanospheres, nanowires, nanotubes, nanorings, and nanotetrapods [16-18]. These materials are normally designated has wide bandgap semiconductors, meaning that they mostly absorb on the UV range of the electromagnetic spectrum, which represents only 3-5% of the solar irradiance at Earth's surface. Due to limited activity of these materials under visible light excitation, the scientific community was prompted to search for modified ZnO and TiO₂ materials with reduced bandgaps, therefore capable of absorbing a wider range of visible light range. Making these materials efficient photocatalysts implied structural and morphological modifications that were achieved by many ways. The use of TiO₂ hybrids containing carbon materials, such as activated carbon, carbon xerogel, carbon nanotubes, nanodiamonds, activated carbon fibres and graphene, has been reported as an effective approach to enhance the semiconductor activity, both under UV and visible/solar light conditions [19-30]. Modification by dye photosensitization [31] or mixing with other semi-conductors [32] has also been tested. Doping with metals, such as Au, has proven to be successful in enhancing photocatalytic activity of both TiO₂ and ZnO [33-37]. Gold is a noble metal that does not undergo photocorrosion and can be strongly anchored on surfaces, exhibiting a characteristic surface plasmon band in the visible region, due to the collective excitation of electrons in the gold nanoparticles [38, 39].

Although Au/TiO₂ based catalysts have been recently used for the photocatalytic reforming of organic molecules, including ethanol [38-43], to the best of our knowledge that has not been yet performed using Au/ZnO materials (even though this type of catalysts has been used for several photocatalytic applications mostly in the fields of water and air decontamination [37, 44-49]). In this work, we loaded gold on several ZnO samples with different micro/nanoscale morphologies. A commercial ZnO sample was also used for comparison purposes. The synthesized materials were used for the photocatalytic production of H₂ from a water-ethanol solution under UV-visible irradiation ($\lambda > 300$ nm). During the photocatalytic runs, H₂ was generated at a constant rate for all the catalytic systems.

2. Experimental

2.1 Synthesis of ZnO materials

Different ZnO materials were synthesized by diverse techniques. Needle-like ZnO (ZnO-n) was prepared by a hydrothermal process: a 4 M NaOH (Aldrich, \geq 97%) aqueous solution was heated to 70 °C under vigorous stirring, and then a 2 M Zn(NO₃)₂·6H₂O (Aldrich, \geq 99%) aqueous solution was added dropwise to the first with 1h stirring. The resulting solid precipitate was filtered, washed and allowed to dry at 60 °C in an oven [50]. Rods of ZnO (ZnO-r) were obtained through a similar process, but the molar ratio between the solutions was 4:1 (instead of 2:1). The temperature was 80 °C and the stirring time was 6 h. Flower-like ZnO (ZnO-f) was produced from a mixture with equal molar amounts of Zn(NO₃)₂·6H₂O and hexamethylenetetramine (Aldrich, 99%). The pH was adjusted to 10.0 using an ammonia solution (Aldrich, 25%). The mixture was heated to 90 °C for 1h in an autoclave. The obtained solid was washed and dried in air. Another sample was prepared by a thermal process (ZnO-t), i.e., calcination of the precursor: zinc acetate dihydrate (Aldrich \geq 99.5%) was heated at 5 °C min⁻¹ up to 600 °C in static air, and maintained there for 2 h [51]. A

commercial sample (ZnO-c) from Strem Chemicals (85-95% ZnO, 3-7% Al₂O₃, 0.5-3% CaO) was used for comparison purposes.

2.2 Gold deposition on ZnO materials

Au was loaded by double impregnation method (for a nominal loading of 1 wt. %), using $HAuCl_4 \cdot 3H_2O$ (Alfa Aesar) as precursor. After impregnation with a chloroauric acid solution (5×10⁻³ M) with sonication, a second impregnation step with addition of a solution of 1 M Na_2CO_3 (Aldrich > 99%) followed with stirring [52]. This was needed for chloride removal, which is well known to cause sintering of gold nanoparticles, making them inactive [53].

2.3 Materials characterization

The morphology of bare ZnO and Au/ZnO was analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a FEI Quanta 400 FEG ESEM/EDAX Genesis X4M (15 keV) instrument.

The materials of Au/ZnO were visualised through high-resolution transmission electron microscopy (HRTEM). High Z-contrast images were also acquired using scanning transmission electron microscopy (STEM) and a high-angle annular dark-field (HAADF) detector. The analyses were carried out in a Cs-corrected FEI Titan 80/300 microscope at INMETRO.

The different forms of ZnO used as support were also analysed by X-ray diffraction (XRD) on a Siemens D-5000 diffractometer, at room temperature, using CuK α radiation (λ =1.5418 Å). Textural characterisation, namely determination of the specific surface area (S_{BET}), was performed by analysis of N₂ adsorption isotherms at -196°C using the BET method, in a Quantachrome NOVA 4200e multi-station apparatus.

The optical absorption spectrum on the UV-Vis range was obtained with a Jasco V-560 UV-Vis spectrophotometer, equipped with an integrating sphere attachment (JASCO ISV-469). The various spectra were recorded in diffuse reflectance mode and transformed by the JASCO software to equivalent absorption Kubelka–Munk units. The bandgaps (Eg) were obtained from the UV-Vis spectra.

Diffuse reflection infrared Fourier transformed (DRIFT) spectroscopic analysis was performed on a Nicolet 510P FTIR Spectrometer. The interferograms were converted by the OMINC software to equivalent absorption units in the Kubelka–Munk scale.

The gold loading was determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Horiba Jobin Yvon Ultima 2 apparatus.

The metal dispersion was calculated as $D_M = (6.n_s.M)/(\rho.N.d_p)$, where n_s is the number of atoms at the surface per unit area $(1.15 \times 10^{19} \text{ m}^{-2} \text{ for Au})$, *M* is the molar mass of gold (196.97 g mol⁻¹), ρ is the density of gold (19.5 g cm⁻³), *N* is Avogadro's number (6.023 × 10²³ mol⁻¹) and d_p is the average particle size (determined by STEM, admitting that particles are spherical).

Photoluminescence (PL) spectra were acquired at room temperature on a Crylas CW 266 nm laser as an excitation source. The laser power was kept in 1 mW and the sample emission was collected by a CCD camera attached to a grating monochromator.

2.3 Photocatalytic reactions

The photogeneration of hydrogen was carried out in a double-wall quartz photochemical reactor. A 7 mg sample of the photocatalyst was suspended in 8 mL of a 1:4 (volume ratio) ethanol:water solution with the help of magnetic stirring. The temperature was maintained at 25°C, by water circulation through the photochemical reactor, using a thermostatic bath. Prior to irradiation, the system was deaerated by Ar bubbling for 30 min to remove any traces

of air. A 300 W Hg–Xe lamp (PerkinElmer; Cermax-PE300) was used as excitation source. The gases produced during the experiments were quantified using gas chromatography at room temperature in an Agilent 6820 GC chromatograph equipped with a thermal conductivity detector (TCD) with a Porapak Q (80/100 mesh) column by using argon as the carrier gas. The amounts of gases produced were measured at intervals of 0.5 h using a gas-tight syringe with a maximum volume of 100 μ L. To check the reproducibility of the photocatalytic activity, each sample was measured three times.

3. Results and discussions

3.1 Catalysts characterization

The ZnO materials were characterised by X- ray powder diffraction. The observed diffraction peaks of all samples match well with the hexagonal wurtzite structure, except in the case of ZnO-c that reveals the presence of alumina (α -Al₂O₃ phase), which is in in agreement with the Strem Chemicals manufacturer information. Loading with gold did not affect the crystallinity of ZnO. Also no Au phase was detected (Figure 1), most likely due to the low loading and low nanoparticle size.

The crystallite sizes of the ZnO samples were derived from the XRD analysis. ZnO-n presents the lower crystallite dimensions (39 nm), followed by ZnO-f (47 nm), ZnO-t (54 nm), ZnO-r (60 nm) and ZnO-c (72 nm). The materials present very low surface areas ranging from 2 to 30 m² g⁻¹ (Table 1), which is very common for zinc oxide [33, 37]. Although the gold loading was predicted as 1 wt.%, ICP analysis revealed the presence of lower percentages of the metal and varying depending on the ZnO material (Table 1). Previous works with Au/CeO₂, Au/MnO_x and Au/ZnO catalysts also showed that DIM method produces catalysts with gold loadings lower than the expected, due to the leaching of part of the metal during the deposition process [33, 54]. For ZnO-n, ZnO-r and ZnO-t, Au

loadings range from *ca.* 0.30-0.40 wt. %, while 0.74% and 0.90 wt. % were obtained for ZnO-c and ZnO-r.

The morphology of the different ZnO materials was observed by SEM. Selected images can be found in Figure 2.

It is interesting to note that the synthesis method and preparation conditions have a significant influence in the morphology of the samples. ZnO-r, ZnO-n and ZnO-f were obtained by hydrothermal routes, but using different temperatures, pressures, reaction times and molar proportions of the reactants. ZnO-n consists in needle-like structures having ca. 600 nm in length (Figure 2a), while ZnO-r shows hexagonal prismatic particles with lengths varying between 800 and 1300 nm (Figure 2b). ZnO-n and ZnO-r were obtained by similar procedures, but at different temperatures (70 °C and 80 °C, respectively), and diverse sodium hydroxide to zinc nitrate molar ratio (2:1 and 4:1, respectively) and dissimilar synthesis times (1h and 6 h, respectively). The morphological differences between both materials are associated with the different velocities of crystal growth, ZnO-n crystals growing faster than ZnO-r, which results in the disappearance of the hexagonal planes that can be observed in ZnO-r [37]. In ZnO-f, needle-like structures of 2 µm of average length grow as bundles coming from a same core (Figure 2c). ZnO-t (Figure 1d) is constituted by a mixture of spheroidal particles (175 nm average diameter) and needle-like structures (700 nm average length). Finally, ZnO-c is constituted by a mixture of larger ZnO particles (100–500 nm) with smaller (10-20 nm diameter) "needle"-like particles of Al₂O₃ (not shown), as already reported in an earlier publication [33].

STEM micrographs (Figures 2e-h) reveal the presence of Au particles of very small dimensions at the surface of the ZnO materials. The average Au particle sizes varied between 5.2 nm (for Au/ZnO-f) and 6.2 nm (for Au/ZnO-r and Au/ZnO-t), as shown in Figures 2i-l. Gold nanoparticles deposited over ZnO-r had mostly spheroidal shape, while metal

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nanoparticles with elongated form were observed for the remaining materials (Figures 2i-1). For Au/ZnO-c, spheroidal Au nanoparticles with sizes ranging from 6 to 20 nm (average size of 12.5 nm) were observed (not shown), as already reported in an previous paper [33].

The UV-Vis spectra of ZnO materials can be observed in Figure 3a, depicting a broad absorption in the UV range (Eg > 3.10 eV), characteristic of ZnO materials [33]. After loading with gold, a new absorption band is shown between 450 and 650 nm (2.76 eV > Eg > 1.91 eV), which is typical of gold surface plasmon (Figure 3b) [36, 55]. Moreover, a shift to lower energies was observed for ZnO-r, ZnO-f and ZnO-c after the introduction of Au nanoparticles (Table 1).

The normalized photoluminescence (PL) spectra of the synthesized materials are shown in Figure 4. An intense PL band common to all the spectra is observed in the visible range, being associated to deep-level-emissions (DLE) originated from atomic point defects such as oxygen vacancies (V_0), oxygen interstitials (O_i), zinc antisites (Zn_0), oxygen antisites (O_{Zn}) or zinc vacancies (V_{Zn}) [56, 57]. Also, the near-band-edge (NBE) emission at UV region is observed. In general, the relative intensity of both bands is a reasonable indicative of the defect amount in the atomic structure [56, 57]. ZnO-t shows the highest emission in the UV, meaning that this material has the lowest concentration of point defects, probably due to the high calcination temperature used in its synthesis (Figure 4a).

The other synthesized ZnO samples show a higher degree of defects justifying the lower emission in the UV. In the case of ZnO-r, some residual emission can be observed, being absent for ZnO-f and ZnO-n, meaning that recombination of photogenerated charges undergo preferably via defect levels rather than via gap (UV).

The PL spectra of the Au-loaded materials (Figure 4b) are similar to the ones of bare ZnO, indicating that recombination mechanisms are similar. The same behaviour was observed for the ZnO-c and Au/ZnO-c materials (not shown).

3.2 Photocatalytic hydrogen generation

The synthesized materials were used for the photocatalytic production of H₂ from a waterethanol solution under UV-visible irradiation ($\lambda > 300$ nm). H₂ was generated at a constant rate for all the catalytic systems.

Results show that bare ZnO materials were capable to promote H₂ photogeneration (Table 2 and Figure 4). However, the rate of hydrogen production varied among the materials. The catalysts with lower performances for H_2 generation were ZnO-c (66 μ mol h⁻¹ g_{cat}⁻¹), followed by ZnO-r (97 μ mol h⁻¹ g_{cat}⁻¹). ZnO-n and ZnO-t show similar rates of H₂ production (c.a. 230 μ mol h⁻¹ g_{cat}⁻¹) while ZnO-f was the best performing catalyst capable to promote H₂ generation at a constant rate of 301 μ mol h⁻¹ g_{cat}⁻¹. Apparently the BET surface area of the materials does not play a role here, since ZnO-c has the highest value (Table 1) and the worse performance. It might be that, even present in a low percentage, the Al₂O₃ present in this sample (as reported earlier [33]) has a detrimental role in its photocatalytic activity. In fact, the higher bandgap of ZnO-c comparing to the other bare ZnO materials (Table 1) can be attributed to the presence of alumina, a wide bangap material (~8.8 eV), resulting in a decrease in the photoefficiency of this sample. It was reported that light-harvesting or light trapping properties were found for certain ZnO surface structures or nanomaterials such as hollow spheres and pore-array structures [58-60]. It is possible that the intricate morphology of ZnO-f, constituted by bundles of needle-like structures deriving from a same core, may scatter the incoming light, enhancing light absorption efficiency, thus increasing the photoefficiency of this material. In fact, we have measured the reflectance of ZnO suspensions (not shown) and observed that for ZnO-f the reflectance is much lower than for ZnO-t and ZnO-n (both presenting similar spectra and also similar photoefficiency), which may result from multiple interface light scattering.

Addition of gold, in general, improved the photocatalytic activity towards H₂ production (Table 2 and Figure 4), with the exception of ZnO-t, where addition of gold was detrimental. The efficiency of H₂ production appears to be related to the size of Au nanoparticles. The most active gold loaded photocatalysts were Au/ZnO-f (427 µmol h⁻¹ g_{cat}⁻¹) and Au/ZnO-n (280 µmol h⁻¹ g_{cat}⁻¹), as shown in Table 2 and Figure 4. Those had the lowest gold nanoparticle sizes (5.4 nm and 5.8 nm, respectively). The samples with largest size (Au/ZnOr and Au/ZnO-t with 6.2 nm, and ZnO-c with 12.5 nm) were not so efficient (values below 231 μ mol h⁻¹ g_{cat}⁻¹). The influence of gold nanoparticle size in photocatalytic activity is well documented [35], although other factors, such as the nature of the support [61, 62], and the interaction of the support with gold [63] also play an important role, just like in heterogeneous catalysis by gold in general [64, 65]. However, Idriss and co-workers [61, 62] reported that gold nanoparticle size did not affect the photoreaction rate of hydrogen production from water-ethanol mixtures over the 3-12 nm range on Au/TiO₂ catalysts. The same authors also noticed that the nature of the support has also a great deal of influence, as they found that anatase was much more efficient that rutile as a support, producing more active materials, for the same gold nanoparticle size [61, 62]. That does not seen to the case in our work, as for the same gold nanoparticle size (6.2 nm) the difference between Au/ZnO-r and Au/ZnO-t performance is not so different (226 and 211 µmol h⁻¹ g_{cat}⁻¹, respectively). Other authors also found that the nanoparticle size of silver on ZnO could affect the photocatalytic activity [66].

A synergy factor (*R*), defined by the ratio between $r_{Au/ZnO, H2}$ and $r_{ZnO, H2}$, has been determined in order to quantify the effect of loading gold on ZnO materials (Table 2). The highest *R* was obtained for ZnO-c and ZnO-r, with 2.98- and 2.33-fold increase in the rate of H₂ production after loading with Au nanoparticles, respectively. For Au/ZnO-n and Au/ZnO-f, an increase

of 20 and 42% was observed, when compared to the bare materials, respectively. However no increase in the rate of hydrogen production was obtained for Au/ZnO-t material.

For better comparison of the results obtained with the different Au-loaded materials, the rates of H₂ production were normalized by the mass of gold present in each catalyst ($r_{[Au/ZnO, H2]Au}$) Table 2) and by the metal dispersion ($r_{[Au/ZnO, H2]Au, DM}$), since ICP and STEM analysis revealed that distinct percentages of gold with different nanoparticle sizes had been loaded on the ZnO samples (Table 1 and Figure 1). Results show that, even normalizing the rates of H₂ production by the mass of gold and by the metal dispersion, Au/ZnO-f remains as the most active photocatalyst (Table 2), which is must be related to the lower dimensions of the Au nanoparticles and to enhanced light trapping properties of the ZnO-f material.

The above results show that several factors such as ZnO purity, morphology, and the amount, shape and dimensions of Au nanoparticles, have influence in the efficiency of ZnO and Au/ZnO materials towards H_2 generation by photoreforming of ethanol.

After being irradiated with light at $\lambda > 300$ nm, it is expected that charge separation occurs, with electrons (e⁻) and holes (h⁺) migrating to the surface of ZnO. Since the Fermi level of Au is lower than that of ZnO, photo-excited electrons can migrate from the surface of the semiconductor to Au nanoparticles, where they can reduce water-protons to produce H₂. In some cases, Au nanoparticles have also the ability of being photoexcited by visible light,

due to surface plasmon band resonance. In fact, in a previous work, we have demonstrated that Au/ZnO-t shows photocatalytic activity towards phenol oxidation under 546 nm irradiation, i.e., exclusively exciting gold nanoparticles [37]. In the irradiation conditions used in this work ($\lambda > 300$ nm), it is expected that both ZnO-t and gold nanoparticles may be simultaneously photoexcited. This may explain the detrimental effect observed by the

introduction of Au in ZnO-t for photocatalytic H_2 generation, as a result of the simultaneous electron transfer between the semiconductor and the metal nanoparticles.

Sakata and Kawai reported the photocatalytic hydrogen generation from water-ethanol mixtures over Pt-loaded TiO₂ [67]. The obtained products were H_2 , CH_4 and CO_2 in the gas phase, and acetaldehyde (CH_3CHO) and acetic acid (CH_3COOH) in the aqueous phase. These authors suggested that surface trapped holes would interact ethanol to form acetaldehyde:

$$2h^+ + C_2 H_5 OH \rightarrow 2H^+ + CH_3 CHO \tag{1}$$

Then acetaldehyde is further oxidizer to acetic acid, following eq. (2):

$$2h^+ + CH_3CHO + H_2O \rightarrow 2H^+ + CH_3COOH \tag{2}$$

While H^+ produced via eqs. (1) and (2) can be reduced by photogenerated electrons producing H_2 , acetic acid is fully decomposed into CO_2 and CH_4 through a photo-Kolbe route.

Nadeem et al. [37] proposed a different reaction pathway for the photocatalytic reforming of ethanol over Au/TiO₂. In that case, ethanol was deprotonated upon adsorption over the catalyst and then each ethoxide injects two electrons into the conduction band of TiO₂ to produce an α -hydroxyethyl radical, which is then oxidized to form acetaldehyde. In other work by Wahab et al. on H₂ production from ethanol using metal-loaded SrTiO₃ catalysts, authors proposed that ethanol decomposition undergo through CH₃CO radical, which may react with surface oxygen resulting in acetate species, or may split to CH₃ radical and CO [68]. Then CH₃ radicals could react with OH radicals yielding methanol, which would easily decompose into H₂ and CH₄.

This later mechanism is believed to be similar to the one occurring for the reactions with the ZnO and Au/ZnO materials used in this work since, apart from H₂, also CH₄ and CO were detected in the gas phase and produced at a constant rate (Figure 5). For bare ZnO materials the rate of gas formation followed the order $r_{H2} > r_{CH4} > r_{CO}$ (Figure 5a).

Addition of gold to ZnO also increased the amounts of CO and CH₄ by-products generated for all systems (Figure 5b). This increase is particularly noticeable for Au/ZnO-r and Au/ZnO-c (some of the samples with the largest Au nanoparticle sizes). In general, lower gold nanoparticle sizes lead to more production of both CH₄ and CO. It has been reported that Au nanoparticle size has a central influence in the selectivity towards CO formation by photocatalytic reforming of alcohols since CO oxidation occurs at the interface between the metal and the semiconductor [69]. Thus, the catalysts showing smaller ZnO nanoparticles would be more efficient towards CO conversion to CO₂. However, there is a striking difference between Au/ZnO-r and Au/ZnO-t, that have the same gold nanoparticle size (6.2 nm) and large differences in CH₄ and CO production (being the former much more active than the latter for the production of these by-products), which indicates that gold particle size cannot be the only factor accounting for the different product yields. It was also reported that defect sites in the semiconductor act as active sites for CO formation [70]. The PL spectrum of Au/ZnO-t reveals the presence of a lower amount of defects comparing with Au/ZnO-r, which may contribute to the lower amount of CO (and CH₄) produced using Au/ZnO-t. All Au/ZnO systems showed amounts of CH₄ larger than those of H₂. Au/ZnO-f was the exception, which may be attributed to its lowest gold nanoparticle size. Therefore this material is a promising photocatalyst, but further research needs to be carried out to make it more selective to H₂.

Conclusions

Bare ZnO samples promoted H_2 photogeneration, being ZnO-f the most efficient in terms of H_2 generation. That can be due to its intricate morphology that may scatter the incoming light, enhancing light absorption efficiency and increasing the photoefficiency.

Loading with Au increased the photoefficiency for all materials, especially that of ZnO-f, which was the most active photocatalyst with a rate of 427 μ mol h⁻¹ g_{cat}⁻¹. That can also be

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related with its lower gold nanoparticle size (5.4 nm). Catalysts with largest sizes (like Au/ZnO-r, Au/ZnO-t with 6.2 nm, and Au/ZnO-c with 12.5 nm) were not so efficient and had highest amounts of CO and CH_4 production, compared to H_2 .

A mechanism involving ethanol decomposition through a CH_3CO radical, which may react with surface oxygen resulting in acetate species, or may split to CH_3 radical and CO seems to take place. Then CH_3 radicals react with OH radicals, yielding methanol that can easily decompose into H_2 and CH_4 .

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Figure Captions



Figure 1. XRD diffractograms of the gold loaded ZnO materials: Au/ZnO-c (a), Au/ZnO-t (b), Au/ZnO-f (c), Au/ZnO-r (d) and Au/ZnO-n (e). *Alumina peaks of ZnO-c.



Figure 2. SEM micrographs of ZnO-n (a), ZnO-r (b), ZnO-f (c) and ZnO-t (d); STEM micrographs of Au/ZnO-n (e), Au/ZnO-r (f), Au/ZnO-f (g) and Au/ZnO-t (h); histograms for Au particle size distribution (i-l).



Figure 3. Diffuse reflectance UV-Vis spectra of ZnO (a) and Au/ZnO (b) materials.



Figure 4. Photoluminescence spectra of ZnO (a) and Au/ZnO (b) materials.



Figure 5. Rates of H₂, CH₄ and CO generation using ZnO (a) and Au/ZnO (b) catalysts.

Tables

Table 1. BET surface area of ZnO samples; Au loading and metal dispersion (D_M) of therespective Au/ZnO materials, and bandgap energies (Eg) of bare and Au-loaded ZnO.

| ZnO | S _{BET} | Au loading | D _M | Eg _{ZnO} | Eg _{Au/ZnO} |
|----------|------------------|------------|----------------|-------------------|----------------------|
| material | $(m^2 g^{-1})$ | (wt. %) | (%) | (eV) | (eV) |
| ZnO-n | 2 | 0.38 | 19.9 | 3.11 | 3.09 |
| ZnO-r | 8 | 0.90 | 18.6 | 3.19 | 3.13 |
| ZnO-f | 4 | 0.29 | 21.4 | 3.15 | 3.07 |
| ZnO-t | 6 | 0.35 | 18.7 | 3.11 | 3.11 |
| ZnO-c | 30 | 0.74 | 9.26 | 3.35 | 3.12 |

| ZnO | r _{ZnO, H2} | r _{Au/ZnO, H2} | R | <i>r</i> [Au/ZnO, H2]Au | $r_{[Au/ZnO, H2]Au, DM}$ |
|----------|---------------------------------|---------------------------------|------|-----------------------------------|--|
| material | $(\mu mol h^{-1} g_{cat}^{-1})$ | $(\mu mol h^{-1} g_{cat}^{-1})$ | | $(\text{mmol }h^{-1}g_{Au}^{-1})$ | $(\text{mmol } h^{-1} g_{Au}^{-1} D_{M}^{-1})$ |
| ZnO-n | 234 | 280 | 1.20 | 73 | 3.67 |
| ZnO-r | 97 | 226 | 2.33 | 25 | 1.34 |
| ZnO-f | 301 | 427 | 1.42 | 147 | 6.87 |
| ZnO-t | 231 | 211 | 0.91 | 60 | 3.21 |
| ZnO-c | 66 | 197 | 2.98 | 26 | 2.81 |

| Table 2. Rate of H ₂ | generation using | $ZnO(r_{ZnO, H2})$ | and Au/ZnO (| $r_{\rm Au/ZnO, H2}$) ca | talysts |
|---------------------------------|------------------|--------------------|--------------|---------------------------|---------|
|---------------------------------|------------------|--------------------|--------------|---------------------------|---------|