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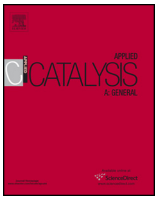

Photocatalytic performance of Au/ZnO nanocatalysts for hydrogen production from ethanol

Maria J. Sampaio[a], João W.L. Oliveira[b], Caroline I.L. Sombrio[b], Daniel L. Baptista[b], Sérgio R. Teixeira[b], Sónia A.C. Carabineiro[a], Cláudia G. Silva[a], Joaquim L. Faria[a,*]

[a] *LCM – Laboratório de Catálise e Materiais – Laboratório Associado LSRE-LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias s/n 4200-465 Porto, Portugal*
[b] *Instituto de Física, Universidade Federal do Rio Grande do Sul, Porto Alegre, RS 91501-970, Brazil*

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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 H_2 from a water–ethanol solution under UV–vis irradiation ($\lambda > 300$ nm). During the photocatalytic runs, hydrogen was generated at a constant rate for all samples, as well as CH_4 and CO. The obtained results show that bare ZnO materials were able to promote H_2 photogeneration, being ZnO-f the most efficient in terms of H_2 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 μmol h^{-1} $g_{cat}{}^{-1}$; 5.4 nm) and Au/ZnO-n (280 μmol 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 μmol h^{-1} $g_{cat}{}^{-1}$). Au/ZnO-f seems to be the most promising photocatalyst, generating the highest amount of H_2 and the lowest quantities of CH_4 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.

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

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* Corresponding author. Fax: +351 225 081 449.
E-mail address: jlfaria@fe.up.pt (J.L. Faria).

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energy, widely abundant in south European and south American countries) are used, then process becomes even more attractive.

Titanium dioxide (TiO_2) 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 TiO_2, 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 TiO_2 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 TiO_2 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 TiO_2 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/TiO_2 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 H_2 from a water-ethanol solution under UV–vis irradiation ($\lambda > 300$ nm). During the photocatalytic runs, H_2 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, ≥97%) aqueous solution was heated to 70 °C under vigorous stirring, and then a 2 M $Zn(NO_3)_2{\cdot}6H_2O$ (Aldrich, ≥99%) aqueous solution was added dropwise to the first with 1 h 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 $Zn(NO_3)_2{\cdot}6H_2O$ 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 1 h 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, ≥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% Al_2O_3, 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 analysed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a FEI Quanta 400 FEG ESEM/EDAX Genesis X4 M (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 CuKα radiation ($\lambda = 1.5418$ Å). Textural characterisation, namely determination of the specific surface area (S_{BET}), was performed by analysis of N_2 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 (1.15×10^{19} m^{-2} 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 (6.023×10^{23} 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.

2.4. 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