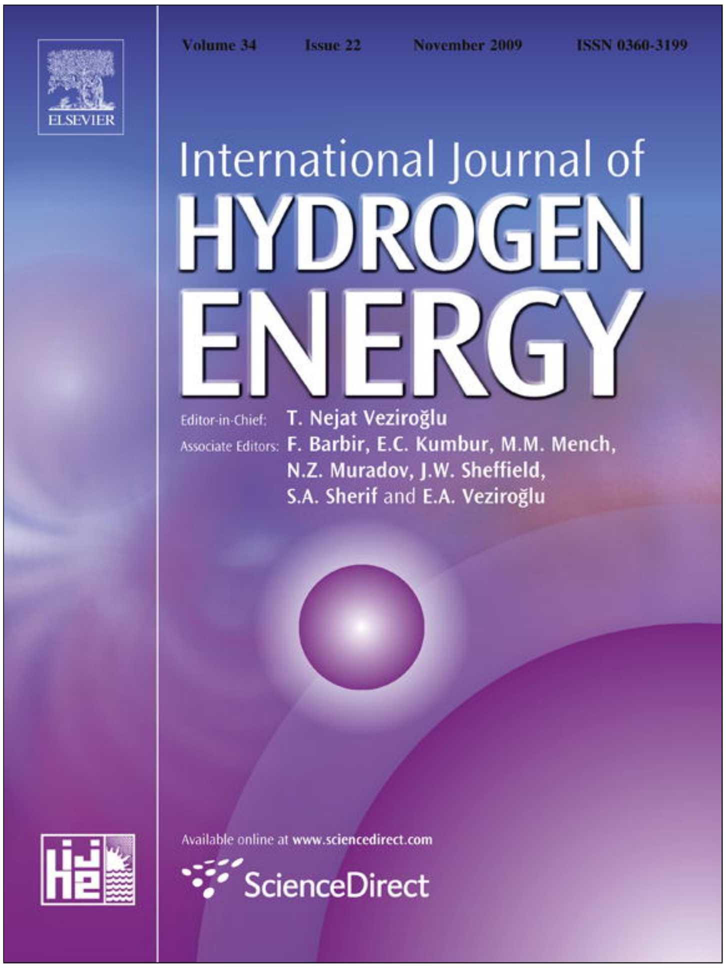
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Synergistic effects in hydrogen production through water sonophotolysis catalyzed by new $La_{2x}Ga_{2y}In_{2(1-x-y)}O_3$ solid solutions

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ABSTRACT

This work presents experimental data regarding hydrogen production by heterogeneous photocatalysis, sonocatalysis and sonophotocatalysis in water/ethanol solutions. Three new metal oxides solid solutions, $LaGa_{0.5}In_{0.5}O_3$, $La_{0.8}Ga_{0.2}InO_3$ and S-doped $La_{0.8}Ga_{0.2}InO_3$ (S:$La_{0.8}Ga_{0.2}InO_3$), have been synthesized and used as catalysts. Their action has been tested in diluted and concentrated suspensions wherein the content of ethanol, acting as sacrificial reagent, has been fixed to 10% in volume. The largest amounts of hydrogen have, always, been achieved from concentrated suspensions and by using S:$La_{0.8}Ga_{0.2}InO_3$ as catalyst. Ultrasounds, generated by 38 kHz and 50 W piezoelectric transducer, were more effective than light coming from a 35 W Xe lamp. Moreover, the hybrid action of light and ultrasounds determined a remarkable synergistic effect on the hydrogen production. Therefore, sonophotocatalysis is a promising way of generating hydrogen from water/ethanol solutions. In the near future, a net hydrogen production is expected to be achieved by improving the proposed process efficiencies.

1. Introduction

Hydrogen could be the energy vector of future; for that, it is expected to find out ways to economically produce it from an abundant chemical species. Water is the ideal starting material since it is available almost everywhere in the world and it is obtained back from H_2 combustion. If it were, the main process for hydrogen production would be the water splitting reaction (see equation 1):

$$H_2O_{(l)} \rightarrow H_{2(g)} + \tfrac{1}{2}\, O_{2(g)} \tag{1}$$

Process (1) is an uphill redox reaction, wherein hydrogen ion is reduced and oxygen ion is oxidized. A free energy of 237 kJ/mol is required to perform it in standard conditions.

In order to give rise to future sustainable economy, it is necessary to exploit renewable energy sources to perform the chemical process (1). This can be done by electrolysis, using electrical energy accumulated directly (photovoltaic cells) or indirectly (hydroelectric or wind generation) from the sun [1–3], by concentrated solar thermochemical processes [4], by photobiological systems [5,6] or by photochemical reactions [7]. Photodecomposition of water in hydrogen and oxygen cannot be achieved directly, since the solar radiation reaching the earth surface is devoid of those UV wavelengths that are absorbed by

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the electrons of water molecules. Therefore, a photocatalyst is needed, i.e. a species that, after absorption of sunlight, triggers the required redox reactions, leading to the production of hydrogen and oxygen. From the viewpoint of large-scale hydrogen production, particulate semiconductor systems are considered to be advantageous because of their simplicity [7,8]. Since most of the solar radiation consists of visible wavelengths, coloured photocatalysts should be synthesized [9]. In this case, it is suitable to assist the photo-production of hydrogen with a sacrificial reagent, i.e. a species that can be oxidized more easily than oxygen and can regenerate the photocatalyst [10]. Sacrificial reagent may be derived by a renewable process in order to run a quasi-carbon free hydrogen production.

To make the water splitting process with hydrogen production easier, it is useful to combine the action of light and heterogeneous photocatalyst with that of ultrasounds [11,12]. The use of ultrasounds into a photocatalytic reaction system might enhance mass transport and catalytic activity, due to surface cleaning and particle size reduction [13].

In this work we present the experimental results regarding the production of hydrogen from water through photocatalysis, sonocatalysis and sonophotocatalysis, by using new solid solutions of lanthanum, gallium and indium oxides (having $La_{2x}Ga_{2y}In_{2(1-x-y)}O_3$ as general formula) as catalysts and bio-ethanol as sacrificial reagent. We reveal that the simultaneous action of ultrasounds and UV-visible electromagnetic waves determines a noticeable synergistic effect: the moles of H_2 produced by sonophotolysis are always larger than the sum of H_2 moles obtained by photolysis and sonolysis, carried out separately.

2. Experimental

2.1. Preparation of catalysts

The chemical reagents, Ga_2O_3 (grade 99.99+%), In_2O_3 (grade 99.999%), La_2O_3 (grade 99.999%), thiourea and ethanol (>99.8%) were purchased by Sigma Aldrich and used as received. To synthesize $LaGa_{0.5}In_{0.5}O_3$ and $La_{0.8}Ga_{0.2}InO_3$, the reagents, Ga_2O_3, In_2O_3 and La_2O_3 were mechanically mixed under the appropriate molar ratios and grinded by a miller. The mixtures were calcined at 1373 K under air atmosphere, in a platinum crucible, for 24 h through a muffle furnace. Sulphur doped $La_{0.8}Ga_{0.2}InO_3$ was prepared as follows: $La_{0.8}Ga_{0.2}InO_3$ was mixed with thiourea in 1:4 molar ratio. The mixed powders were calcined at 773 K under air atmosphere for 5 h. After calcination, the resulting powder was washed with distilled water. The occurred products formation was ascertained by recording the X-ray diffraction spectra (through a Philips X'PERT PRO diffractometer) and the UV-visible reflectance spectra (through a Cary 4000 spectrophotometer, equipped by a DRA900 Diffuse Reflectance Accessory). SEM images revealed that the average dimensions of the particles were hundreds of nanometers.

2.2. Sono- and/or photocatalysis experiments

The experimental setup, employed to carry out the experiments of sonocatalysis, photocatalysis and sonophotocatalysis, is sketched in Fig. 1 A. It consists of a reactor, a source of ultrasounds and a source of UV-visible and near-IR electromagnetic radiation (sunlight spectrum). The reactor is made of AISI 304 stainless steel with a high pure quartz glass plate as a cover, shown in Fig. 1B. It is surrounded by a cooling system that maintains the temperature at 298 K during the experiments. Moreover, it is provided with three cylindrical pipes: one to insert the sample, i.e. water, ethanol and the catalyst; another, connected to a porous septum, to allow the collection of the produced gas through a gas-tight syringe; the last one to connect the upper side of the reactor to a vacuum pump and to a line of argon (grade 99,9999%) filling the free volume of the reactor at the pressure of 1 bar (this pressure assured better values for the sonophotolysis tests [14]). Temperature and pressure inside the reactor are constantly monitored through

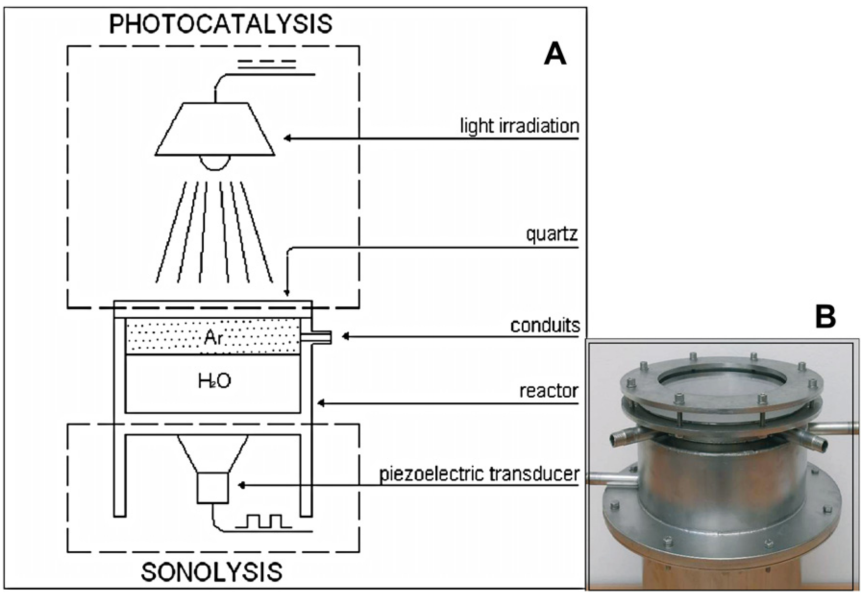

Fig. 1 – (A) Scheme of the experimental apparatus. (B) Picture of the reactor.

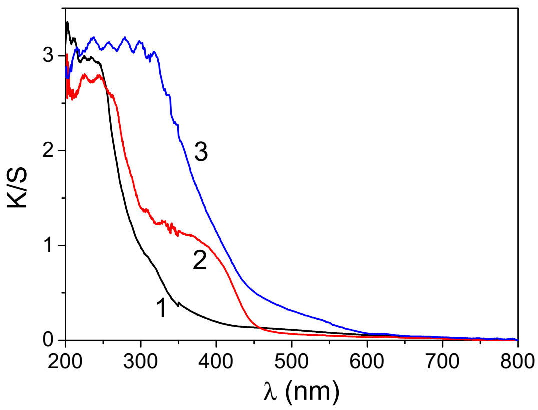

Fig. 2 – UV-visible absorption spectra of $LaGa_{0.5}In_{0.5}O_3$ (1, black trace), $La_{0.8}Ga_{0.2}InO_3$ (2, red trace) and $S{:}La_{0.8}Ga_{0.2}InO_3$ (3, blue trace), plotted in Kubelka-Munk units (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

a thermocouple and a pressure probe, respectively. The ultrasound source, located on the bottom side of the reactor, is constituted by a piezoelectric transducer, producing mechanical waves of 38 kHz at 50 W. The source of UV-visible and near-IR electromagnetic radiation is a 35 W Xe lamp, located 0.05 m above the reactor (having a diameter of 30 cm).

Samples, processed by the reactor, consisted of 0.4 g of catalyst suspended in 200 mL or 1100 mL of water/ethanol (10 % vol.) solutions. The two volumes were chosen in order to test the effect of two different surface/volume ratios for the water-ethanol mixture.

The amount of evolved hydrogen was measured by gas cromatography (CP-4900, Varian). The experiments of photo-, sono- and sonophotocatalysis for the different samples have been repeated at least two times. The uncertainties, defined as average standard deviations, are ±0.05 μmoles for the amount of hydrogen produced by photocatalysis, and ±0.5 μmoles for that obtained by sono- and sonophotocatalysis.

The viscosities of the suspensions have been measured by a capillary viscosimeter.

3. Results and discussion

3.1. *Properties of catalysts*

Binary solid solutions of Ga_2O_3 with In_2O_3, having $Ga_{2-x}In_xO_3$ as general formula, are known to be active photocatalysts for hydrogen production from water, in the presence of methanol as sacrificial reagent [15]. Ga_2O_3 is a wide band gap semiconductor able to produce hydrogen from water, whereas In_2O_3 is a semiconductor with a medium band gap that does not reduce water, but when mixed with Ga_2O_3, shifts the absorption spectrum of the $Ga_{2-x}In_xO_3$ solid solutions towards the visible region. The higher the value of x, the tighter the band gap is. Semiconductors with a restricted band gap can absorb a broader portion of the solar spectrum.

Aiming at the preparation of photocalysts suitable to produce H_2 by reduction of water, ternary solid solutions of general formula $La_{2x}Ga_{2y}In_{2(1-x-y)}O_3$ have been synthesized. They have been obtained by acid-base reactions among La_2O_3, Ga_2O_3 and In_2O_3, carried out in solid phase at high temperature (T = 1373 K for 24 h) (the details of their structural and photophysical properties will be presented into a paper that is in preparation). La_2O_3 is a semiconductor with a very wide band gap (5.2 eV) wherein lanthanum ion is a strong reducing agent.

In this paper we present the photo-, sono-, and sonophotolytic activity of three catalysts having the following chemical

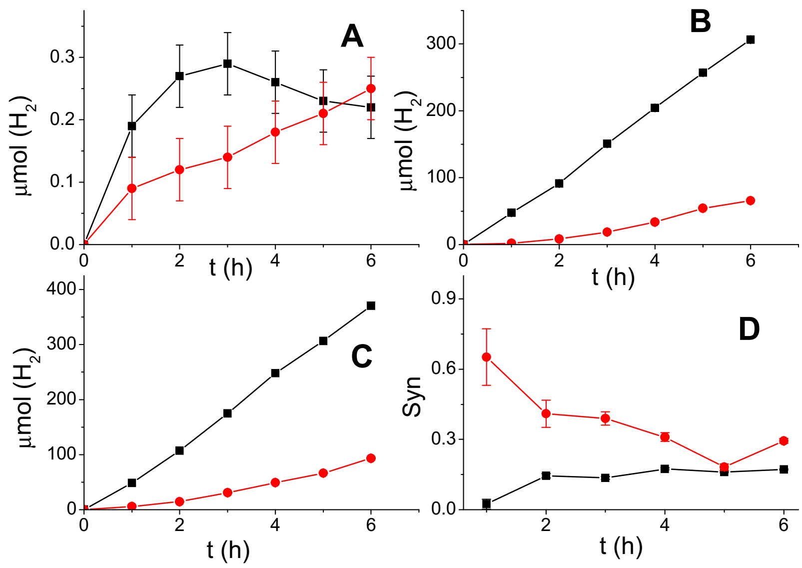

Fig. 3 – Production of hydrogen (μmol) as function of time (hours): (A) photocatalysis, (B) sonocatalysis, (C) sonophotocatalysis and (D) synergy for 0.4 g of $LaGa_{0.5}In_{0.5}O_3$ in 200 mL (black squared points) and 1100 mL (red circled points) of water/ethanol solutions (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 1 – Data of hydrogen production (μmol) by photocatalysis (light), sonocatalysis (US), sonophotocatalysis (light+US) and Synergy (Syn.) for the samples consisting of 0.4 g of $LaGa_{0.5}In_{0.5}O_3$ suspended in 200 mL and 1100 mL of water/ethanol solutions.

Time (h)	H_2 (μmol)				H_2 (μmol)			
	light 200 mL	US 200 mL	light+US 200 mL	Syn.[a] 200 mL	light 1100 mL	US 1100 mL	light+US 1100 mL	Syn.[a] 1100 mL
0	0	0	0	–	0	0	0	–
1	0.19	47.4	48.7	0.02 ± 0.02	0.09	2.0	6.0	0.65 ± 0.12
2	0.27	91.4	107.1	0.14 ± 0.01	0.12	8.5	14.6	0.41 ± 0.06
3	0.29	150.7	174.6	0.135 ± 0.006	0.14	18.6	30.7	0.39 ± 0.03
4	0.26	204.4	247.8	0.174 ± 0.004	0.18	33.5	48.8	0.31 ± 0.02
5	0.23	257.0	306.5	0.161 ± 0.003	0.21	54.0	66.2	0.18 ± 0.01
6	0.22	306.6	370.4	0.172 ± 0.003	0.25	65.8	93.5	0.29 ± 0.01

a The uncertainties assigned to the values of Synergy have been estimated as a priori maximum absolute error, through the formula of error propagation.

formula: $LaGa_{0.5}In_{0.5}O_3$, $La_{0.8}Ga_{0.2}InO_3$ and S: $La_{0.8}Ga_{0.2}InO_3$. Their absorption spectra, reported in Kubelka-Munk units, are depicted in Fig. 2. $LaGa_{0.5}In_{0.5}O_3$ is a white powder, which only absorbs ultraviolet radiation, having wavelengths (λ) shorter than 380 nm. By decreasing the content of La and Ga, and increasing that of In, the spectra of the ternary solutions $La_{2x}Ga_{2y}In_{2(1-x-y)}O_3$ are expected to shift towards the red. In fact, $La_{0.8}Ga_{0.2}InO_3$ is a pale yellow powder: it absorbs also in the visible region, with $\lambda < 450$ nm. By doping $La_{0.8}Ga_{0.2}InO_3$ with sulphur atoms, the spectrum undergoes a further shift towards the red: S:$La_{0.8}Ga_{0.2}InO_3$ is a dark yellow powder, that begins to absorb at 600 nm. S atoms give rise to energy levels above the valence band that is defined by the oxygen atoms. These intermediate levels confer to the catalysts the capability of absorbing a wider portion of the solar spectrum.

3.2. *Production of hydrogen*

The catalytic action of $LaGa_{0.5}In_{0.5}O_3$, $La_{0.8}Ga_{0.2}InO_3$ and S:$La_{0.8}Ga_{0.2}InO_3$ to produce H_2 from water has been tested by suspending 0.4 g of powder into 200 mL or 1100 mL of water/ethanol (10 vol %) solutions. Ethanol has been chosen as sacrificial reagent, since that produced by biomass fermentation can be employed in the prospect of a sustainable process of H_2 synthesis. By this way, ethanol is obtained by a renewable process with no carbon emission. A 35 W Xe lamp and a piezoelectric transducer of 38 kHz and 50 W have been used as sources of electromagnetic and mechanical waves, respectively. They have been applied separately, in photolytic and sonolytic experiments, and jointly in sonophotolytic experiments.

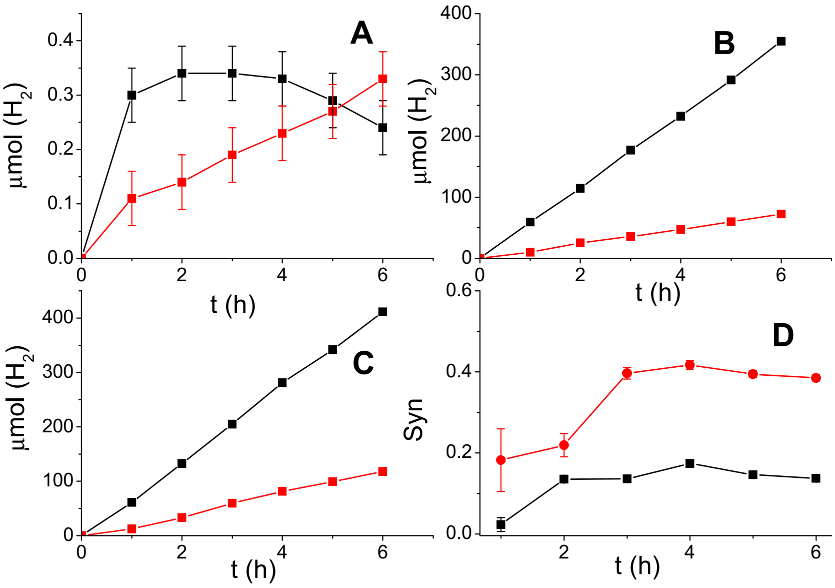

Fig. 4 – Production of hydrogen (μmol) as function of time (hours): (A) photocatalysis, (B) sonocatalysis, (C) sonophotocatalysis and (D) synergy for 0.4 g of $La_{0.8}Ga_{0.2}InO_3$ in 200 mL (black squared points) and 1100 mL (red circled points) of water/ethanol solutions (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 2 – Data of hydrogen production (μmol) by photocatalysis (light), sonocatalysis (US), sonophotocatalysis (light+US) and Synergy (Syn.) for the samples consisting of 0.4 g of $La_{0.8}Ga_{0.2}InO_3$ suspended in 200 mL and 1100 mL of water/ethanol solutions.

Time (h)	H_2 (μmol)				H_2 (μmol)			
	light 200 mL	US 200 mL	light+US 200 mL	Syn.[a] 200 mL	light 1100 mL	US 1100 mL	light+US 1100 mL	Syn.[a] 1100 mL
0	0	0	0	–	0	0	0	–
1	0.30	59.2	61.0	0.02 ± 0.02	0.11	10.1	12.5	0.18 ± 0.08
2	0.34	114.3	132.6	0.14 ± 0.01	0.14	25.5	32.9	0.22 ± 0.03
3	0.34	176.6	204.8	0.136 ± 0.005	0.19	35.8	59.7	0.40 ± 0.01
4	0.33	232.1	281.3	0.174 ± 0.003	0.23	47.1	81.2	0.42 ± 0.01
5	0.29	291.5	341.7	0.146 ± 0.002	0.27	59.7	99.1	0.40 ± 0.01
6	0.24	354.6	411.2	0.137 ± 0.002	0.33	72.3	118.1	0.39 ± 0.01

a The uncertainties assigned to the values of Synergy have been estimated as a priori maximum absolute error, through the formula of error propagation.

It has already proved that photolysis of water and ethanol solutions in the presence of a catalyst, such as TiO_2, produces H_2 and acetaldehyde. Only after prolonged period of irradiation, acetaldehyde can be further oxidized to acetic acid; finally, CH_3COOH decomposes into CH_4 and CO_2 [16]. Hydrogen and the typical pyrolysis and combustion products of ethanol, such as acetaldehyde and acetic acid, are produced even when water-alcohol mixtures are exposed to ultrasound irradiation [17,18]. Examples of sonophotocatalysis of pure and sea-water can be found in the literature by using TiO_2 as photocatalyst [19–21]. The hybrid action of mechanical and electromagnetic waves has been ascertained to exert a synergistic effect on the yield of formation of hydrogen and the other products of water decomposition. Such synergistic effect has been also observed in sonophotocatalytic decomposition reactions of water pollutants; for instance degradation of 2-chlorophenol, acid orange 8, acid red 1 [22] and 2,4,6-trichlorophenol [23]. In ref. [22], the synergy has been quantified as the normalised difference between the decomposition rate constants obtained under sonophotocatalysis and the sum of those obtained under separate photocatalysis and sonolysis. Herein, the synergy will be defined through the Eq. (2) below:

$$\mathrm{Syn} = \frac{\mu\mathrm{mol}_{(\mathrm{light+US})} - \left(\mu\mathrm{mol}_{(\mathrm{light})} + \mu\mathrm{mol}_{(\mathrm{US})}\right)}{\mu\mathrm{mol}_{(\mathrm{light+US})}} \tag{2}$$

where $\mu mol_{(light+US)}$ are the H_2 micromoles produced by the combined action of light and ultrasounds, $\mu mol_{(light)}$ are the H_2 micromoles produced by photocatalysis, whereas $\mu mol_{(US)}$ are those obtained by sonocatalysis. If $Syn = 0$, there is no synergistic effect; if $Syn = 0.5$, it means that the hybrid action of the two energy sources engenders the production of a doubled H_2 quantity with respect to that obtained through the separate actions of photolysis and sonolysis.

In Fig. 3, the amounts of H_2 produced by photocatalysis (3A), sonocatalysis (3B) and sonophotocatalysis (3C) with 0.4 g

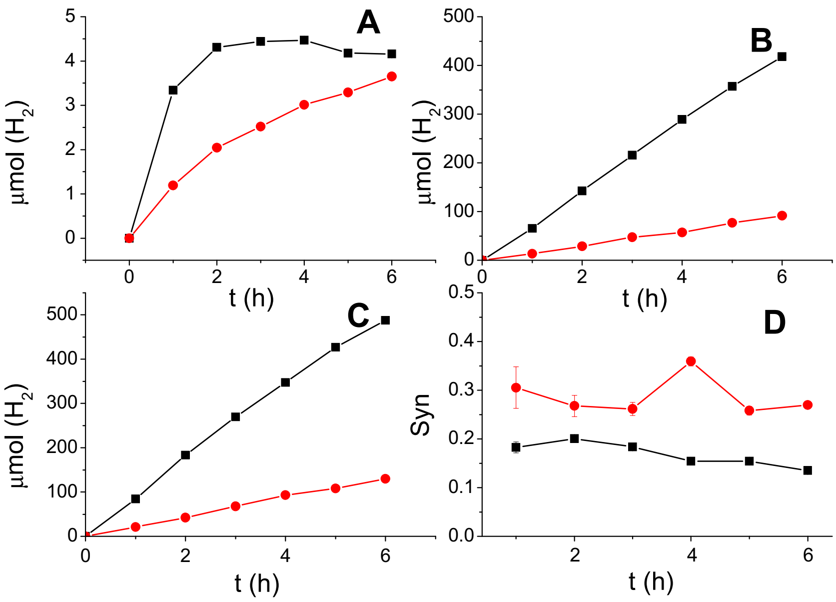

Fig. 5 – Production of hydrogen (μmol) as function of time (hours): (A) photocatalysis, (B) sonocatalysis, (C) sonophotocatalysis and (D) synergy for 0.4 g of S:$La_{0.8}Ga_{0.2}InO_3$ in 200 mL (black squared points) and 1100 mL (red circled points) of water/ethanol solutions (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 3 – Data of hydrogen production (μmol) by photocatalysis (light), sonocatalysis (US), sonophotocatalysis (light+US) and Synergy (Syn.) for the samples consisting of 0.4 g of S:$La_{0.8}Ga_{0.2}InO_3$ suspended in 200 mL and 1100 mL of water/ethanol solutions.

Time (h)	H_2 (μmol)				H_2 (μmol)			
	light 200 mL	US 200 mL	light+US 200 mL	Syn.[a] 200 mL	light 1100 mL	US 1100 mL	light+US 1100 mL	Syn.[a] 1100 mL
0	0	0	0	–	0	0	0	–
1	3.34	65.6	84.4	0.18 ± 0.01	1.19	13.4	21.0	0.31 ± 0.04
2	4.31	142.5	183.5	0.200 ± 0.005	2.04	29.1	42.5	0.27 ± 0.02
3	4.44	215.6	269.6	0.184 ± 0.004	2.52	47.7	68.0	0.26 ± 0.01
4	4.47	289.4	347.5	0.154 ± 0.003	3.01	56.8	93.3	0.36 ± 0.01
5	4.18	356.9	426.8	0.154 ± 0.002	3.29	77.0	108.2	0.26 ± 0.01
6	4.16	417.8	487.9	0.135 ± 0.002	3.65	91.5	130.2	0.27 ± 0.01

a The uncertainties assigned to the values of Synergy have been estimated as a priori maximum absolute error, through the formula of error propagation.

of $LaGa_{0.5}In_{0.5}O_3$, suspended in 200 mL (black squared points) and 1100 mL (red circled points) water/ethanol (10%) solutions are shown (the data are also reported in Table 1). The photocatalysis allowed about 0.2 μmoles of H_2 to be stored after 6 h of irradiation in both the 200 mL and the 1100 mL solution. Whereas the rate of H_2 production was nearly constant in the case of the diluted (1100 mL in vol) suspension, it was irregular in the case of the concentrated (200 mL as total volume) suspension: at the beginning, it was sharp, and after 3 h it became practically null. Larger quantities of H_2 were stored by sonocatalysis, being tens of μmoles in the case of the diluted suspension and even hundreds of μmoles in the case of the concentrated suspension. A further increase in H_2 production was achieved by sonophotocatalysis, exhibiting a significant synergistic effect (shown in Fig. 3 D and in Table 1), especially for the diluted suspension.

The results obtained by using $La_{0.8}Ga_{0.2}InO_3$ as catalyst are reported in Fig. 4 and Table 2. The lowest amounts of H_2 were collected by photocatalysis. As seen before, the rate of H_2 production was roughly constant in the case of diluted suspension, whereas it was rather irregular in the case of concentrated suspension, since at the beginning was high and then, after 3 h, became practically null (Fig. 4A). The largest quantities of H_2 were attained by sonophotocatalysis (Fig. 4C). The combined action of ultrasounds and light determined appreciable synergistic effects (Fig. 4D), especially in the case of the diluted suspension, although working with the concentrated suspension guaranteed the storage of a larger number of H_2 μmoles.

The μmoles of H_2 synthesized by using S:$La_{0.8}Ga_{0.2}InO_3$ as catalyst, are shown in Fig. 5 and Table 3. Also in this case, as in the preceding ones, the rate of H_2 μmoles production obtained by photocatalysis was irregular in the case of the concentrated suspension: at the beginning, it was fast and then became zero (Fig. 5A). Better results were achieved by sonocatalysis, exhibiting linear growths of H_2 μmoles as a function of irradiation time (Fig. 5B). Finally, the hybrid action of mechanical and electromagnetic waves favored a synergistic effect that was larger in the case of diluted suspension (Fig. 5D), although the largest amounts of H_2 were attained always in the case of concentrated suspensions.

Comparing the performances of the three catalysts, it results that S:$La_{0.8}Ga_{0.2}InO_3$ was the best in the photocatalytic, sonocatalytic and sonophotocatalytic experiments, whereas $LaGa_{0.5}In_{0.5}O_3$ was always the worst.

The photocatalytic activity of the three semiconductors is in relation with their absorption spectra: S:$La_{0.8}Ga_{0.2}InO_3$ is the semiconductor absorbing the broadest portion of solar spectrum and therefore the best photocatalyst; $La_{0.8}Ga_{0.2}InO_3$ absorbs the blue and the UV, whereas $LaGa_{0.5}In_{0.5}O_3$ only absorbs in the ultraviolet region, whereby the latter is the worst photocatalyst. By considering the performances of other photocatalysts appearing in the literature [15,24–28], and also taking into account that in our experiments a low power Xe lamp was used as source of irradiation and no Pt or NiO were used as co-catalysts, it can be inferred that S:$La_{0.8}Ga_{0.2}InO_3$ has exhibited a good activity. As a further support to this consideration, the semiconductor $GaInO_3$, having Pt as cocatalyst, was prepared as described in Ref. [15] and its photocatalytic activity tested by our apparatus. It emerged that $GaInO_3$ did not produce hydrogen, although it exhibited a rate of hydrogen evolution of the order of 30 μmoles per hour upon the irradiation with a 300 W Xe lamp.

The different sonocatalytic activity of the three solids is understandable by estimating the mechanical energy of ultrasounds that is dissipated as heat, and therefore not useful for splitting water, due to the shearing motions of medium molecules and viscous forces. The amount of wasted energy depends on the value of sound absorption coefficient (α, see Eq. (3) below) [29]. The larger the α value, the higher is the fraction of ultrasounds converted into heat. The α coefficient was estimated through measurements of cinematic viscosity (η_c) and the application of Eq. (3), as shown below:

$$\alpha = \frac{(5\eta_c\omega^2)}{(6c^3)} \tag{3}$$

Table 4 – Values of cinematic viscosity (η_c) and sound absorption coefficient (α) for the three catalysts suspended in water/ethanol (10%) solutions.

Sample	η_C [m²/s]	α [m^{-1}]
$LaGa_{0.5}In_{0.5}O_3$	0.0127	0.179
$La_{0.8}Ga_{0.2}InO_3$	0.0117	0.166
S:$La_{0.8}Ga_{0.2}InO_3$	0.0115	0.161

Table 5 – Rate of H_2 production (μmol/h) for the diluted (0.4 g of catalyst in 1100 mL) and concentrated (0.4 g of catalyst in 200 mL) suspensions measured in photolysis (light), sonolysis (US) and sonophotolysis (US + light) experiments and Synergy values determined as in Ref. [20].

Sample	light (μmol/h)	US (μmol/h)	US+light (μmol/h)	Synergy
$LaGa_{0.5}In_{0.5}O_3$ in 200 mL[a]	0.13	51.9	63.1	0.18
$LaGa_{0.5}In_{0.5}O_3$ in 1100 mL	0.037	11.7	15.5	0.25
$La_{0.8}Ga_{0.2}InO_3$ in 200 mL[a]	0.17	58.8	69.4	0.15
$La_{0.8}Ga_{0.2}InO_3$ in 1100 mL	0.050	12.1	20.6	0.41
$S:La_{0.8}Ga_{0.2}InO_3$ in 200 mL[a]	2.15	70.8	82.6	0.12
$S:La_{0.8}Ga_{0.2}InO_3$ in 1100 mL	0.58	15.3	22.0	0.28

a The rate of H_2 production determined in the photocatalytic experiments in concentrated suspensions has been calculated by considering just the first three experimental points.

where ω is the ultrasound frequency and c is the sound speed. The values for the three powders suspended in water/ethanol (10%) solutions are reported in Table 4.

It emerged that $S:La_{0.8}Ga_{0.2}InO_3$ exhibited the lowest value of thermal sound absorption, whereas $LaGa_{0.5}In_{0.5}O_3$ the largest. Therefore, as expected, $S:La_{0.8}Ga_{0.2}InO_3$ was the best sonocatalyst and $LaGa_{0.5}In_{0.5}O_3$ the worst. The extent of H_2 produced by the three sonocatalysts is noticeable if compared with that produced by TiO_2 upon more powerful sources of ultrasounds having even higher frequencies [19–21].

All three catalysts displayed appreciable synergistic effects in the sonophotocatalytic experiments. When a heterogeneous catalysis is carried out under the hybrid action of light and ultrasounds, the mechanical waves promote mass transport [30] of reactants to solid surface. Moreover, microjets produced by cavitation, are so strong to erode the surfaces of catalysts, determining an enhancement of their activity [11,22,31,32]. Finally, water and ethanol degradation species, produced by light irradiation of solid particles, can provide extra nuclei for bubble formation [33].

Focusing on the rate of hydrogen production, the best results have been obtained always in the case of concentrated (0.4 g of catalyst in 200 mL of water/ethanol) suspensions rather than in the case of diluted ones (0.4 g of catalyst in 1100 mL of water/ethanol), as it can be easily inferred by an analysis of the data reported in Table 5. The rates have been estimated by a linearization (not shown in the Figures) of all points collected in each type of experiment, except for the photolysis in concentrated suspensions, wherein just the first three points have been considered. In fact, the photolysis performed in 200 mL of liquid, have showed, always, a strong reduction of slope after 3 h of irradiation, reaching almost a plateau value. This trend may be due to a deactivation of the catalyst [8]. The sonolysis carried out in 200 mL of solution have exhibited rates almost five times faster than those obtained in 1100 mL of water/ethanol. The choice of a reduced volume of liquid guarantees a lesser dispersion of mechanical energy into heat. A quantification of the synergy, based on the kinetic constant values, as it has been proposed in Ref. [22], is also reported in Table 5. It appears that the largest synergistic effect always occurred in the case of diluted suspensions, in agreement with the estimates made by application of Eq. (2).

4. Conclusion

This work presents the results of H_2 production by photocatalysis, sonocatalysis and sonophotocatalysis of water/ethanol solutions in the presence of newly synthesized metal oxides solid solutions, acting as catalysts. Ethanol has been chosen as sacrificial reagent, since it may be derived by biomass fermentation, which can be employed in the prospect of a renewable hydrogen economy. The compounds herein described, having $LaGa_{0.5}In_{0.5}O_3$, $La_{0.8}Ga_{0.2}InO_3$ and $S:La_{0.8}Ga_{0.2}InO_3$ as molecular formula and prepared through solid state acid-base reactions, have been tested as photo-, sono- and sonophoto-catalysts. Promising experimental results have been achieved.

$La_{0.8}Ga_{0.2}InO_3$ is a more active photocatalyst than $LaGa_{0.5}In_{0.5}O_3$, since it absorbs a broader portion of the solar spectrum, due to the higher content of indium atoms. The doping of $La_{0.8}Ga_{0.2}InO_3$ by sulphur atoms, determines the introduction of intermediate energetic levels between the semiconductor conduction and valence bands, whereby $S:La_{0.8}Ga_{0.2}InO_3$ absorbs an even more extended amount of solar energy. It derives that $S:La_{0.8}Ga_{0.2}InO_3$ is the best photocatalyst.

The sequence of sonocatalytic power for the three solids reflects that of photocatalysis, i.e. $S:La_{0.8}Ga_{0.2}InO_3$ and $LaGa_{0.5}In_{0.5}O_3$ are the best and the worst sonocatalysts, respectively. This phenomenology becomes understandable by considering the magnitude of the thermal sound absorption coefficient (α) of their suspensions. The larger the α, the lower the sonocatalytic activity is.

Finally, the hybrid action of light and ultrasounds favors a remarkable synergistic effect in H_2 production. The extent of synergy depends on the mass of liquid (water and ethanol) introduced into the reactor: it is more pronounced in diluted rather than in concentrated suspensions. Evidently, the larger the mass of liquid, the faster the mass transport of reactants to solid surface is. However, the largest amounts of H_2 μmoles have been achieved always from the concentrated suspensions: probably, the use of a lesser quantity of water/ethanol solution allows the dissipation of mechanical energy of ultrasounds as heat to be reduced.

The general goal of this research is getting hydrogen with a net energy balance: produced hydrogen energy content must be greater than energy spent in the process. Actually, there is a long way to achieve it because of the tiny amount of produced hydrogen with respect to the energy spent on mechanical source. However, further viable improvements encourage us to go on by implementing the following items:

- synthesis of new solid solutions to be used as catalysts and optimisation of their durability;
- optimization of water/ethanol ratio;

- maximization of acoustical matching between the source and liquid under test;
- optimization of source frequency and wave shape;
- optimization of surface/volume ratio of liquid under test;
- implementation of more efficient techniques to get a sudden separation of produced hydrogen.

Further experiences will be carried out by practicing the previous improvements and energetic parameters will be estimated.

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