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(71) **Applicant**: **COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH** [IN/IN]; an Indian registered body incorporated, under the Regn. of Soc. Act (Act XXI of 1860), Anusandhan Bhawan, Rafi Marg, New Delhi - 110 001 (IN).

(72) **Inventors**: **DEVI, Nandini, R.**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008 (Maharashtra) (IN). **NARENDRANATH, Soumya Bharathi**; National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008 (Maharashtra) (IN).

(74) **Agent**: **DUTT, Ranjna Mehta**; Remfry & Sagar, Attorneys at Law, Remfry House at the Millennium Plaza, Sector 27, Gurgaon 122 009 New Delhi (IN).

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(54) Title: WATER SPLITTING ACTIVITY OF LAYERED OXIDES

(57) **Abstract**: The invention discloses an efficient and economical process for H2 evolution by water splitting, catalyzed by layered oxides that function in UV and visible light.

WATER SPLITTING ACTIVITY OF LAYERED OXIDES

FIELD OF THE INVENTION

Present invention relates to an efficient and economical process for H_2 evolution by water splitting, catalyzed by layered oxides that function in UV and visible light. Particularly, present invention discloses catalysts that efficiently evolve H_2 in the presence and absence of a co-catalyst.

BACKGROUND AND PRIOR ART OF THE INVENTION

Photo-catalytic hydrogen generation from water is one of the most favorable ways to generate clean energy. Water splitting using semiconductor powder catalysts is a promising and preferred process because of the simplicity and ease of handling.

Semiconductor oxides like TiO_2 and ZnO are widely used in photocatalysis due to unique electronic structures facilitating the formation of electron-hole pairs, on irradiation with light of appropriate energy, which can be utilized in electron transfer processes. However, efficient utilization of these charge carriers is possible only if charge recombination is avoided.

Recombination occurs when photo generated electrons reoccupy valence band and depends on the positions of valence and conduction bands, or electron and hole conduction pathways within the oxide lattice. On irradiation with light of appropriate energy, electrons and holes are generated in bulk of the semiconductor particles and travel to the surface, eventually being utilized in water reduction and oxidation reactions respectively, on catalytically active surface sites or external co-catalysts deployed on the surface. During these processes, there are several possible pathways for recombination of the electron hole pair leading to energy wastage, such as grain boundaries, lattice defects and surface sites.

Recombination can be prevented if photo generated electrons and holes are well separated from each other spatially, i.e. photogeneration and utilization sites as well as conduction pathways are physically separated in space within the structure of the semiconductor. Consequently, catalytic activity, which depends on the availability of the photogenerated electrons, can be enhanced if such a spatial separation is provided.

Another important parameter depends on the structural characteristics of valence and conduction bands, wherein holes and photogenerated electrons and holes are located respectively and in semiconductors with bulk 3D structures, they are structurally close to each other enhancing the chances of recombination. Hence, structures with inherent separation of photogenerated charges spatially, are ideal for efficient photocatalysis. Such a phenomenon is exploited by nature in utilizing solar energy whereby photogenerated charges are separated spatially by cascade processes. Solid oxide structures can be envisaged which have intrinsic structural anisotropy leading to separate sites for charge generation and electron conduction pathways, effectively separating holes and electrons.

In view of the aforesaid, a suitable photocatalytic material should possess sufficiently small band gap for utilizing more abundant visible light region in the solar spectrum. The valence band and conduction band positions with respect to reduction and oxidation potentials of water should be appropriate to drive overall water splitting.

Lately, a lot of attention is garnered by layered semiconductor oxides, like $K_4Nb_6O_{17}$, members of Ruddlesden-Popper series of perovskites, layered perovskites, $Sr_2Ta_2O_7$ and $Sr_2Nb_2O_7$ as catalysts for H_2 generation. Typically, these structures consist of sheets of transition metal oxides separated by alkali or alkaline earth metal ions, giving rise to anisotropy to certain extent restricting movement of charges through interlayer spaces. However, in these layered compounds, the attempt is to introduce catalytic sites within the interlayer spaces thereby achieving partial space separation of the charges or spatially separate H_2 and O_2 evolution sites reducing the backward reaction. Moreover, high band gap energies of these compounds limit their usage to only UV light region.

Layered structures with well-defined conduction pathways separated from photo generation sites can be envisaged to address the problems posed by layered oxides effectively. $InMO_3\ (ZnO)_m$ are a series of oxides form one such family of compounds which are conventionally studied for their excellent thermoelectric properties as well as transparent conducting oxides. The enhanced conductivity is suggested to be due to a spatial separation of the carrier donors located in insulating layers and the conducting layers which transfer the carriers effectively. Spatial separation in $InMO_3(ZnO)_m$ is found to be much higher compared to contemporary semiconductors. This is manifested in the anisotropic nature of the electrical conductivity. Measurements on thin film and single crystals reveal higher conductivity along a-b plane. Kawazoe and co-workers (*Un'no, N. Hikuma, T. Omata, N. Ueda, T. Hashimoto, and H. Kawazoe, Jpn. J. Appl. Phys., Part 2 32, L1260 (1993), T. Omata, N. Ueda, K. Ueda, and H. Kawazoe, Appl. Phys. Lett. 64, 1077 (1994), K. Yanagawa, Y. Ohki, T. Omata, H. Hosono, N. Ueda, and H. Kawazoe, Appl. Phys. Lett. 64, 2071 (1994)*) suggested that layers formed by edge sharing MO_6 octahedra, where M is a p-block metal ion, may act as electron conducting pathways facilitating electrical conductivity. The unique electronic and band structure resulting from such a structural anisotropy makes this series, potential materials for addressing recombination issues associated with semiconductor photocatalysts.

In this context, there remains a need in the art for simple and economical photocatalytic water splitting process catalyzed by structurally anisotropic compounds with photo-generation sites and electron conduction pathways which are spatially separated structurally.

Therefore, it will be of advantage to explore photo catalysts that have above mentioned properties and structures and provide them as efficient photo catalysts for systems to evolve H_2 by water splitting. But such catalysts should preferably satisfy the need to maintain the costs of the process of H_2 generation. Rather it would be pertinent to state here that the catalyst should not be the reason for the process to not satisfy the need for an economic alternative. It would be further advantageous to provide a catalyst that functions well at visible and UV range.

OBJECTS OF THE INVENTION

Main object of the present invention is to provide a photocatalytic process for H_2 evolution by water splitting using a catalyst active in UV and visible light.

Another object of the present invention is to provide a process of H_2 evolution by water splitting using a catalyst that is independent of a co catalyst.

SUMMARY OF THE INVENTION

Accordingly, present invention provides a photocatalytic water splitting process for H_2 generation catalyzed by InA(ZnO)*m* in the visible and UV light range, wherein A is selected from an oxide of Fe or Ga and m = 1-5, comprising:

i. dispersing InA(ZnO)*m* powder in a reactant solution comprising water and methanol in ratio of 4:1 in a gas closed irradiation system;

ii. irradiating the reactant mixture as obtained in step (a) to obtain hydrogen.

In an embodiment of the present invention, the catalyst are selected from the group consisting of $InFeO_3(ZnO)m$ and $InGaO_3(ZnO)m$, wherein m=1 – 5.

In another embodiment of the present invention, the irradiation process is carried out in UV or visible light region.

In yet another embodiment of the present invention, the said process is carried for a period of 1-12 hours.

In yet another embodiment of the present invention, optionally the process is carried out in the presence of a metal co-catalyst selected from the group consisting of NiO, CuO and Pt.

In yet another embodiment of the present invention, NiO is loaded onto $InGaO_3(ZnO)m$, where m = 1- 5.

In yet another embodiment of the present invention, CuO is loaded onto $InGaO_3(ZnO)m$, where m = 1- 5.

In yet another embodiment of the present invention, Pt is loaded onto $InFeO_3(ZnO)m$, where m = 1- 5.

In yet another embodiment of the present invention, the hydrogen evolution rate is in the range of 7 to 11 milli mol/g/h and 0.8 to 3.58 milli mol/g/h in the presence of catalyst $InFeO_3(ZnO)m$ and $InGaO_3(ZnO)m$ respectively.

In yet another embodiment, present invention provide a photocatalyst composition $InA(ZnO)_m$, wherein A is selected from an oxide of Fe or Ga and m = 1-5 for use as catalyst in water splitting reactions for H_2 generation.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts the powder XRD pattern of $InFeO_3(ZnO)_1$.

Figure 2 depicts the effect of irradiation time on hydrogen generation by $InFeO_3$ $(ZnO)_1$ without loading Pt under visible light irradiation.

Figure 3 depicts the powder XRD pattern of $InFeO_3(ZnO)_2$.

Figure 4 depicts the effect of irradiation time on hydrogen generation by $InFeO_3$ $(ZnO)_2$ with Pt loading under UV irradiation.

Figure 5 depicts the effect of irradiation time on hydrogen generation by $InFeO_3$ $(ZnO)_2$ without loading Pt under UV irradiation.

Figure 6 depicts the effect of irradiation time on hydrogen generation by $InFeO_3$ $(ZnO)_2$ without loading Pt under visible irradiation.

Figure 7 depicts the effect of irradiation time on hydrogen generation by $InFeO_3$ $(ZnO)_2$ with Pt loading under visible irradiation.

Figure 8 depicts the powder XRD pattern of $InFeO_3(ZnO)_3$.

Figure 9 depicts the effect of irradiation time on hydrogen generation by $InFeO_3$ $(ZnO)_3$ without loading Pt under visible irradiation.

Figure 10 depicts the powder XRD pattern of $InFeO_3(ZnO)_4$.

Figure 11 depicts the effect of irradiation time on hydrogen generation by $InFeO_3(ZnO)_4$ without loading Pt under visible irradiation.

Figure 12 depicts the comparison of water splitting activity in visible light without Pt impregnation for the three catalysts.

Figure 13 depicts H_2 evolution with IGZ $InGaO_3(ZnO)m$, where m = 1- 4 catalysts under UV light irradiation.

Figure 14 depicts H_2 evolution with 1 wt%, 2 wt% NiO loaded IGZ catalyst.

Figure 15 depicts H_2 evolution with 2 wt% NiO loaded IGZ catalysts.

Figure 16 depicts H_2 evolution with 1 wt%, 2 wt% CuO loaded IGZ catalyst at 4 hours.

Figure 17 depicts H_2 evolution with 2 wt% CuO loaded IGZ catalysts.

Figure 18 depicts H_2 evolution from IGZ1 with different CuO loading.

DETAILED DESCRIPTION OF THE INVENTION

The invention provides an efficient and economic process for H_2 evolution by water splitting employing layered oxides as photo catalysts, which are functional in UV and visible light.

In an aspect, the present invention provides a process for H_2 evolution, wherein the photocatalyst is $InA(ZnO)_m$, wherein m = 1-5, A is selected from an oxide of Fe or Ga, such that the catalyst evolves H_2 in UV as well as visible range.

In another aspect the present invention provides a process of evolution of H_2 carried out optionally in the presence of a co-catalyst selected from Pt, CuO or NiO.

Terminologies UV and visible light range used in the specification refer to wavelengths in the range of 180-800 nm.

Accordingly, the present invention discloses a photocatalytic water splitting process for H_2 generation catalyzed by $InA(ZnO)_m$, wherein A is selected from an oxide of Fe or Ga and m = 1-5 in the absence of a metal co-catalyst and is carried out in the UV or visible range.

The present invention discloses a photocatalytic process for H_2 generation in the presence of a catalyst InA (ZnO)*m*, wherein A is selected from an oxide of Fe or Ga and m = 1-5.

Further, the present invention discloses a photocatalytic process for H2 generation in the presence of a layered oxide catalyst InA (ZnO)*m*, wherein A is selected from an oxide of Fe or Ga and m = 1 – 5 comprising:

a. dispersing InA(ZnO)*m* powder in a reactant solution comprising water and methanol in a ratio of 4:1 in a gas closed irradiation system, and
b. irradiating the reactant mixture obtained in step a.

Accordingly, the photocatalytic activity of InA(ZnO)*m* is determined by measuring the H_2 evolution in reactions that are carried out in a gas-closed system having a dead volume in the range of 45 – 55 ml.

The instant photocatalyst InA(ZnO)*m*, wherein A is selected from an oxide of Fe or Ga and m = 1 – 4 is dispersed by magnetic stirring in the reactant solution (25 mL) in an irradiation cell made of quartz.

The reactant solution for water splitting comprises (20 mL) pure/distilled water and (5 mL) methanol in a ratio of 4:1.

The reactant mixture is irradiated and methanol as the sacrificial reagent is oxidized by the resulting photogenerated holes.

The present invention discloses a water splitting catalyst for H_2 generation selected from the group consisting of $InFeO_3(ZnO)m$ and $InGaO_3(ZnO)m$, where m=1 – 5.

The present invention discloses a photocatalytic water splitting process for H_2 evolution, wherein the catalysis is carried out in the UV range and visible range of light.

The light source used for irradiation in the closed system is 400 W mercury lamp for UV irradiation and 400 W Tungsten lamp for visible irradiation.

The present invention discloses a photocatalytic process in the presence of a catalyst having formula InA(ZnO)m, wherein the said process is carried for a period of 1 to 8 hours.

The evolving gas mixture from the closed system is taken in a syringe at an interval of 1 hour. The amount of H_2 evolved was determined using gas chromatography (Agilent GC with Carbosphere column and N_2 as carrier gas).

The present invention discloses a photocatalyst, InA $(ZnO)_m$, wherein A is selected from an oxide of Fe or Ga and m = 1-5 for catalyzing water splitting reactions for H2 generation.

The instant catalyst InA (ZnO)*m*, is prepared by grinding indium oxide (In_2O_3), a metal oxide selected from FeO_3 or $GaO_3Fe_2O_3$; and ZnO under acetone in an agate mortar and pestle and subjecting it to calcination at 700°C, 900°C and 1000°C overnight with intermitted grinding in a muffle furnace. The resulting powder is pelleted by adding 2.5% polyvinyl alcohol in an aqueous solution as binder. The pellet is sintered two times at 1350°C for 15h. The catalyst is characterized by XRD. Pt is loaded onto $InFeO_3(ZnO)m$, where m = 1 – 5, by wet impregnation method and heated at 400 °C for 1 hour. Metal oxides selected from NiO and CuO are used as co-catalysts for water splitting reactions catalyzed by $InGaO_3(ZnO)m$, where m = 1 – 5.

The present invention discloses a process for catalyzing H_2 generation wherein the process is optionally co-catalysed by metals or metal oxides selected from the group consisting of, but not limited to Pt, CuO or NiO.

The present invention discloses a photocatalytic water splitting process, wherein the hydrogen evolution rate is in the range of 7 to 11 milli mol/g/h in the presence of catalyst $InFeO_3(ZnO)m$. The hydrogen evolution rate is in the range of 0.8 to 3.58 milli mol/g/h in the presence of catalyst $InGaO_3(ZnO)m$.

The present invention discloses the use of the instant photocatalyst composition InA(ZnO)m, wherein A is selected from metal oxides of Ga or Fe and m =1 -5 for catalyzing a water splitting reaction for the evolution of H_2.

EXAMPLES

Following examples are given by way of illustration therefore should not be construed to limit the scope of the invention.

Example 1

i. Synthesis of $InFeO_3 (ZnO)_1$

For 1 g of $InFeO_3(ZnO)_1$, 0.4627 g, 0.2661 g and 0.2712 g of In_2O_3, Fe_2O_3 and ZnO were weighed respectively and ground thoroughly under acetone in an agate mortar and pestle. The mixed powders were transferred to a platinum crucible and calcined at 700°C, 900°C and 1000°C overnight with intermitted grinding in a muffle furnace. The resulting powder was made into pellet by adding 2.5% polyvinyl alcohol in aqueous solution as binder. The pellet was sintered two times at 1350°C for 15h.

ii. Characterization of $InFeO_3 (ZnO)_1$

X ray Diffraction

The phase formation was confirmed with XRD. Powder X-ray diffraction (XRD) was carried out in a PANalytical X'pert Pro dual goniometer diffractometer working under 40 kV and 30 mA. The radiation used was Cu Kα (1.5418 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg–Brentano geometry with 1° slit at the source and receiving sides. An X'celerator solid-state detector with a scan speed of 0.012° min^{-1} was employed.

The powder XRD patterns depicted in Figure 1, 3, 8 and 10, show highly crystalline diffraction peaks, clearly indicating the formation of required structures, JCPDS Card Numbers 40-0250, 40-0243, 40-024, 40-0245 for IFZ1, IFZ2, IFZ3 and IFZ4 respectively, with reference to Kimizuka, N *et al.*, *Solid State Chem.* **1988**, *74*, 98-109.

The XRD pattern (Fig. 1) matches that of the reported compound corresponding to JCPDS PDF number 40-0250.

iii. Photocatalytic activity

$InFeO_3$ $(ZnO)_1$ was dispersed in 20 ml water and 5 ml methanol by means of a magnetic stirrer in a gas closed irradiation cell made of quartz having 70 ml capacity. Here methanol was taken as sacrificial reagent which gets oxidized by the resulting photogenerated holes. The light source was 400 Watt tungsten lamp for visible irradiation. The amount of H_2 evolved was determined using gas chromatography (Agilent GC with Carbosphere column and N_2 as carrier gas). The reaction was carried out for 5 hours. The evolving gas mixture was taken in a syringe at an interval of 1 hour and injected into the GC. With reference to Table 1 and Figure 2, H_2 evolution is observed to be greater than 1 milli mole for five hours, in the absence of a co catalyst selected from Pt or NiO.

Table 1: Water splitting activity of $InFeO_3(ZnO)_1$

Catalyst	Irradiation	Irradiation Time (h)	H_2 evolved (μmol/g/h)
$InFeO_3(ZnO)_1$_without Pt	Visible	1	1689.437
		2	1741.901
		3	1463.899
		4	1421.402
		5	1413.016

Example 2

i. Synthesis of $InFeO_3$ $(ZnO)_2$

For 1 g of $InFeO_3 (ZnO)_2$ 0.3639 g, 0.2093 g and 0.4267 g of In_2O_3, Fe_2O_3 and ZnO were weighed respectively and ground thoroughly under acetone in an agate mortar and pestle. The mixed powders were transferred to a platinum crucible and calcined at 700°C, 900°C and 1000°C overnight with intermitted grinding in a muffle furnace. The resulting powder was made into pellet by adding 2.5% polyvinyl alcohol in aqueous solution as binder. The pellet was sintered two times at 1350°C for 15h.

ii. Characterization of $InFeO_3 (ZnO)_2$

X ray Diffraction

The phase formation was confirmed with XRD. Powder X-ray diffraction (XRD) was carried out in a PANalytical X'pert Pro dual goniometer diffractometer working under 40 kV and 30 mA. The radiation used was Cu Kα (1.5418 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg–Brentano geometry with 1° slit at the source and receiving sides. An X'celerator solid-state detector with a scan speed of $0.012° \text{ min}^{-1}$ was employed. The XRD pattern (Fig.3) matches that of the reported compound corresponding to JCPDS PDF number 40-0243.

iii. Impregnation of Platinum

Tetraamine platinum nitrate ($[Pt(NH_3)_4](NO_3)_2$) was used as the platinum precursor. In order to load 2% platinum 0.002 g of $[Pt(NH_3)_4](NO_3)_2$ was weighed and dissolved in minimum amount of water and added to 0.049g of $InFeO_3(ZnO)_2$, mixed well and dried at 60°C. The mixture was transferred to an alumina crucible and heated at 400°C for 1 h.

iv. Photocatalytic activity

The 2% platinum loaded $InFeO_3 (ZnO)_2$ was dispersed in 20 ml water and 5 ml methanol by means of a magnetic stirrer in a gas closed irradiation cell made of quartz having 70 ml capacity. Here methanol was taken as sacrificial reagent which gets oxidized by the resulting photogenerated holes. The light source was 400 W mercury lamp for UV and 400 W Tungsten lamp for visible irradiation. The amount of H_2 evolved was determined using gas chromatography (Agilent GC with Carbosphere column and N_2 as carrier gas). The reaction was carried out for 1 to 5hours as tabulated herein. The evolving gas mixture was taken in a syringe at an interval of 1 hour and injected into the GC. The experiments were carried out with bare and platinum loaded catalyst under UV and visible irradiation. With reference to Figures 4-7 and Tables 2, 3, 4 and 5 it is observed that H_2 evolves in the presence of co catalyst exemplified as Pt, in both UV and visible ranges.

Table 2

Catalyst	Irradiation	Irradiation Time (h)	H_2 evolved (μmol/g/h)
$InFeO_3(ZnO)_2$ with Pt	UV	2	233.5063
		3	199.6466
		4	174.612
		5	158.0367

Table 3

Catalyst	Irradiation	Irradiation Time (h)	H_2 evolved (μmol/g/h)
$InFeO_3(ZnO)_2$ without Pt	UV	2	445.5616
		3	517.2267
		4	407.1339
		5	209.6826

Table 4

Catalyst	Irradiation	Irradiation Time (h)	H_2 evolved (μmol/g/h)
$InFeO_3(ZnO)_2$ without Pt	Visible	1	1761.588
		2	1536.928
		3	1284.246
		4	1114.3

Table 5

Catalyst	Irradiation	Irradiation Time (h)	H_2 evolved (μmol/g/h)
$InFeO_3(ZnO)_2$ with Pt	Visible	1	1686.829
		2	1230.631
		3	1310.478

Example 3

i. Synthesis of $InFeO_3$ $(ZnO)_3$

For 1 g of $InFeO_3$ $(ZnO)_3$ 0.2999 g, 0.1725 g and 0.5275 g of In_2O_3, Fe_2O_3 and ZnO were weighed respectively and ground thoroughly under acetone in an agate mortar and pestle. The mixed powders were transferred to a platinum crucible and calcined at 700°C, 900°C and 1000°C overnight with intermitted grinding in a muffle furnace. The resulting powder was made into pellet by adding 2.5% polyvinyl alcohol in aqueous solution as binder. The pellet was sintered two times at 1350°C for 15h.

ii. Characterization of $InFeO_3$ $(ZnO)_3$

X ray Diffraction

The phase formation was confirmed with XRD. Powder X-ray diffraction (XRD) was carried out in a PANalytical X'pert Pro dual goniometer diffractometer working under 40 kV and 30 mA. The radiation used was Cu Kα (1.5418 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg–Brentano geometry with 1° slit at the source and receiving sides. An X'celerator solid-state detector with a scan speed of $0.012° \text{ min}^{-1}$ was employed.

The XRD pattern (Fig. 8) matches that of the reported compound corresponding to JCPDS PDF number 40-0244.

iii. Photocatalytic activity

$InFeO_3(ZnO)_3$ was dispersed in 20 ml water and 5 ml methanol by means of a magnetic stirrer in a gas closed irradiation cell made of quartz having 70 ml capacity. Here methanol was taken as sacrificial reagent which gets oxidized by the resulting photogenerated holes. The light source was 400 Watt tungsten lamp for visible irradiation. The amount of H_2 evolved was determined using gas chromatography (Agilent GC with Carbosphere column and N_2 as carrier gas). The reaction was carried out for 1 to 6 hours. The evolving gas mixture was taken in a syringe at an interval of 1 hour and injected into the GC. It may be concluded from Figure 9 and Table 6 that the catalyst of this example evolves H_2 up to 1 milli mole even without presence of co catalyst. Further, the catalyst of this example has exhibited stability and activity over 6 hours.

Table 6: Water splitting activity of $InFeO_3(ZnO)_3$

Catalyst	Irradiation	Irradiation Time (h)	H_2 evolved (μmol/g/h)
$InFeO_3(ZnO)_3$_without Pt	Visible	1	766.4058
		2	747.9462
		3	788.8368
		4	984.5972
		5	1052.739
		6	960.1463

Example 4

i. Synthesis of $InFeO_3$ $(ZnO)_4$

For 1 g of $InFeO_3$ $(ZnO)_4$ 0.2551 g, 0.1467 g and 0.5982 g of In_2O_3, Fe_2O_3 and ZnO were weighed respectively and ground thoroughly under acetone in an agate mortar and pestle. The mixed powders were transferred to a platinum crucible and calcined at 700°C, 900°C and 1000°C overnight with intermitted grinding in a muffle furnace. The resulting powder was made into pellet by adding 2.5% polyvinyl alcohol in aqueous solution as binder. The pellet was sintered two times at 1350°C for 15h.

ii. Characterization of $InFeO_3$ $(ZnO)_4$

X ray Diffraction

The phase formation was confirmed with XRD. Powder X-ray diffraction (XRD) was carried out in a PANalytical X'pert Pro dual goniometer diffractometer working under 40 kV and 30 mA. The radiation used was Cu Kα (1.5418 Å) with a Ni filter and the data collection was carried out using a flat holder in Bragg–Brentano geometry with 1° slit at the source and receiving sides. An X'celerator solid-state detector with a scan speed of 0.012° min^{-1} was employed. The XRD pattern (Fig. 10) matches that of the reported compound corresponding to JCPDS PDF number 40-0245.

iii. Photocatalytic activity

$InFeO_3$ $(ZnO)_4$ was dispersed in 20 ml water and 5 ml methanol by means of a magnetic stirrer in a gas closed irradiation cell made of quartz having 70 ml capacity. Here methanol was taken as sacrificial reagent which gets oxidized by the resulting photogenerated holes. The light source was 400 Watt tungsten lamp for visible irradiation. The amount of H_2 evolved was determined using gas chromatography (Agilent GC with Carbosphere column and N_2 as carrier gas). The reaction was carried out for 5 hours. The evolving gas mixture was taken in a syringe at an interval of 1 hour and injected into the GC. With reference to

Table 7 and Figure 11, H_2 evolution is observed to be greater than 1 milli mole for five hours, in the absence of a co catalyst selected from Pt or NiO.

Table 7: Water splitting activity of $InFeO_3(ZnO)_4$

Catalyst	Irradiation	Irradiation Time (h)	H_2 evolved (μmol/g/h)
$InFeO_3(ZnO)_4$_without Pt	Visible	1	1406.202
		2	1368.77164
		3	1330.18205
		4	1679.50397
		5	1754.50057

Example 5

Photocatalytic water splitting activity of $InGaO_3ZnO$

Photocatalytic water splitting activities for the instant IGZ ($InGaO_3ZnO$) compounds were evaluated with or without a co-catalyst. The results of hydrogen evolved with IGZ catalyst in the absence of a co-catalyst are tabulated in **Table 8** and represented graphically in **Fig. 13**. The experiments were performed for 2 hours under UV light irradiation.

Table 8: H_2 evolution with IGZ catalysts without co-catalyst under UV light

Catalysts	H_2 evolved (milli mol/g)
IGZ1	3.31258
IGZ2	3.36874
IGZ3	4.48085
IGZ4	4.72560

The H_2 evolution experiments using $InGaO_3ZnO$ catalysts were performed in presence of visible light irradiation. However, H_2 evolution was negligible.

Therefore, co-catalysts such as CuO, NiO in combination with IGZ catalysts were used in order to enhance the water splitting activity in the visible region. 1 wt% and 2 wt% NiO loaded IGZ catalysts were used for water splitting under both UV and visible light irradiations for 4 hours.

Even though these catalysts were shown to be active for water splitting under UV light, it did not indicate any visible light activity. The amount of hydrogen evolved under

UV light when using 1wt % and 2wt% NiO co-catalyst is tabulated in the **Table 9** and also represents graphically in **Fig. 14**.

Table 9: H_2 evolution with 1wt%, 2 wt% NiO loaded IGZ catalyst

Catalysts	**H_2 evolved in 4h, UV light irradiation**	
	1% NiO	**2% NiO**
IGZ1	5.49722	13.57300
IGZ2	6.80806	14.35979
IGZ3	6.14817	11.48355
IGZ4	8.35684	12.55806

From **Fig 14**, it is observed that NiO co-catalyst functions efficiently for $InGaO_3(ZnO)_m$ (m= 1 -4) series under UV irradiation. 2wt% NiO loaded IGZ exhibits enhanced activity compared to 1 wt% NiO loaded. This proves the role of co-catalyst in water splitting.

2wt% NiO loaded IGZ samples were used for detailed study by varying time of light irradiation. The results obtained from these experiments are graphically represented in **Fig. 15**. From the figure it is observed that as time of irradiation increases, the water splitting activity also increases. The NiO loaded IGZ based photocatalysts work under UV light irradiation.

As known from earlier experiments, IGZ water splitting catalysts were found to be less active under visible light.

In view of the weak activity of IGZ catalyst under visible light, it is necessary to provide a photocatalyst which functions under visible light. Sunlight consists 50% visible light and only 4 % UV light. In order to utilize solar energy efficiently, a photocatalyst which is visible light active for water splitting is more favorable.

It is reported that CuO loaded photocatalysts work efficiently under visible light irradiation. Water splitting experiments with 1 wt%, 2 wt% CuO loaded IGZ catalysts were conducted under visible light irradiation and the results obtained from these experiments are tabulated in **Table 10** and graphically represented in **Fig 16**.

Table 10: H_2 evolution with1 wt%, 2wt% CuO loaded IGZ catalysts at 4 hours under visible light.

Catalysts	**H_2 evolved (milli mol/g)**	
	1 wt% CuO	2 wt% CuO
IGZ1	2.99879	5.18061
IGZ2	3.62655	4.54663
IGZ3	2.18242	3.23298
IGZ4	3.392526	3.35715

From the **Figure 16** it is observed that the 2 wt% CuO loaded IGZ catalysts shows more water splitting activity than the corresponding 1 wt% CuO loaded IGZ catalysts. This proves that the addition of CuO as co-catalyst improves the activity. More experiments were conducted with 2 wt% CuO loaded IGZ catalysts by varying time of visible light irradiation and the results are graphically represented in **Fig. 17**.

It is observed that as time of irradiation increases, H_2 production also increases. Experiments were also done by varying the CuO loading in IGZ1 catalyst viz. 1 wt%, 4 wt% and 10 wt% CuO and the results obtained are tabulated in Table 11 and graphically represented in **Figure18**.

Table 11: H_2 evolution with IGZ1 catalyst with different CuO loading.

IGZ1	**Amount of H_2 evolved (Milli mol/g) under visible light for 2 h**
1 wt% CuO	1.49939
2 wt% CuO	2.58468
4 wt% CuO	1.645000
10 wt% CuO	0.69134

Results shown in **Table 11**, indicate that IGZ1 loaded with 2 wt% CuO exhibits enhanced water splitting activity in visible light irradiation. Increase in loading concentration of CuO results in a decrease in the water splitting activity therefore increase in concentration of metal oxide adversely affects the water splitting activity.

Moreover, loading with 2 wt% CuO loaded IGZ catalysts indicates better hydrogen evolution activity.

ADVANTAGES OF THE INVENTION

- Economical process since metal or metal oxide co-catalyst is optional.
- Photo catalyst is UV and visible active, with more activity in visible, especially in absence of co catalyst.

We claim:

1. A photocatalytic water splitting process for H_2 generation catalyzed by InA(ZnO)*m* in the visible and UV light range, wherein A is selected from an oxide of Fe or Ga and m = 1-5, comprising:

   a) dispersing InA(ZnO)*m* powder in a reactant solution comprising water and methanol in ratio of 4:1 in a gas closed irradiation system;

   b) irradiating the reactant mixture as obtained in step (a) to obtain hydrogen.

2. The photocatalytic water splitting process according to claim 1, wherein the catalyst are selected from the group consisting of InFeO3(ZnO)m and InGaO3(ZnO)m, wherein m=1 – 5.

3. The photocatalytic water splitting process according to claim 1, wherein the irradiation process is carried out in UV or visible light region.

4. The photocatalytic water splitting process according to claim 1, wherein the said process is carried for a period of 1-12 hours.

5. The photocatalytic water splitting process according to claim 1, wherein optionally the process is carried out in the presence of a metal co-catalyst selected from the group consisting of NiO, CuO and Pt.

6. The photocatalytic water splitting process according to claim 5, wherein NiO is loaded onto InGaO3(ZnO)m, where m = 1- 5.

7. The photocatalytic water splitting process according to claim 5, wherein CuO is loaded onto InGaO3(ZnO)m, where m = 1- 5.

8. The photocatalytic water splitting process according to claim 5, wherein Pt is loaded onto InFeO3(ZnO)m, where m = 1- 5.

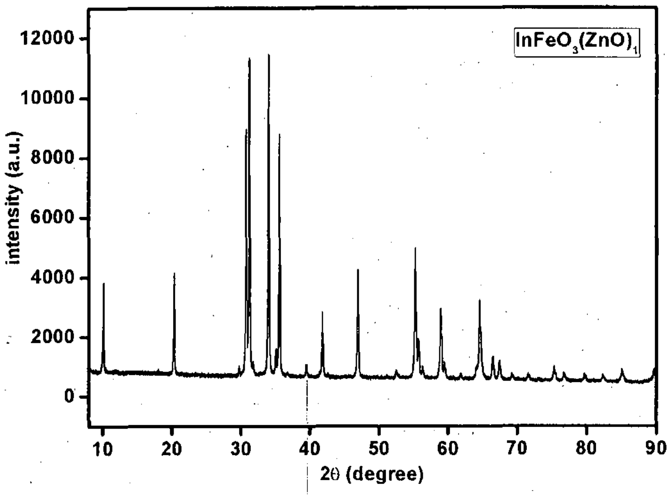
9. The photocatalytic water splitting process according to claim 2, wherein the hydrogen evolution rate is in the range of 7 to 11 milli mol/g/h and 0.8 to 3.58 milli mol/g/h in the presence of catalyst InFeO3(ZnO)m and InGaO3(ZnO)m respectively.

10. A photocatalyst composition InA(ZnO)m, wherein A is selected from an oxide of Fe or Ga and m = 1-5 for use as catalyst in water splitting reactions for H_2 generation.

CSIR, INDIA

No. of Sheets: 12

Sheet No.1



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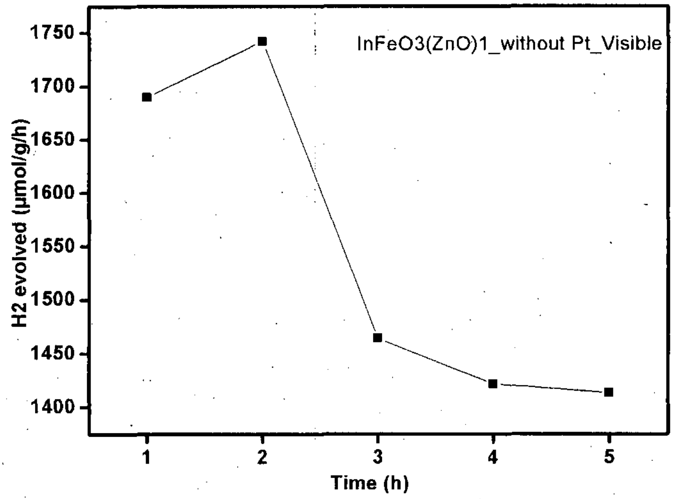

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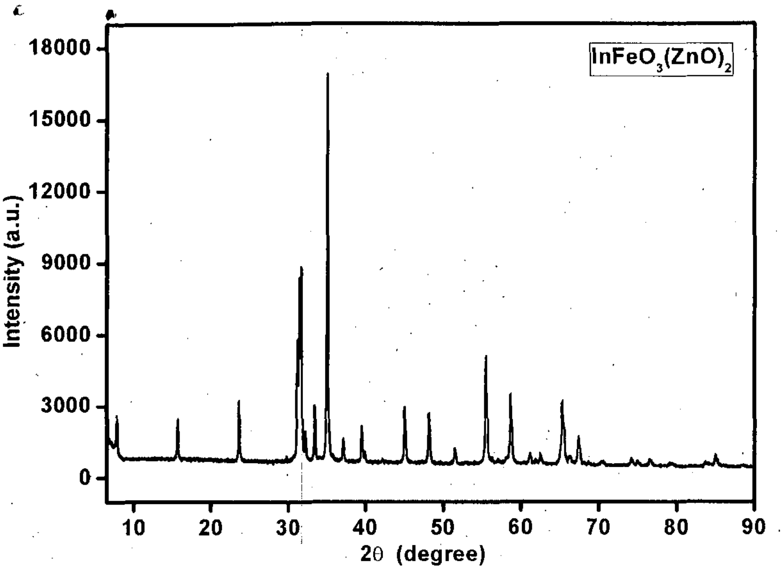

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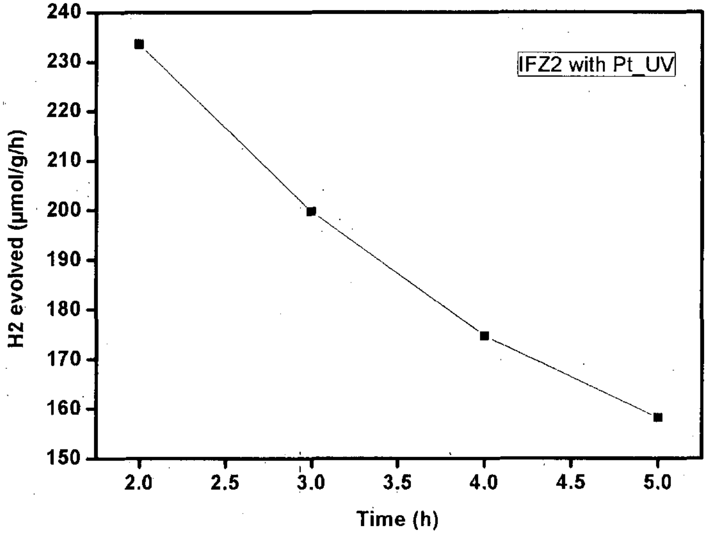

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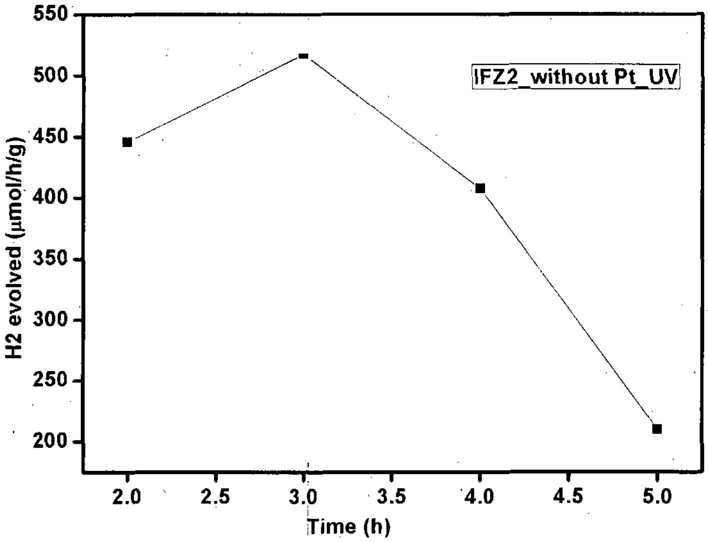
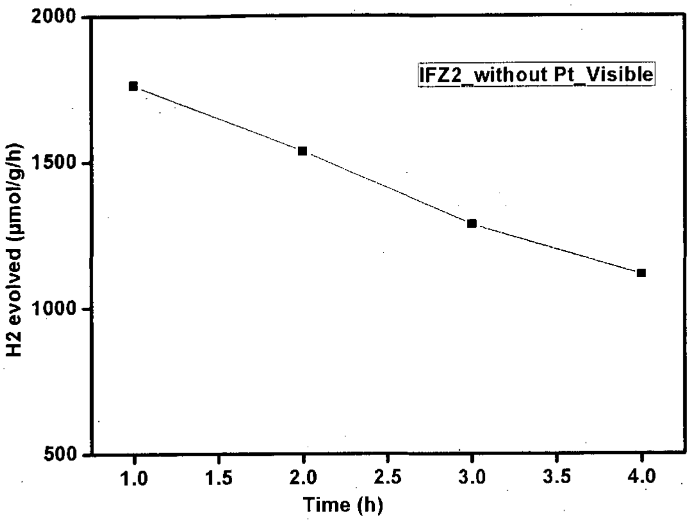


Figure 5



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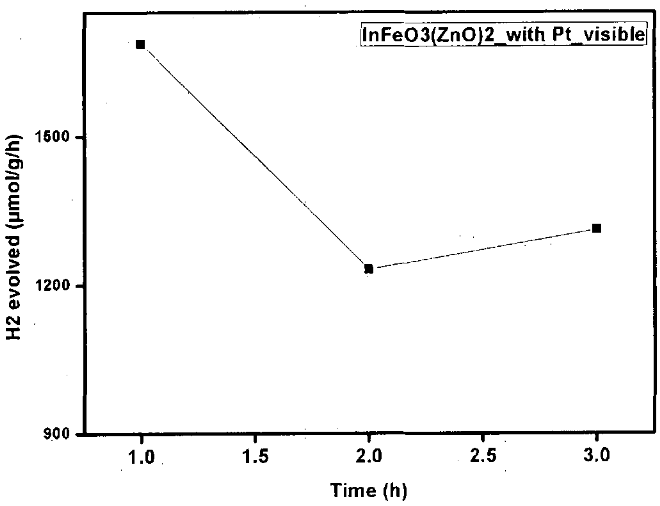

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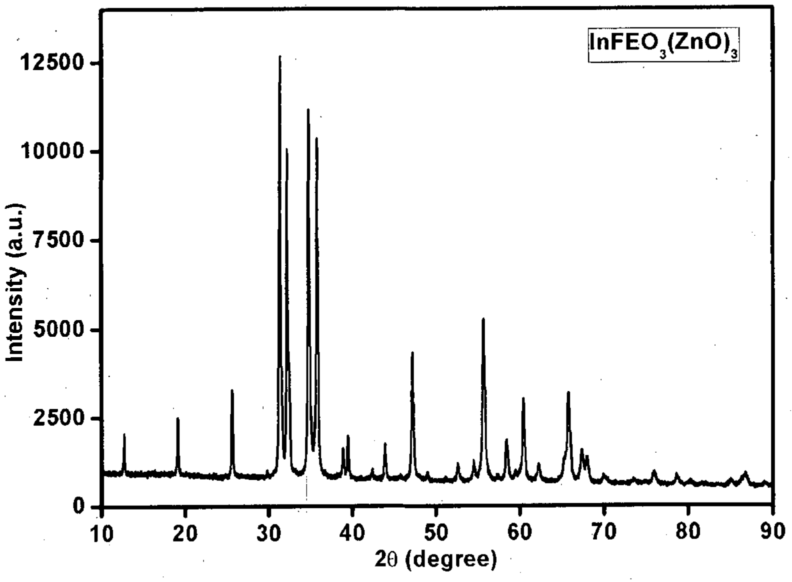

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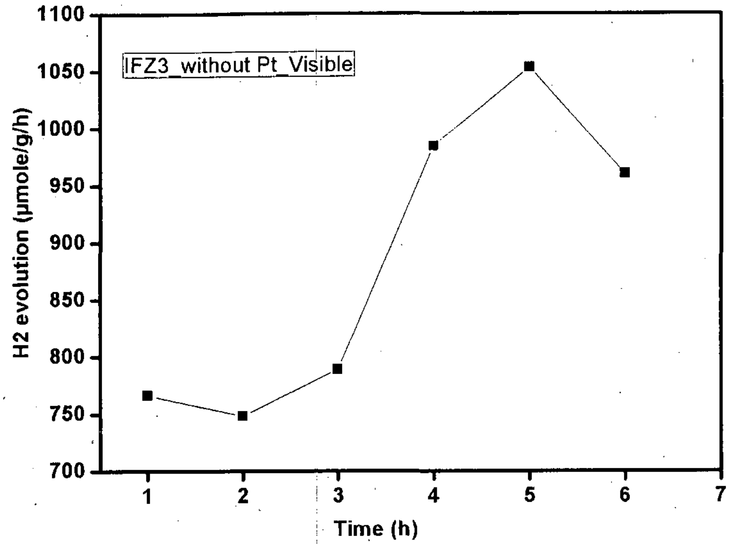


Figure 9

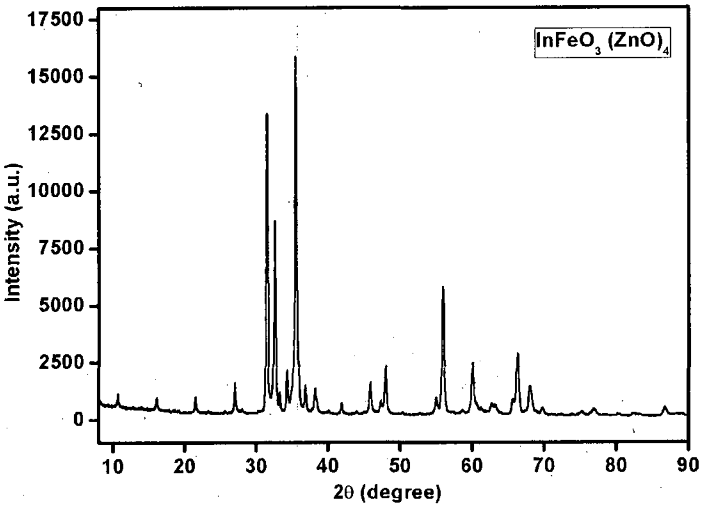


Figure 10

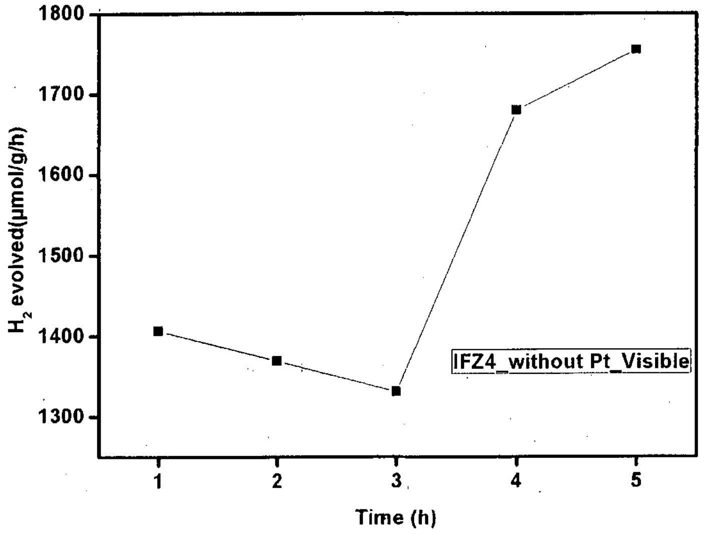
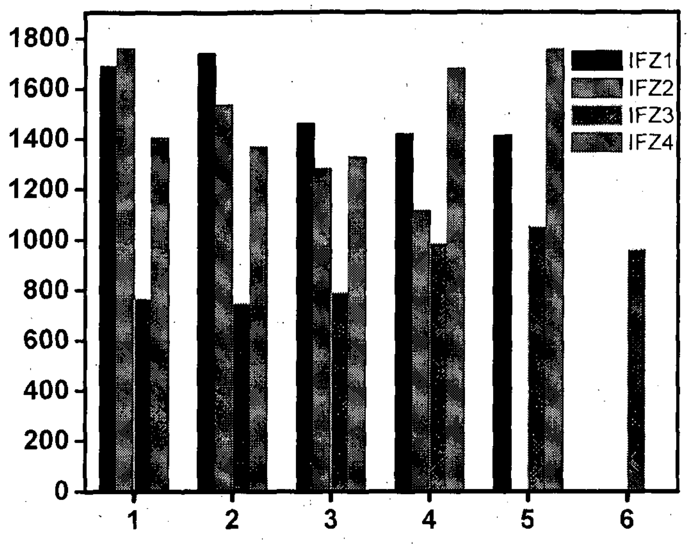


Figure 11



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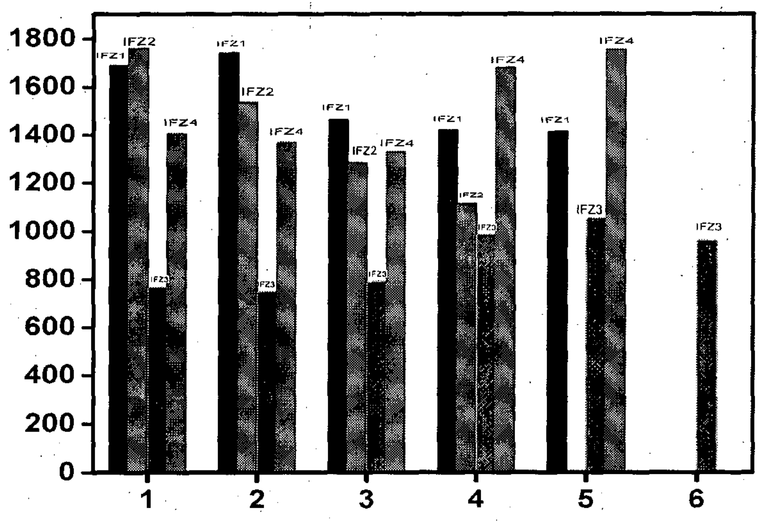


Figure 13

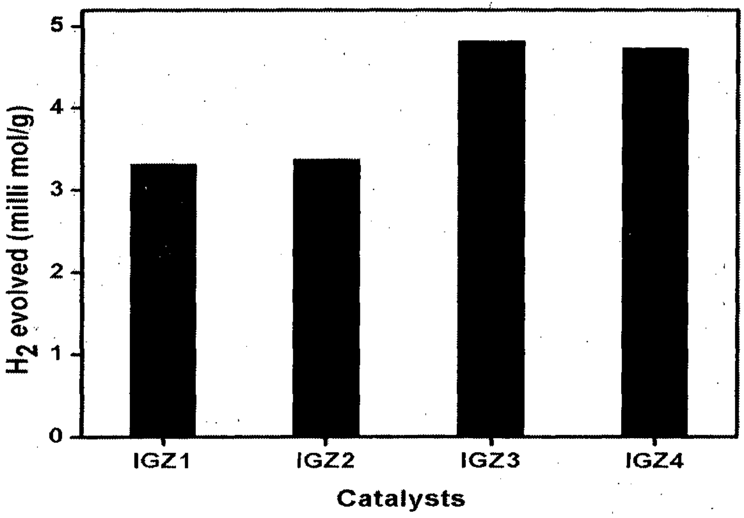


Figure 14

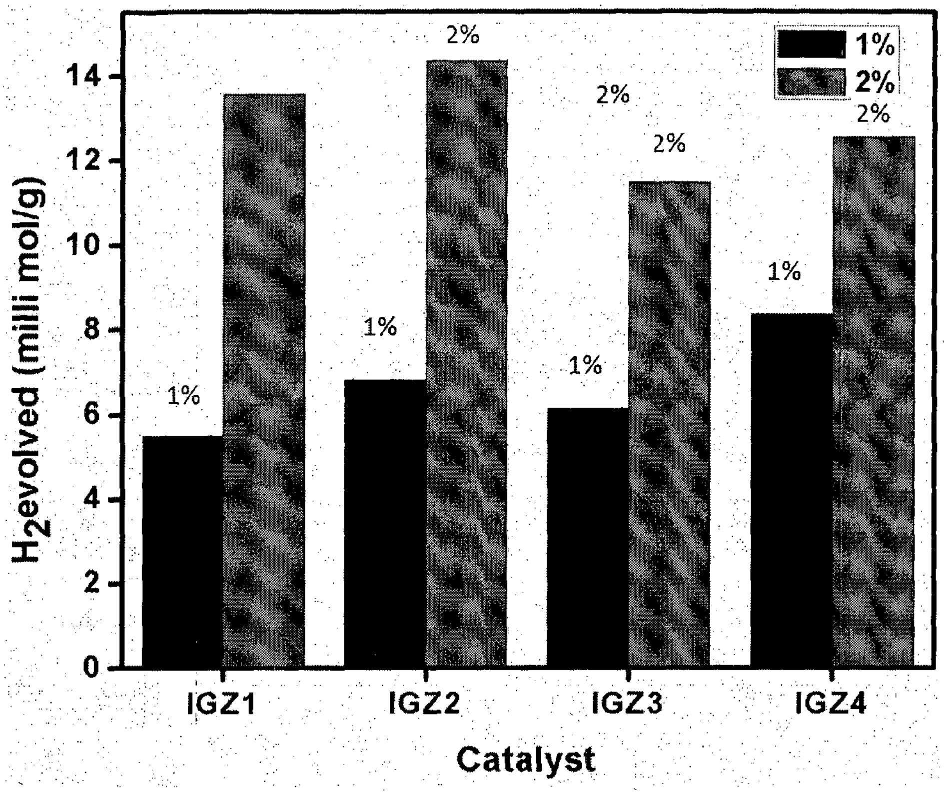


Figure 15

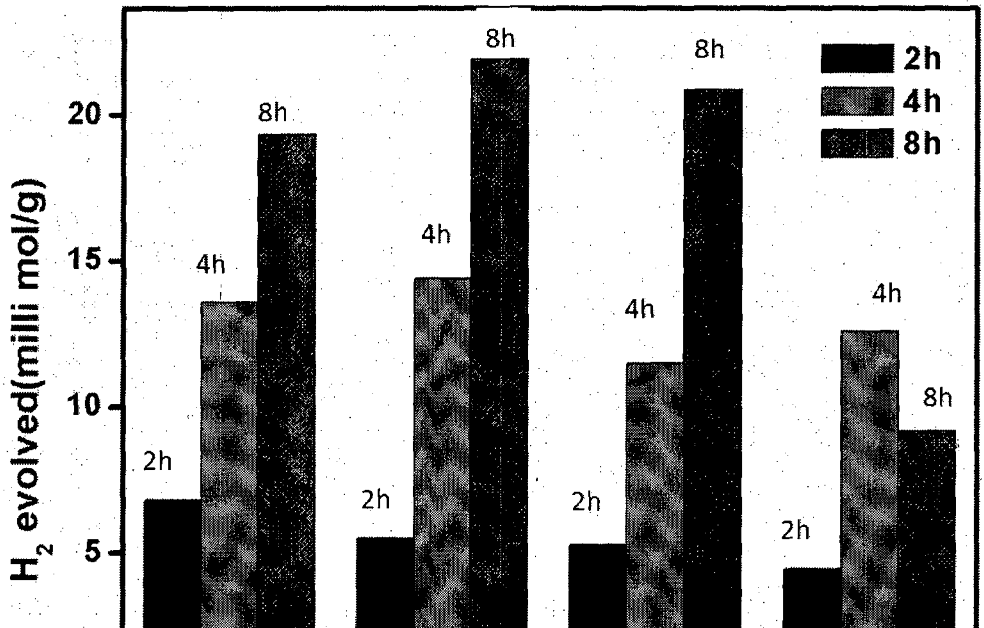


Figure 16

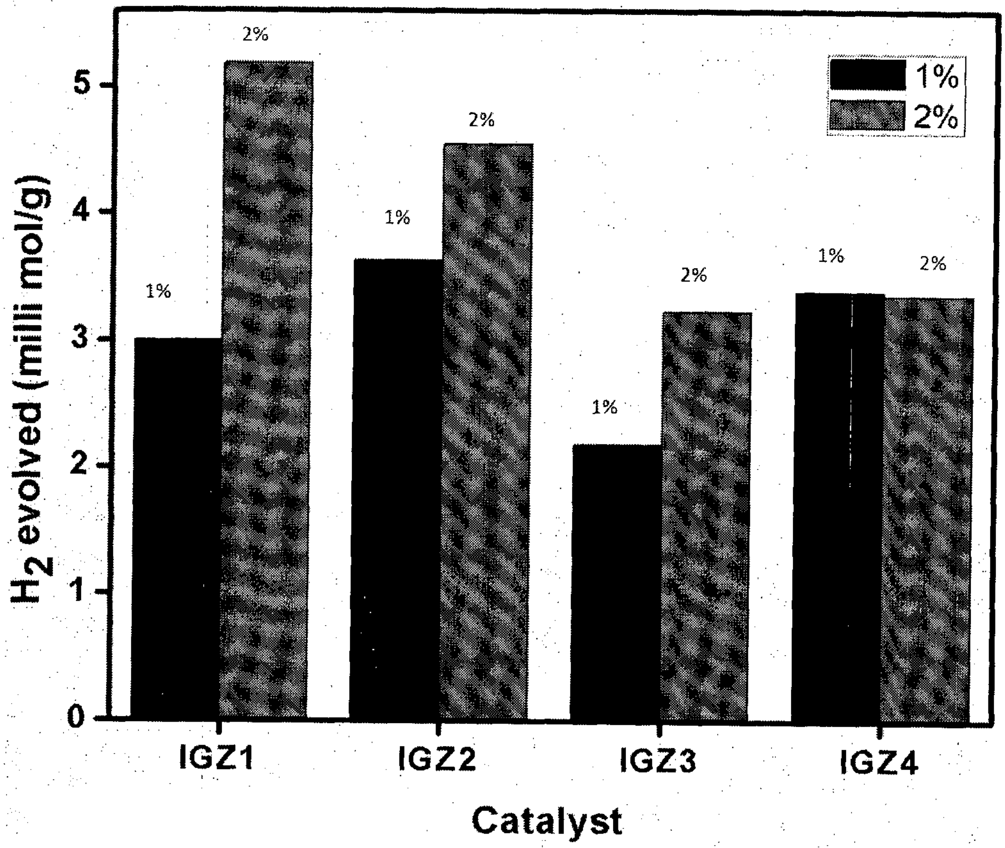


Figure 17

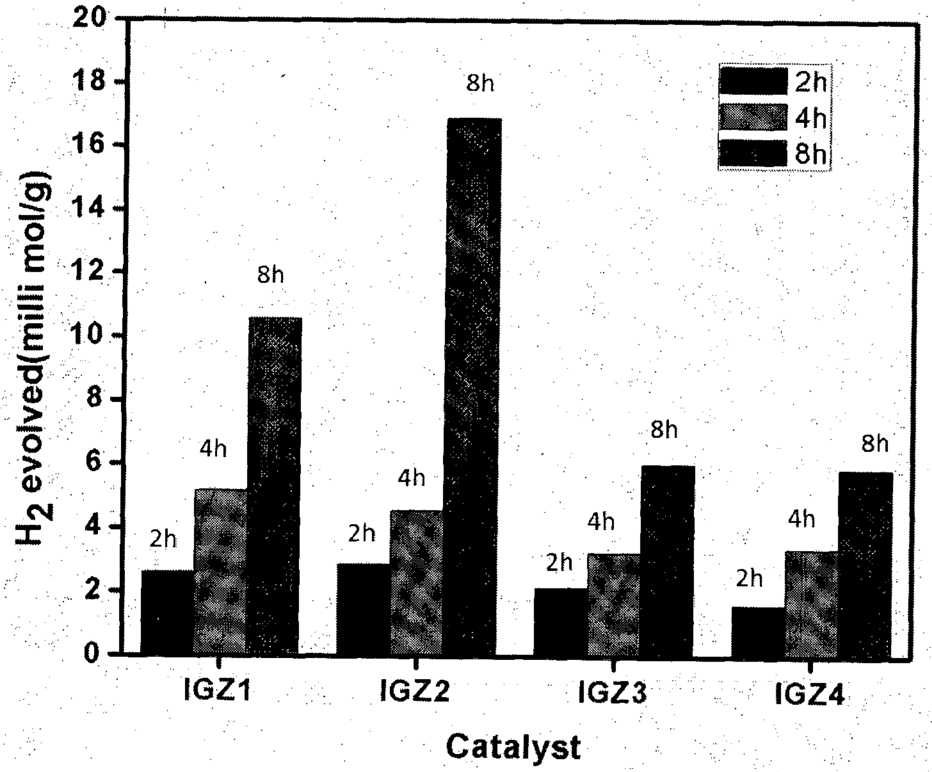
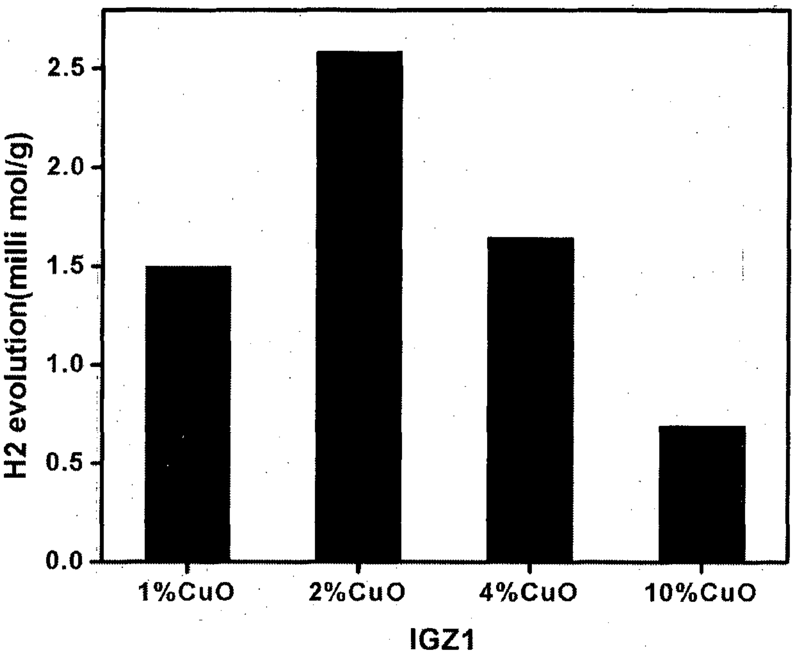


Figure 18


H2 evolution(milli mol/g)
0.0
0.5
1.0
1.5
2.0
2.5
1%CuO
2%CuO
4%CuO
10%CuO
IGZ1

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2014/000560

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/825 B01J23/08 B01J35/00 B01J37/00 B01J37/02
B01J37/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search 12 January 2015	Date of mailing of the international search report 30/01/2015
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Fischbach, Malaika

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	ISABELLE KELLER ET AL: "Synthesis and Crystal Structures of InGaO 3 (ZnO) m (m = 2 and 3)", ZEITSCHRIFT F&#XFFFD;R ANORGANISCHE UND ALLGEMEINE CHEMIE, vol. 635, no. 12, 1 October 2009 (2009-10-01), pages 2065-2071, XP055161185, ISSN: 0044-2313, DOI: 10.1002/zaac.200900199 abstract -----	10
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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