Cite this: Green Chem., 2012, 14, 2790

www.rsc.org/greenchem

PAPER

An eco-friendly, highly stable and efficient nanostructured p-type N-doped ZnO photocatalyst for environmentally benign solar hydrogen production[†]

Ashwini P. Bhirud,^a Shivaram D. Sathaye,^b Rupali P. Waichal,^c Latesh K. Nikam^a and Bharat B. Kale^{*a}

Received 7th April 2012, Accepted 10th July 2012 DOI: 10.1039/c2gc35519a

We have investigated an economical green route for the synthesis of a p-type N-doped ZnO photocatalyst by a wet chemical method. Significantly, hazardous H₂S waste was converted into eco-friendly hydrogen energy using the p-type N-doped ZnO photocatalyst under solar light, which has previously been unattempted. The as-synthesized p-type N-doped ZnO shows a hexagonal wurtzite structure. The optical study shows a drastic shift in the band gap of the doped ZnO in the visible region (3.19–2.3 eV). The doping of nitrogen into the ZnO lattice is conclusively proved from X-ray photoelectron spectroscopy analysis and Raman scattering. The morphological features of the N-doped ZnO are studied from FESEM, TEM and reveal particle sizes to be in the range of ~4–5 nm. The N-doped ZnO exhibits enhanced photocatalytic hydrogen generation (~3957 μ mol h⁻¹) by photodecomposition of hydrogen sulfide under visible light irradiation, which is much higher as compared to semiconductor metal oxides reported so far. It is noteworthy that a green catalyst is investigated to curtail H₂S pollution along with production of hydrogen (green fuel) using solar light, *i.e.*, a renewable energy source. The green process investigated will have the potential to synthesize other N-doped metal oxides.

1. Introduction

Major natural energy sources, namely oil, are depleting fast. Therefore, researchers across the world are focusing their efforts on renewable alternative sources of energy. Simultaneously, environmental problems are becoming more and more serious with the development of industry and economy. Therefore, the emphasis of using conventional physics and chemistry has shifted to the use of unconventional green routes in the processes of tapping various energy sources. Direct splitting of H₂O, H₂S or an organic waste using a particulate photocatalyst remains a promising route to producing H₂ that is environmentally clean and a recyclable form of energy. Water is an ideal hydrogen source and therefore, photocatalysts that could produce hydrogen from water splitting under sunlight have been actively sought.¹⁻³ Apart from water, H₂S could become an alternative source of hydrogen as H₂S splitting requires less energy compared with the photocatalytic decomposition of water. H₂S is cheaply available in large quantities as a byproduct in coal and petroleum industries, natural gas, oil wells and geothermal plants.^{4,5} In most cases, the toxic H₂S has to be converted into an environmentally friendly end product. Thus, simultaneous hydrogen

^b759/83 Deccan Gymkhana, Pune 411004, India

production and H₂S decomposition is a highly desirable process. H₂S can be effectively decomposed by photocatalytic processes, preferably under visible light irradiation to produce hydrogen, the clean fuel. This will not only effectively harness the abundant solar energy, but also clean up the environment. The Claus process is currently used for the decomposition of H₂S.⁶ The conventional Claus process comprises the reaction between H2S and SO₂, yielding elemental sulphur and water vapour. Thus, the Claus process is not a solution to generate H₂ from H₂S. Also, the direct thermal decomposition of H₂S for the production of hydrogen and elemental sulphur is energy intensive and economically more unviable. As a result, there has currently been an immense emphasis on the development of photocatalysts, which are active in the visible range for the production of hydrogen. Unfortunately, the photocatalysts investigated under the visible region are still limited in number.⁷ Recently, a CdS-TiO₂ nanocomposite film, ⁸ CdIn₂S₄ bipyramids/flowers/nanotubes, ^{9,10} a CdS photocatalyst, ¹¹ a β -In₂S₃ dandelion flower, ¹² Cu-doped ZnO nanoparticles,¹³ and metal oxides,^{14,15} have been used for the photodecomposition of H₂S. It is also noticed that the photodecomposition of H₂S by sulfide semiconductor photocatalysts, especially CdS, is not workable due to photocorrosion of the catalyst during the process. Therefore, there is a need to develop a stable semiconductor photocatalyst for hydrogen production, which would be efficient, economical and sustain against photocorrosion. 'Metal oxides' is the most obvious and popular choice for consideration, which fulfil the desired properties mentioned above. Most of the studies have been focused on large band gaps and stable semiconductor oxides, such as TiO₂ and ZnO, wherein electron-hole pairs are generated under photoexcitation

^aCentre for Materials for Electronic Technology, Panchawati, Off Pashan Road, Pune 411008, India. E-mail: kbbb1@yahoo.com, bbkale@cmet.gov.in; Fax: +91-20-25898085; Tel: +91-20-25898390

^cNational Chemical Laboratory (NCL), Dr. Homi Bhabha Road, Pune-411008, India

[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/c2gc35519a

by UV light only. In many respects, ZnO is more suited in dye sensitised solar cell devices than TiO_2 due to its excellent electron mobility and its processability into many shapes and forms as well as adjusting its band-gap to suit its applications in the solar spectrum region.

A step forward to extend the spectral response of ZnO to the visible spectral region is due to impurity doping. An initial approach to shift the optical response of ZnO from the UV (3.2 eV) to the visible spectral range has been the doping of transition metal elements into ZnO.¹⁶ However, metal-doping has several drawbacks. The doped materials have been shown to suffer from thermal instability and metal centres formed as a consequence of doping metals, act as electron traps, which is reducing the photocatalytic efficiency. Recently, it was shown that the desired photo-response of ZnO can be better achieved by using anionic dopants rather than metal ions. Suitable group V elements, such as N, P and As, are used as anionic dopants in ZnO.^{17,18} The doping of ZnO has limitations and hence n-type doping is easily obtained, while it is difficult achieve p-type materials.^{19,20} Nitrogen has been considered as the best candidate for synthesizing p-type ZnO because it has a similar ionic radius as oxygen and also the smallest ionization energy among the group V elements.^{21,22} N-doping into ZnO has been tried by employing various nitrogen precursors such as NH₃, N₂O, NO, N₂, Zn₃N₂ and MMHy.²

Herein, we report the green synthesis of p-type N-doped ZnO using a simple wet chemical method. Significantly, nanostructured p-type N-doped ZnO has been used for the decomposition of H_2S using sunlight for the production of hydrogen which has previously been unattempted. We have synthesized the photocatalyst by a simple chemical method. Characterization of the assynthesized N-doped ZnO photocatalyst was done by XRD and FESEM, revealing its crystal structure and surface morphology. The incorporation of the 'N' impurity into ZnO was confirmed by Raman spectra and X-ray photoelectron spectroscopy (XPS).

2. Results and discussion

In the present investigation, the zinc–urea intermediate complex was obtained from molten urea and ZnCl₂. To understand the mechanism of formation of ZnO by this route, the intermediate, most likely a Zn–urea complex, was characterized using TG-DTA for its thermal decomposition behaviour.

Fig. 1 shows the TG-DTA curves obtained for the Zn-urea intermediate complex with a dynamic heating program. Its thermal decomposition occurs in four stages as indicated by the weight loss in TG (Table 1). The DTA curve shows corresponding heat changes during the course of the reaction.

The TG curve shows that the 3% weight loss is observed at the first stage of the decomposition of the product, at 160 °C, which is higher than expected, which is due to the loss of adsorbed water molecules. This stage is followed by the 13% weight loss in the 160–260 °C range, which can be attributed to the loss of two NH₃ and one NO₂ molecules. The broad endotherm in the DTA curve shown at these stages also confirm the removal of H₂O, NH₃ and NO₂. At this stage, the product would be a Zn–urea complex consisting of Zn–urea decomposition products, wherein Zn and nitrogen from the urea products



Fig. 1 TG-DTA curve of the Zn-urea intermediate.

Table 1 Weight loss stages of the intermediate (Zn-urea complex)

Weight loss stages (°C)	Loss of molecules	% Weight loss ^a	
0–160	Adsorbed H ₂ O	3 (1)	
160-260	$2NH_3 + 2NO_2$	13 (14)	
260-350	$2HCl + 2NO_2$	29 (30)	
350-520	$4\text{CO}_2 + \text{NO}_2$	34 (32)	

^a Figures in parenthesis are predicted values.

would be in close proximity. A further weight loss of 29% is observed in the range 260–350 °C. This may be attributed to the loss of two HCl and two NO₂ molecules. The corresponding endothermic DTA curve obtained also confirms the removal of HCl and NO₂. Similarly, the weight loss observed in the range 350-520 °C is around 34%, which is due to the loss of four CO₂ and one NO₂ molecules. The loss of CO₂ and NO₂ is due to complete combustion of the Zn–urea complex and excess biuret. Accordingly, the exothermic peak is observed at corresponding temperatures. The total weight loss was observed around 79%, which is matching with the extent of ZnO formed from the complex and excess biuret. The weight losses observed at respective stages is in fairly good agreement with those predicted. Considering the stepwise weight loss, the following reaction has been proposed.



No further loss is observed in thermal studies, indicating the formation of a stable phase of ZnO, as subsequently revealed in XRD studies.

Fig. 2 shows the XRD patterns of the as-synthesized products (S1–S5), prepared under different conditions. It is clear from



Fig. 2 XRD spectrum of samples (a) undoped ZnO (S1) treated at 800 °C for 3 h and N-doped ZnO treated at different reaction temperatures for 3 h at (b) 500 °C (S2), (c) 600 °C (S3), (d) 700 °C (S4) and (e) 800 °C (S5).

Table 2 Type of conduction of ZnO samples

Sample	S 1	S2	S3	S4	S5
Type of conduction	n	р	р	р	n

Fig. 2 that the products (S1–S5) show identical XRD pattens. All the peaks are assigned to the standard hexagonal wurtzite ZnO crystal structure (JCPDS 36-1451) and no additional peaks are observed, which infers the formation of phase pure ZnO. Also, this suggests the possibility of induction of nitrogen into the ZnO lattice which has not affected the ZnO crystal structure. The absence of phases such as ZnN, Zn (OH)₂, *etc.*, are note-worthy.²⁴

The type of conductivity of all the end products (S1–S5) is determined by using a well known 'hot probe' method.^{25,26} The type of electrical conduction properties of samples S1, S2, S3, S4 and S5 are indicated in Table 2.

The sample S1 shows n-type conduction and the other samples, S2, S3 and S4, were changed from n-type conduction to p-type conduction by annealing at 500, 600 and 700 °C, respectively. Surprisingly, this p-type conductivity is transformed to n-type for sample S5 formed by annealing at 800 °C.

Thus, the result of finding the type of conductivity by the hot probe method shows that ZnO gets converted to 'p-type material' when heated in the temperature range 500–700 °C for 3 h in a partly nitrogenous atmosphere derived by urea products under the present experimental conditions. This is obviously due to the replacement of oxygen by nitrogen in the ZnO lattice.^{18,27} The absence of a 'p-type' nature in sample S5 can be explained as follows.



Fig. 3 UV-DRS spectra of samples (a) undoped ZnO (S1) treated at 800 °C for 3 h and N-doped ZnO treated at different reaction temperatures for 3 h at (b) 500 °C (S2), (c) 600 °C (S3), (d) 700 °C (S4) (e) 800 °C (S5).

 $Zn-N \rightarrow Zn-O$ transformation would be facilitated with the increase in temperature of reaction. Also, it is known that undoped ZnO is always 'n-type'. At the temperature of 800 °C, even though the Zn-N \rightarrow Zn-O transformation takes place, it may not go to completion within the limited period of heating (3 h). S5 may have some nitrogen left in the lattice but its effect is overtaken by the 'defects' of undoped ZnO formed at high temperature, which is an 'n-type' material.

We observed that there is a one to one correspondence in these observations, namely, when there is a dominant presence of nitrogen in the lattice of ZnO, the sample assumes P-type conduction as shown by the 'hot probe' method. This p-type to n-type conversion is further supported by the results on the studies of Raman spectroscopy and XPS results.

The ultraviolet-visible diffuse reflectance spectra (UV-DRS) of ZnO (S1) and N-doped ZnO (S2–S5) are shown in Fig. 3. The nature of absorption band with a sharp 'cut off' at 388 nm (band gap = 3.19) of sample S1, is assigned to the phase pure ZnO formation. The band gap of samples S2–S5 were observed to be 2.3, 2.4, 2.5 and 2.5 eV, respectively. The samples S2–S5 show drastic red shifts in band gaps, which is due to N-doping. The N-doped ZnO lattice shall have defects formed in the lattice. The location of such defects in the band diagram would be above the valance band. The amount of doped nitrogen shall determine the width of the defect band. Such a band picture can explain all the optical absorption observations of the present study.

Thus, sample S2 shows more absorption in the visible region than the other samples, indicating maximum doping of nitrogen. It is well known that the Zn–O bond is more stable than Zn–N. Therefore, transformation of Zn–N \rightarrow Zn–O is thermodynamically favoured. As the temperature of the reaction is increased, this transformation results in lowering of the amount of nitrogen in the ZnO lattice and consequently lowering of absorption in visible region.

The PL study (ESI[†] (SI-1)) shows emission peaks at 380, 393 and 389 nm for the sample S1, S2 and S5, respectively. There is



Fig. 4 Raman spectrum of samples (a) undoped ZnO (S1) treated at 800 °C for 3 h and N-doped ZnO treated at different reaction temperature for 3 h at (b) 500 °C (S2), (c) 600 °C (S3), (d) 700 °C (S4), (e) 800 °C (S5).

a red shift observed due to the replacement of oxygen by nitrogen in ZnO. Apparently, the red shift has been influenced by the N-doping as well as the creation of defects during the thermal process.²⁸

Raman scattering was performed for the undoped and N-doped ZnO, as illustrated in Fig. 4. In all the spectra, a common Raman line is located at 437 cm^{-1} (Fig. 4a–c), which corresponds to the E₂ (high) vibrational mode which implies the existence of the wurtzite structure for both undoped and the N-doped ZnO. The peak located at 333 cm⁻¹ corresponds to the second order (E₂ (high) – E₂ (low)).²⁹ The other modes at A₁ (275–277 cm⁻¹), A₃ (509 cm⁻¹) and A₁ (LO) (580 cm⁻¹) can be assigned to local vibration modes (LVMs) of nitrogen in ZnO.³⁰ Raman modes at 275 cm⁻¹ was attributed to the localized vibration of Zn atoms, where parts of their first nearest neighbour O atoms are replaced by N atoms in the ZnO lattice.³¹ Also, the Raman peaks observed at 509 and 580 cm⁻¹ is related to the presence of nitrogen.^{32,33} It may be noted that the nitrogen related peaks, namely $(275-277 \text{ cm}^{-1})$, (509 cm^{-1}) and (LO)(580 cm⁻¹) are absent in samples S1 and S5. The Raman spectroscopic observations, thus, confirms N-doping in the lattice and concomitantly shows that sample S1 and S5 do not have an effective presence of nitrogen.

The presence of nitrogen and its concentration in N-doped ZnO was analyzed by XPS. During the thermal treatment, the complex decomposes into ZnO but traces of 'Cl' get adsorbed on the surface during cooling of the sample. The traces of 'Cl' were removed by washing with copious amounts of hot water and its complete removal is confirmed by XPS (Fig. 5a). The full XPS spectrum of the N-doped ZnO (Fig. 5a) showed only



Fig. 5 XPS patterns of N-doped ZnO synthesized at 500 °C for 3 h (S2) (a) Survey spectrum and high-resolution spectra for (b) Zn2p, (c) O1s, (d) N1s.

peaks that were assignable to Zn, O, C and N. High resolution XPS spectra of the Zn2p and O1s lines are shown in Fig. 5b and c. The core lines of $Zn2p_{3/2}$ and $2p_{1/2}$ are located at 1021.8 eV and 1044.7 eV, respectively. In Fig. 5 the high resolution scanning XPS spectra of O1s after deconvolution shows that oxygen exists at least in three forms with the following binding energies: 530.5, 532.0, 533.5 eV. The peak at 530.5 eV is mainly assigned to the oxygen atoms coordinated with Zn atoms.³⁴ The peak at 532 eV corresponds to oxygen adsorbed on sample surface probably as (-OH).³⁵ The peak at 533.5 eV is likely to be due to water molecules on the surface.³⁶ Fig. 5d show that N1S peaks appeared at 395.7, 397.9, 400 eV which indicate nitrogen incorporation. Three peaks are assigned to N-Zn, N-C and N-H bonds respectively.37,38 Oxygen to nitrogen atomic ratio of 1:0.38 is estimated by XPS. The XPS results are consistent with the Raman results, which demonstrate successful N-doping into the ZnO. The XPS of sample S3, S4 and S5 are given in ESI⁺ (SI-2).

Oxygen to nitrogen atomic ratios for the samples S3 and S4 are 1:0.32 and 1:0.41, and for the S5 sample there is no nitrogen. It is interesting to note that more nitrogen is shown to be present in sample S4 than in sample S3. This is understandable as the reaction temperature of S4 is higher than that of S3 and therefore more nitrogen is present on the surface of the sample due to the nitrogen out-diffusion process. Such removal of nitrogen from N-doped ZnO is reported in the literature.³⁹ XPS is a surface sensitive technique which efficiently detects these subtle variations of concentration.

The morphology and particle size of the nanostructured compounds were investigated by FESEM and TEM. Fig. 6 shows the FESEM images of samples S1–S5, indicating the morphologies of undoped and all N-doped ZnO samples. The FESEM of sample S1 (Fig. 6a, b) shows the agglomerated hexagons of sizes ~3–6 μ m. The FESEM of the N-doped ZnO sample S2 (Fig. 6c, d) shows a spongy structure, whereas samples S3 (Fig. 6e, f) and S4 (Fig. 6g, h) show agglomerated nanoparticles with sizes of ~50–60 nm and ~50–100 nm, respectively. However, sample S5 (Fig. 6i, j) reveals distorted hexagons of sizes ~4–5 μ m.



Fig. 6 FESEM of samples (a, b) undoped ZnO (S1) treated at 800 °C and N-doped ZnO treated at different reaction temperature for 3 h at (c, d) 500 °C (S2), (e, f) 600 °C (S3), (g, h) 700 °C (S4), (i, j) 800 °C (S5).

Since the morphology of sample S2 was not clear in FESEM (spongy structure), we have characterized the sample with TEM (Fig. 7a–d). In the TEM images (Fig. 7a, b) we observed \sim 50–100 nm sized nanocubes as the primary growth. Interestingly, growth of secondary nanoparticles of size \sim 4–5 nm over the nanocubes was observed. The secondary growth is perhaps seen as a spongy structure in the FESEM. Such a spongy structure with highly crystalline nanoparticles (Fig. 7b) is likely to have a high surface area.

The electron diffraction (Fig. 7c) dots can be indexed as the (100), (101), (102) and (201) planes of the hexagonal wurtzite



Fig. 7 TEM of N-doped ZnO treated at 500 °C for 3 h (S2).



Scheme 1 Schematic representation of formation mechanism of undoped and N-doped ZnO.

phase of the N-doped ZnO, which is consistent with the XRD results. Fig. 7d shows a high-resolution TEM (HRTEM) image of the nanocubes. The lattice fringes show that the nanocubes are well crystalline and the observed d-spacing corresponds to the (101) plane of N-doped ZnO.

After careful evaluation of the above results, the over-all mechanism of N-doped ZnO formation by the 'urea route' can be visualized as below.

The formation mechanism of undoped and N-doped ZnO is represented in Scheme 1. When ZnCl₂ and urea are mixed in alcoholic medium and heated at 150 °C, a ZnCl₂ based Zn–urea complex is formed (Scheme 1). However, the product remains

hygroscopic when exposed to the atmosphere. We have performed the reaction using excess urea so as to have a larger number of nitrogen species available for doping. Hence, along with the complex some unreacted biuret is also formed.⁴⁰ Further, the complex along with biuret (as per eqn (1)) is annealed at 500, 600, 700 and 800 °C on the basis of the precise thermal study by TG-DTA. The thermal study shows a four-stage weight loss to obtain ZnO. Our main aim is to dope nitrogen through urea, of which we have achieved at 500 °C.

On the basis of the critical assignment of weight loss and corresponding exo/endothermal changes in DTA observed during thermal decomposition of the Zn–urea complex we have proposed the reaction, eqn (1). According to the TG-DTA, further thermal treatment from 160–260 °C shows gradual decomposition of the complex and biuret in the form of NO₂ and NH₃, as explained in the TG-DTA section. After 260 °C the gradual weight loss of the complex and biuret is continuous and there may be formation of $ZnO_{1-x}N_x$ at 500 °C along with HCl, NO₂ and CO₂.

Urea and its decomposed products, such as a biuret, are in intimate contact with the complex and hence the species containing nitrogen in these decomposed products can act as a nitrogen source for doping in ZnO, which is being formed at high temperatures in an air atmosphere.⁴¹ Ammonia that is evolved at the second stage (160-260 °C) is partially adsorbed by means of dissociative chemisorption on the surface of the intermediate (Zn-urea complex) formed at that stage. During chemisorption, the lone pair of electrons of the nitrogen atom is condensed on the surface, due to which an equal number of hydroxyl groups and amide ions are formed on the surface.²⁶ At high temperature (500 °C) N-doping takes place during the formation of ZnO. The formation of $ZnO_{1-x}N_x$ at 500 °C is already confirmed by Raman and XPS. The decomposition of $ZnO_{1-r}N_r$ starts after 500 °C and at 800 °C pure phase ZnO has been formed (Scheme 1), which is also confirmed by Raman and XPS. The schematic representation (Scheme 1) also shows the morphological transformation of N-doped ZnO at different temperatures.

The FESEM image of sample S1 shows well developed hexagons. It is not surprising because it does not contain intentionally added impurities in the matrix. The addition of impurities/ dopants hampers the growth of the basic structures of the crystals. Sample S2 shows the secondary growth of tiny nanoparticles of size $\sim 4-5$ nm on $\sim 50-100$ nm size nanocubes (Fig. 7) of the N-doped ZnO, as presented in Scheme 1. Sample S3 shows the disappearance of tiny nanoparticles (spongy structure demonstrated by FESEM Fig. 6c, d) and the formation of bigger nanoparticles as compared to sample S2. This is consistent with the earlier proposed mechanism, that as the temperature increases the ZnN \rightarrow ZnO transformation occurs leading to a decrease in N-doping. Consequently, the numbers of defects are also lowered and thus the bigger particles are formed due to high temperature. At high temperatures, the formation of bigger particles via aggregation of smaller particles due to sintering is quite obvious. The same trend continues for S4 and S5 samples. FESEM and Raman of sample S5 is similar to sample S1, and implies minimization of N-doping. The S5 sample is expected to have a negligible nitrogen content, as suggested earlier because of its out-diffusion process, and therefore is likely to have fewer defects, compared to the defects in samples S2-S4.

In the case of sample S5, it was expected to achieve the same morphology, *i.e.*, basic hexagons as obtained for sample S1. However, due to the small number of defects, their influence in the distorted hexagons obtained in sample S5 is well understood. The band gap of N-doped ZnO is red shifted drastically as compared to ZnO, which is due to N-doping, as N-doping produces external strain as well as lattice strain.^{42,43} This strain also affects the total morphology of the N–ZnO. Hence, different morphologies are obtained for the N-doped samples.

Photocatalytic activity

The photocatalytic activity of the undoped and N-doped ZnO samples for hydrogen generation *via* photodecomposition of H_2S was performed. The freshly prepared undoped and N-doped ZnO powders were employed for examining the photocatalytic hydrogen generation activities.

Table 3 shows the hydrogen evolution rate from the photodecomposition of H₂S using undoped and N-doped samples, *i.e.*, S1–S5, respectively. The photocatalytic activity of sample S1 (undoped ZnO) showed a moderate hydrogen evolution rate, *i.e.*, around 1874 µmol h⁻¹, while the N-doped ZnO samples S2, S3, S4 and S5 showed 3957, 3480, 2875 and 2448 µmol h⁻¹, respectively. The maximum H₂ evolution, *i.e.*, 3957 µmol h⁻¹, was obtained for sample S2. The hydrogen evolution *versus* irradiation time plots for catalysts S1–S5 are shown in Fig. 8. The linearity of the graphs clearly show the steady evolution rate of the undoped and N-doped ZnO samples. However, overall the

Table 3 Photocatalytic activity of undoped and N-doped ZnO samplesfor hydrogen evolution^a

Sample	S1	S2	S3	S4	S5
$H_2 \ (\mu mol \ h^{-1})$	1874	3957	3480	2875	2448

 a Catalyst, 0.2 g; 200 ml (0.25 M aqueous KOH solution); 300 W Xe lamp (oriel).



Fig. 8 Time versus volume of H_2 (µmol) evolution of the as-synthesized (a) undoped ZnO (S1) and (b–e) N-doped ZnO (S5–S2) samples.

N-doped ZnO sample S2 shows higher activity as compared to undoped ZnO (S1) and the other metal oxides.^{14,15} Significantly, the photocatalytic activity of N-doped ZnO was observed to be much higher as compared to sulfide semiconductors, such as CdS, CdIn₂S₄, In₂S₃, *etc.*,^{9–12} reported so far.

The higher hydrogen evolution rate for sample S2 is observed, which is due to the higher doping concentration of nitrogen than the other samples and also due to the secondary growth of nanoparticles (\sim 4–5 nm) over the primary growth of nanocubes. Due to N-doping, the band gap of the N-doped ZnO has been shifted completely in the visible region and hence, maximum visible light absorption is favoured. Thus, the maximum evolution rate obtained is justified. Accordingly, it is observed that the evolution rate decreases in the case of samples S3–S5, which is due to lowered levels of N-doping.

During the photodecomposition reaction, in 0.25 M KOH solution (pH of 12–13), the weak diprotic acid H₂S (two p K_a values are 7.0 and 11.96) dissociates and maintains equilibrium with hydrosulphide HS⁻ ions. The oxide semiconductor absorbs light and generates electron–hole pairs. The photogenerated valence band hole (h⁺_{VB}) upon band gap excitation of the powder samples of N-doped ZnO oxidizes the HS⁻ ions to sulphur (2S), liberating protons. The conduction band electron (e⁻_{CB}) from the N-doped ZnO photocatalyst reduces protons to produce molecular hydrogen.

$$H_2S + OH^- \leftrightarrow HS^- + H_2O$$
 (2)

Semiconductor N–ZnO
$$\rightarrow h^+_{VB} + e^-_{CB}$$
 (3)

Oxidation reaction :
$$2HS^- + 2h^+_{VB} \rightarrow 2S + 2H^+$$
 (4)

Reduction reaction :
$$2H^+ + 2e^-_{CB} \rightarrow H_2$$
 (5)

The p-type N-doped ZnO shows higher photocatalytic activity, which may be because of the availability of a larger number of holes (due to p-type doping), that ultimately accelerates the production of protons and increases molecular hydrogen generation (eqn (4) and (5)). However, the detailed mechanism requires more experimentation which is in progress.

It is noteworthy that this is the first time that we have reported enhanced hydrogen generation from waste H_2S using an ecofriendly, stable N-doped ZnO as a photocatalyst under solar light. The stability of the photocatalyst has also been examined by reusing the photocatalyst samples (S2) and we obtained the same results (SI-3†). The XRD of the reused catalyst did not show any changes in the phase purity of the N-doped ZnO (SI-4†), which implies good stability of the catalyst.

3. Experimental section

3.1 Synthesis of N-doped ZnO

The synthesis of the N-doped ZnO was performed by using a wet chemistry technique. Analytical grade zinc chloride $(ZnCl_2)$, urea and absolute ethanol were purchased from the local chemical manufacturer (Qauligene chemicals) and were used as received. In a typical synthesis, to 0.5 M ZnCl₂ solution in absolute ethanol, urea (1:2 w/w) was added slowly with constant

stirring until a homogeneous solution was achieved. This solution was then kept in oven at 150 °C to obtain a white product, which was found to be hygroscopic. The hygroscopic product was preserved in a desiccator, and then further subdivided for heat treatment at 500 °C, 600 °C, 700 °C and 800 °C for 3 h to obtain brown products, which are no longer hygroscopic. For comparison, we also synthesized the undoped (S1) sample. It was synthesized by heat treating a 0.5 M ZnCl₂·3H₂O solution (without any additives like urea) at 150 °C to obtain the product, which was further annealed at 800 °C for 3 h. The other products with dopants were annealed at 500 °C, 600 °C; 700 °C and 800 °C for 3 h. After annealing at the different temperatures, all samples (including S1) were washed with copious amounts of hot distilled water until all chlorine is removed, and were labeled as S2, S3, S4 and S5 respectively. These products were then subjected to UV-DRS, XRD, Raman, XPS, FESEM, TEM analysis for their characterization.

3.2. Characterization

Thermogravimetric (TG) and differential thermal analysis (DTA) of the intermediate was carried out at a heating rate of $10 \,^{\circ}\text{C} \,^{\text{min}^{-1}}$ in air (SETARAM-16/18). The optical properties of the powder samples were studied using an UV-visible-near infrared spectrometer (UV-VIS-NIR, Perkin Elmer Lambda-950). The crystalline phases and the crystallite size of the photocatalyst was identified using an X-ray powder diffraction (XRD) technique (XRD-D8, Advance, Bruker-AXS) with Cu Ka radiation. Room temperature micro Raman scattering (RS) was performed using a HR 800-Raman Spectroscopy, Horiba Jobin Yvon, France, with an excitation at 632.81 nm by a coherent He-Ne ion laser and a liquid nitrogen cooled CCD camera to collect and process the scattered data. The chemical bonds of these N-doped ZnO samples were examined using X-ray photoelectron spectroscopy (XPS, ESCA-3000, VG Scientific Ltd, England) with a base pressure greater than 1.0×10^{-9} Pa and Mg K α radiation (1253.6 eV) was used as an X-ray source operated at 150 W. The morphologies of the N-doped ZnO nanostructures were characterized by field emission scanning electron microscopy (FESEM, Hitachi, S-4800) and high resolution transmission electron microscopy (HRTEM, JEOL, 2010F). For HRTEM studies, samples were prepared by dispersing the powder in acetone, followed by sonication in an ultrasonic bath for 2 min and then drop-casting the dispersion on a carboncoated copper grid and by subsequent drying in a vacuum.

3.3. Photodecomposition of H₂S

The cylindrical quartz photochemical reactor was filled with 200 ml 0.25 M aqueous KOH and purged with argon for 1 h. Hydrogen sulphide (H₂S) was bubbled through the solution for about 1 h at the rate of 2.5 ml min⁻¹ at 299 K. N-doped ZnO (0.2 g) was introduced into the reactor and irradiated with a visible light source Xe-lamp (300 W, LOT ORIEL GRUPPE, EUROPA, LSH302, see ESI† SI-5 for Xe lamp spectrum) with constant stirring. The escaped hydrogen sulfide was trapped in a NaOH solution. The amount of hydrogen gas evolved was collected in a graduated cylinder and measured. The evolved

hydrogen was then analyzed for its purity using a gas chromatograph (Model Shimadzu GC-14B, MS-5 Å column, TCD, Ar carrier). All the samples (S1–S5) were tested for their catalytic activity under identical conditions.

4. Conclusions

In nutshell, the synthesis of a p-type N-doped ZnO catalyst was demonstrated by a simple wet chemical method. Significantly, the efficient and stable production of eco-friendly hydrogen using hazardous H₂S waste with the help of abundantly available solar light was demonstrated for the first time using the p-type N-doped ZnO catalyst. The optical study clearly shows a shift in the band gap to the visible region (3.19-2.3 eV) due to N-doping, which is in good agreement with the Raman and XPS studies. XPS confirms the bond formation of nitrogen with zinc in the ZnO lattice with an oxygen-to-nitrogen atomic ratio of 1:0.38. The lowering of the amount of N-doping with increasing temperature agrees well with the XPS results. In the case of the N-doped ZnO catalyst obtained at 500 °C (S2), nanocubes of the size $\sim 50-100$ nm were obtained as the primary growth, while the secondary growth was nanoparticles of size \sim 4–5 nm over the nanocubes. The naked N-doped ZnO sample prepared at 500 °C showed excellent photocatalytic activity (3957 μ mol h⁻¹) for the hydrogen production under visible light irradiation, which is much higher as compared to the oxide semiconductor catalysts reported so far. Significantly, the catalyst is highly stable and can be used repeatedly. The green route investigated herewith, will have potential applications in the production of other N-doped metal oxides.

Acknowledgements

The authors would like to thank the Department of Information and Technology, Govt of India, New Delhi for financial support and Dr D. P. Amalnerkar, Executive Director, C-MET for their kind support. The authors are very grateful and also wish to express their gratitude to the nanocrystalline materials group C-MET, Pune for their support. The authors would also acknowledge to Dr K. R. Patil for XPS analysis and Dr V. H. Rane for the GC analysis.

Notes and references

- P. Xu, T. Xu, J. Lu, S. Gao, N. S. Hosmane, B. Huang, Y. Dai and Y. Wang, *Energy Environ. Sci.*, 2010, **3**, 1128; F. Dionigi, P. C. K. Vesborg, T. Pedersen, O. Hansen, S. Dahl, A. Xiong, K. Maeda, K. Domen and I. B. Chorkendorff, *Energy Environ. Sci.*, 2011, **4**, 2937; J. Shi, H. Cui, Z. Liang, X. Lu, Y. Tong, C. Su and H. Liu, *Energy Environ. Sci.*, 2011, **4**, 466; K. Maeda, D. Lu, K. Teramura and K. Domen, *Energy Environ. Sci.*, 2010, **3**, 471; M. Liu, L. Wang, G. Lu, X. Yao and L. Guo, *Energy Environ. Sci.*, 2011, **4**, 1372.
- 2 H. G. Kim, D. W. Hwang and J. S. Lee, J. Am. Chem. Soc., 2004, 126, 8912.
- 3 H. G. Kim, P. H. Borse, W. Choi and J. S. Lee, *Angew. Chem., Int. Ed.*, 2005, 44, 4585.
- 4 M. Barbeni, E. Pelizzetti, E. Borgarello, N. Serpone, M. Gratzel and L. Balducci, *Int. J. Hydrogen Energy*, 1985, 10, 249.
- 5 N. Buhler, K. Meier and J. P. Reber, J. Phys. Chem., 1984, 88, 3261.
- 6 M. P. Elsner, M. Menge, C. Muller and D. W. Agar, *Catal. Today*, 2003, 79–80, 487.
- 7 H. Kato and A. Kudo, J. Phys. Chem., 2004, 106, 5029.

- 8 W. So, K. Kim and S. Moon, *Int. J. Hydrogen Energy*, 2004, 29, 229.
- 9 A. P. Bhirud, N. S. Chaudhari, L. K. Nikam, R. S. Sonawane, K. R. Patil, B. J. Ook and B. B. Kale, *Int. J. Hydrogen Energy*, 2011, **36**, 11628.
- 10 B. B. Kale, J. O. Baeg, S. M. Lee, H. Chang, S. J. Moon and C. W. Lee, *Adv. Funct. Mater.*, 2006, 16, 1349.
- 11 S. k. Apte, S. N. Garje, G. P. Mane, A. Vinu, A. D. Naik, D. P. Amalnerkar and B. B. Kale, *Small*, 2011, 7, 957.
- 12 S. D. Naik, T. C. Jagadale, S. K. Apte, R. S. Sonawane, M. V. Kulkarni, S. I. Patil, S. B. Ogale and B. B. Kale, *Chem. Phys. Lett.*, 2008, 452, 301.
- 13 K. G. Kanade, B. B. Kale, J. -O. Baeg, S. M. Lee, C. W. Lee, S. -J. Moon and H. Chang, *Mater. Chem. Phys.*, 2007, **102**, 98.
- 14 E. Subramanian, J. O. Baeg, B. B. Kale, S. M. Lee, S. J. Moon and K. J. Kong, *Bull. Korean Chem. Soc.*, 2007, 28, 2089.
- 15 B. B. Kale, J. O. Baeg, K. J. Kong, S. J. Moo, S. M. Lee and W. W. So, *Int. J. Energy Res.*, 2010, 34, 404.
- 16 K. C. Barick, S. Singh, M. Aslam and D. Bahadur, *Microporous Mesoporous Mater.*, 2010, **134**, 195; D. Jung, *Solid State Sci.*, 2010, **12**, 466; M. C. Zlatko, D. T. L. Alexander, S. Andrzej, M. C. Marijana, L. Forró and M. Arnaud, *Cryst. Growth Des.*, 2010, **10**, 4437; J. Zhao, H. Liang, J. Sun, Q. Feng, S. Li, J. Bian, L. Hu, G. Du, J. Ren and J. Liu, *Phys. Status Solid A*, 2011, **208**, 825; Y. Liu, T. Wang, X. Sun, Q. Fang, Q. Lv, X. Song and Z. Sun, *Appl. Surf. Sci.*, 2011, **257**, 6540; C. Wu, L. Shen, Y. C. Zhang and Q. Huang, *Mater. Lett.*, 2011, **65**, 1794; T. Xia, Y. Zhao, T. Sager, S. George, S. Pokhrel, N. Li, D. Schoenfeld, H. Meng, S. Lin, X. Wang, M. Wang, Z. Ji, Z. J. I. Zink, L. Madler, V. Castranova, S. Lin and A. E. Nel, *ACS Nano*, 2011, **5**, 1223.
- 17 D. Fan, R. Zhang and Y. Li, *Solid State Commun.*, 2010, **150**, 1911; H. von Wenckstern, H. Schmidt, M. Brandt, A. Lajna, R. Pickenhain, M. Lorenz, M. Grundmann, D. M. Hofmann, A. Polity, B. K. Meyer, H. Saal, M. Binnewies, A. Börger, K.-D. Becker, V. A. Tikhomirov and K. Jug, *Prog. Solid State Chem.*, 2009, **37**, 153; S. P. Wang, C. X. Shan, B. H. Li, J. Y. Zhang, B. Yaoa, D. Z. Shen and X. W. Fan, *J. Cryst. Growth*, 2009, **311**, 3577.
- 18 X. Yang, A. Wolcott, G. Wang, A. Soba, R. C. Fitzmorris, F. Qian, J. Z. Zhang and Y. Li, *Nano Lett.*, 2009, 9, 2331.
- 19 S. B. Zhang, S.-H. Wei and A. Zunger, Phys. Rev. Lett., 2000, 84, 1232.
- 20 S. B. Zhang, S. H. Wei and A. Zunger, Phys. Rev. B, 2001, 63, 075205.
- 21 C. H. Park, S. B. Zhang and S. H. Wei, Phys. Rev. B, 2002, 66, 073202.
- 22 K. Iwata, P. Fons, A. Yamada, K. Matsubara and S. Niki, J. Cryst. Growth, 2000, 209, 526.
- 23 Z. Z. Ye, J. G. Lu, H. H. Chen, Y. Z. Zhang, L. Wang, B. H. Zhao and J. Y. Huang, *J. Cryst. Growth*, 2003, **253**, 258; X. L. Guo, H. Tabata and T. Kawati, *J. Cryst. Growth*, 2002, **544**, 237; C. Wang, Z. Ji, K. Liu, Y. Xiang and Z. Ye, *J. Cryst. Growth*, 2003, **259**, 279.
- 24 C. W. Zou, X. D. Yan, J. Han, R. Q. Chen, W. Gao and J. Metson, *Appl. Phys. Lett.*, 2009, **94**, 171903.
- 25 G. Golan, A. Axelevitch, B. Gorenstein and V. Manevych, *Microelectron. J.*, 2006, 37, 910.
- 26 B. V. Zeghbroeck, Principles of Semiconductor Devices, 2004, ch. 2, pp. 161–162.
- 27 T. Morimoto, H. Yanal and M. Nagao, J. Phys. Chem., 1976, 80, 471.
- 28 C. Persson, C. Platzer-Bjorkman, J. Malmstron, T. Torndahl and M. Edoff, *Phys. Rev. Lett.*, 2006, **97**, 146403.
- 29 J. Serrano, A. H. Romero, F. J. Manjon, R. Lauck, M. Cardona and A. Rubio, *Phys. Rev. B*, 2004, **69**, 094306.
- 30 K. Saito, Y. Hosokai, K. Nagayama, K. Ishida, K. Takahashi, M. Konagai and B. P. Zhang, J. Cryst. Growth, 2004, 272, 805.
- 31 X. Zhu, H. Z. Wu, D. J. Qiu, Z. Yuan, G. Jin, J. Kong and W. Shen, *Opt. Commun.*, 2010, 283, 2695.
- 32 B. Sieber, H. Liu, G. Piret, J. Laureyns, P. Roussel, B. Gelloz, S. Szunerits and R. Boukherroub, J. Phys. Chem. C, 2009, 113, 13643.
- 33 G. T. Du, Y. Ma, Y. T. Zhang and T. P. Yang, *Appl. Phys. Lett.*, 2005, 87, 213103.
- 34 S. Anandana, A. Vinu, K. L. P. Sheeja Lovely, N. Gokulakrishnan, P. Srinivasu, T. Mori, V. Murugesan, V. Sivamurugan and K. Ariga, J. Mol. Catal. A: Chem., 2007, 266, 149.
- 35 S. F. Chen, S. J. Zhang, W. Liu and W. Zhao, J. Hazard. Mater., 2008, 155, 320.
- 36 S. F. Chen and L. Chen, Mater. Chem. Phys., 2006, 98, 116.
- 37 H. Wang, H. P. Ho, K. C. Lo and K. W. Cheah, J. Phys. D: Appl. Phys., 2007, 40, 4682.
- 38 C. L. Perkins, S. H. Lee, X. Li, S. E. Asher and T. J. Coutts, J. Appl. Phys., 2005, 97, 034907.

- 39 A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma and M. Kawasaki, *Nat. Mater.*, 2005, 4, 42.
- 40 Q. F. Ana, P. Marina, V. Aurea, M. del Francisco, G. H. Mar and M. G. C. Jose, *Chem. Mater.*, 2010, **22**, 6529.
- 41 C. Giordano, C. Erpen, W. Yao, B. Milke and M. Antonietti, *Chem. Mater.*, 2009, **21**, 5136.
- 42 A. M. Smith, A. M. Mohs and S. Nie, *Nat. Nanotechnol.*, 2009, 4, 63.
- 43 M. Onuki and S. Kubo, J. Phys. Soc. Jpn., 1962, 17, 1516.