



Laser induced photocatalytic generation of hydrogen and oxygen over NiO and TiO₂

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Abstract

A comparative study of photocatalytic splitting of water into hydrogen and oxygen over NiO and TiO₂ was carried out using 355 nm laser radiations as a light source. The effect of dissolved metal ions on photocatalytic splitting of water over these catalysts was also studied by using Fe³⁺, Ag⁺ and Li⁺ ions to enhance the efficiency of the process by suppressing the non-productive electron–hole recombination. The dependence of products yield on incident laser energy, amount of catalyst (particle density), stirring rate and laser beam diameter was also investigated for activity comparison of these catalysts. It was demonstrated for the first time that by using a high photon flux source such as laser, the problems of longer exposure time and low photonic efficiencies could be resolved which is common problem with conventional UV lamp based photocatalysis.

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1. Introduction

The major part of the energy consumed today, comes from chemical energy stored in the fossil fuels. The deposits of fossil fuels are rapidly depleting and their combustion has led to severe pollution and stress to the environment. The environmental impact of rise in pollution is manifested in the form of global warming, acid rain formation, ozone depletion and climate change. Due to rapid depletion of the fossil reserves, grave situation of the environment, growing interest has been developed for the search of new alternative non-fossil and environmental friendly energy sources. Hydrogen is considered as the best option in this regard, as its combustion leads to the formation of water as exhaust. Based on heterogeneous photocatalysis approach, the main desire of the community is to use two inexpensive sources, i.e. water and sunlight for the production of hydrogen but this desire is still a

dream as no photocatalyst fulfills the prerequisites required for complete splitting of water into its components with high efficiencies. Due to these reasons, efforts are under way for the production of hydrogen in controlled quantities, with high efficiencies, using water, semiconductors and cheaply available light sources other than sunlight [1–10].

Photocatalytic splitting of water is based upon the illumination of the aqueous colloidal suspension of semiconductor powder with light of wavelength having energy equal to or greater than the band gap of semiconductor producing electron–hole pair. The hydroxyl radicals (OH•) produced by the donation of electrons by adsorbed water to the valence band holes are responsible for the production of O₂ while the other portion of dissociated water, i.e. H⁺ ions produces H₂ by capturing the conduction band electrons. The important parameter with respect to photocatalyst, in this regard, is the positions of the conduction and valence band edges. To produce hydrogen the conduction band edge of the photocatalyst should have a sufficiently high negative value compared to H⁺/H₂ ($E = 0.0$ V versus NHE) redox couple [11–21].

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Among metal oxide semiconductors, TiO_2 ($E_g = 3.2 \text{ eV}$) is the most extensively studied photocatalyst. In this study, based on its p-type semiconductor properties, with a band gap of 3.5 eV [22], and the suitable valence and conduction band edges for hydrogen and oxygen production, NiO was selected to study the photocatalytic splitting of water and compared its activity with that of TiO_2 . NiO is the least studied for its photocatalytic properties but well-studied as heterogeneous catalyst especially as hydrogenation catalyst [23,24]. Heterogeneous photocatalysis is still in the developing stage and several hidden aspects of photocatalytic processes are yet to be explored. The two basic inherited problems associated with the commercial application of heterogeneous photocatalysis are the long reaction time and low quantum or photonic efficiencies. By solving these two basic problems, heterogeneous photocatalysis can be introduced as cheap and versatile technique for synthesis and environmental purposes.

In this study, the above-mentioned two basic problems associated with heterogeneous photocatalytic processes are addressed and it was demonstrated that by using a high photon flux source such as laser, the problems of longer exposure time and low photonic efficiencies could be resolved. Another aspect of this study is the evaluation of photocatalytic activity of the catalysts, i.e. NiO and TiO_2 under strong UV photon flux of 355 nm . In addition, the measurement of pH changes during illumination was found very useful in explaining the contribution of various reactions in the evolution of H_2 and O_2 , with or without metal ions, which was not possible otherwise.

2. Experimental

The setup used to study the photocatalytic splitting of water is discussed in detail elsewhere [25–27]. To study the photocatalytic splitting of water over NiO and TiO_2 , both the catalysts were subjected to identical experimental conditions. While using laser as light source, it was observed that the change in experimental parameters such as laser energy, amount of catalyst (particle density), stirring rate and laser beam diameter significantly affects the product yield. The parameters, i.e. stirring rate and laser beam diameter were adjusted to a fixed value and kept constant for all studies while the other parameters, i.e. laser energy and amount of catalyst were carefully optimized on the basis of evolved oxygen for NiO and kept constant for TiO_2 for comparison. The destructive effect of focused laser beam was minimized by expanding the diameter of the beam to 1 cm by using lenses and mirrors.

The photocatalytic splitting of water NiO and TiO_2 was studied by suspending an optimized amount (300 mg) of NiO and TiO_2 semiconductor powders in 60 ml of deionized water. Argon was used as purge gas to remove dissolved gases and the progress of the purging process was monitored by analyzing the gas samples from the dead volume of the

reaction cell. All the experiments were performed in batches and the quantity of evolved gases was estimated by analyzing the gas samples at regular interval of 10 min by using a SHIMADZU GC-17A gas chromatograph equipped with a 30 m , wide bore molecular sieve 5A PLOT column and a TCD detector. Argon was used as carrier gas. Both the catalysts were exposed to optimized laser energy of 100 mJ as higher energies were found detrimental. All the experiments were performed at room temperature and atmospheric pressure.

3. Results and discussion

The change in photon flux and the particle density (amount of photocatalyst) affect the product yield significantly. These parameters were optimized based on maximum yield of oxygen for NiO and kept constant for TiO_2 for comparison.

The oxygen yield for various concentrations of NiO was measured for fixed interval of time and is plotted in Fig. 1, where a sharp increase in O_2 yield from 50 to 300 mg and a slow increase in O_2 yield for further increase in catalyst concentration can be noticed. A high activity of NiO was observed for O_2 production through water splitting, particularly in the range 50 – 300 mg . Although, there was an increase in oxygen yield with the further increase in the amount of catalyst i.e. for 400 and 500 mg , but not as sharp as in range 50 – 300 mg . This behavior indicates that the extent of non-productive processes, such as electron–hole recombination and photon losses by light scattering, increases with the increase in catalyst concentration beyond certain limit. Based on these results an amount of 300 mg was used for rest of the experiments.

Fig. 2 depicts the amount of oxygen formed (yield) plotted against the laser energy for NiO catalysts at 355 nm laser irradiation. It can be noticed that the oxygen yield shows strong dependence on the incident photon flux (laser energy). A linear increase in the oxygen yield has been observed in the 50 – 100 mJ laser energy range. Although, the O_2 yield also increases for 100 – 200 mJ range but loses its linearity. The initial increase of oxygen yield with the laser energy could be attributed to the fact that the generation of electron–hole pair increases with the incident laser photon flux, which in turn enhances the water splitting process to generate O_2 . This is because at constant stirring rate the total number of catalyst particles exposed per unit area remains the same and the additional photons, beyond a limiting value, does not contribute significantly towards oxygen production rather consumed in non-productive processes.

The photocatalytic evolution of H_2 and O_2 as a function of time was studied by illuminating the colloidal suspension containing the optimized amount of NiO and TiO_2 with a 355 nm laser, as light source, for 90 min . The yield of the two gases was recorded after regular intervals of 10 min . The possibility of H_2 and O_2 generation by multi-photon

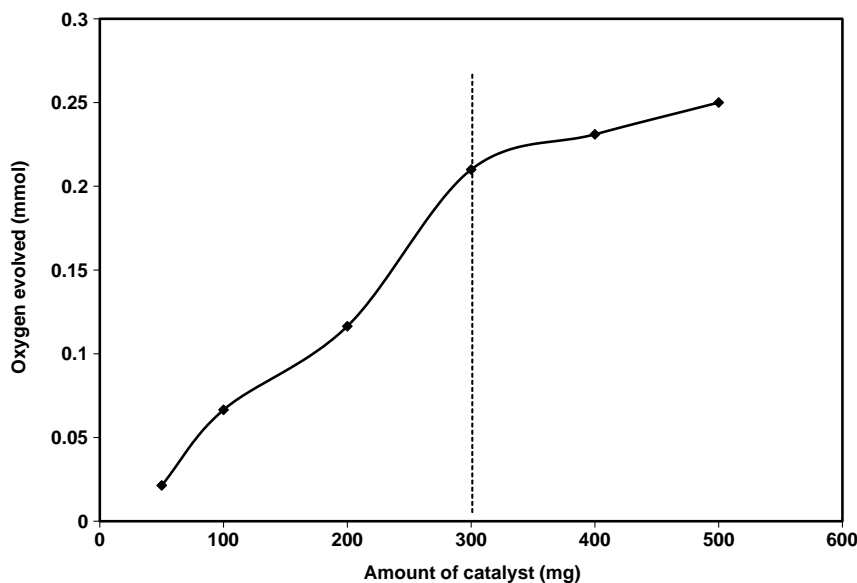


Fig. 1. Optimization of catalyst particle density for photocatalytic studies over NiO.

photolysis of water was ruled out by performing a blank experiment (without NiO and TiO₂) under the same experimental conditions.

It was observed that with the increase in laser exposure time the color of NiO suspension changed from dark green to black while from white to gray for TiO₂. In addition, the formation of hydrogen compared to oxygen was non-stoichiometric for both the catalysts even in the presence of highly suitable conduction band edges of -0.5 and -0.48 V for NiO and TiO₂, respectively [22]. The original color of the catalysts was not regenerated even when the illuminated suspensions were kept in dark. Both the catalysts regained their original green and white colors, when heated at 400 – 500 °C in an oxidizing environment, confirming the

release of lattice oxygen from the catalyst under illumination. The possible explanation of above-mentioned changes and the existing correlation between them is as under.

NiO has slightly distorted cubic rock salt structure and the non-polar (1 0 0) plane is the most stable surface. In this configuration, each Ni atom exists as Ni²⁺. Absorption of photon of energy equal to or greater than the band gap energy ($E > E_g$) causes the transfer of an electron from the valence band of oxygen (2p) to the conduction band of Ni (3d) atom and causes the reduction of Ni²⁺ to Ni⁺. This electron transfer process weakens the Ni²⁺–O bond allowing lattice oxygen to be driven out creating a “defect” or “trap” site and leads to the formation of a hole in the valence band [23,24]. The hole in the valence band oxidize the

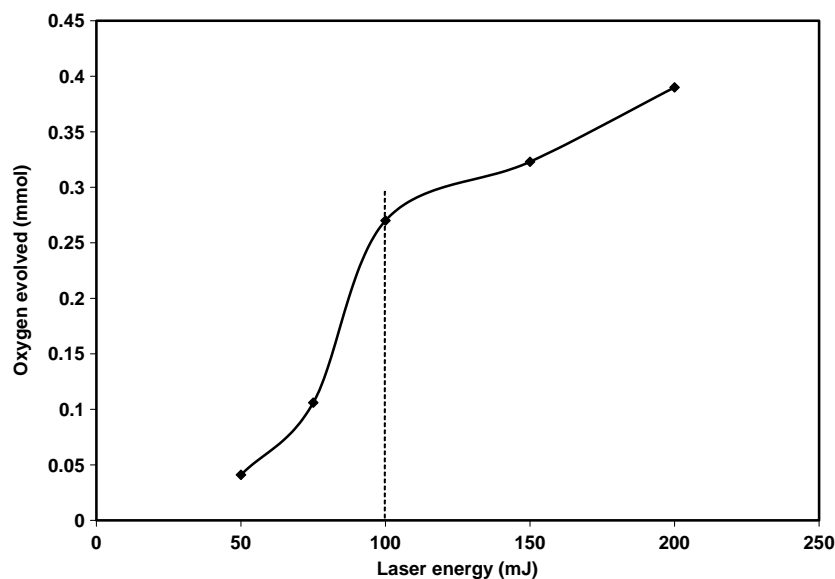
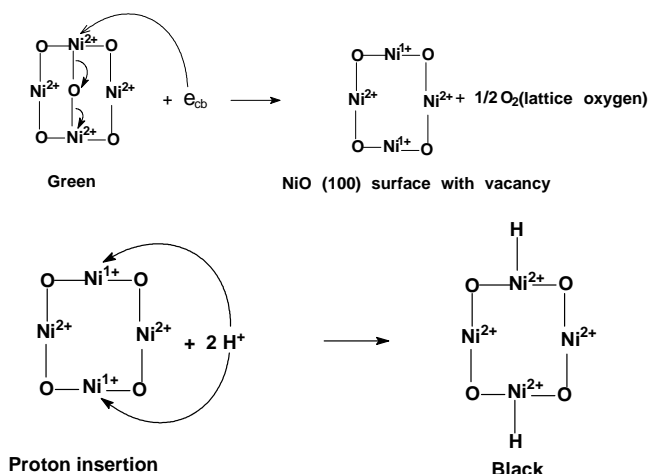
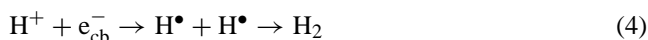
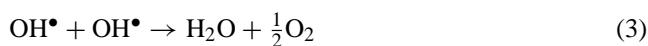
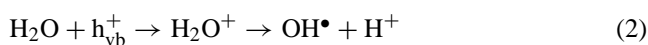
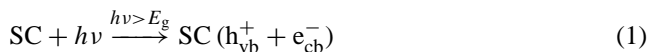


Fig. 2. Optimization of laser energy for photocatalytic studies over NiO.



Scheme 1.

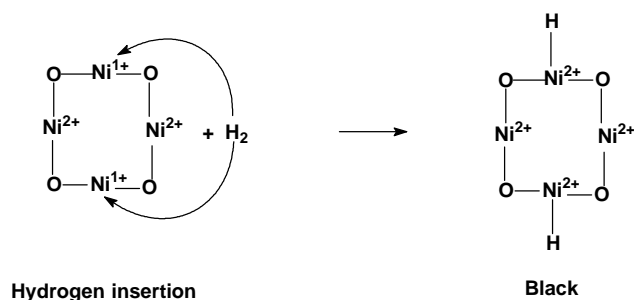
adsorbed water producing O_2 and H^+ ions in the solution. The lattice oxygen released by the reduction of catalyst serves as additional source of oxygen and disturbs the stoichiometry of the evolved gases. The H^+ ions produced as the result of photocatalytic oxidation of water, in the presence of favorable conduction band edge, are capable of capturing the conduction band electron before it being diffused to the bulk or trapped to create defect sites, to give H^\bullet radicals or H_2 gas as indicated in Eqs. (1)–(4):



Here SC, $h\nu$ and h_{vb}^+ represent semiconductor catalyst, laser photon and valence band hole, respectively.

Another reason for the loss of stoichiometry is the consumption of H^+ ions or H_2 gas is the reversible insertion of H^+ ions in the photogenerated defect sites (Scheme 1) to give H_xNiO_{1-x} type species or the homolytic insertion of molecular hydrogen (H_2) (Scheme 2).

It is clear from the above-mentioned mechanism (Scheme 1) that a measurable fraction of H^+ ions produced

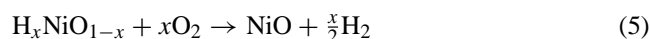


Scheme 2.

by photocatalytic splitting is consumed in the photoreduction of the NiO causing an overall decrease in the yield of H_2 as given in Fig. 3. Another contributing factor in this regard is the possibility of homolytic addition of molecular hydrogen to the defect sites (Scheme 2).

TiO_2 (rutile) has slightly distorted monoclinic structure. It consists of TiO_6 octahedra arranged in various corner-sharing or edge-sharing configurations [28,29]. In this configuration, each titanium atom exists as Ti^{4+} . The absorption of photon of energy equal to or greater than the band gap energy ($E > E_g$) causes the transfer of an electron from the valence band of oxygen (2p) to the conduction band of Ti (3d) atom and causes the reduction of Ti^{4+} to Ti^{3+} . This electron transfer process introduces the weakening of titanium–oxygen bond, allowing lattice oxygen to be driven out creating a “defect” or “trap” site. This photon-induced generation of defect sites imparts a gray color to the catalyst.

As mentioned, earlier this process is reversible only at elevated temperatures in the presence of oxygen:



A comparison of hydrogen and oxygen production is presented in Figs. 3 and 4, where it can be observed that the activity of both NiO and TiO_2 increases with the increase in defect sites or with the reduction of the catalyst. Although the yield of hydrogen and oxygen increases with time over both the catalysts, a decrease in the rate of production of both hydrogen and oxygen (Fig. 5) was observed for NiO while for TiO_2 an increase in the rate of production of hydrogen and decrease in the rate of production of oxygen (Fig. 6) was observed.

To explore the factors, which affect the yield of H_2 , the pH changes during the illumination, in the argon environment, were measured for both the catalysts. The change in pH as a function of laser exposure time are presented in Fig. 7, where a large increase in pH for NiO compared with that of TiO_2 can be observed. In a period of 60 min, the pH changes from ~ 5.2 to ~ 11.5 for NiO while for TiO_2 the rise in pH was 2.1 pH units. A significant feature associated with this increase in pH is the shifting of valence and conduction band edges. The relation given below is used to estimate the shifts in valence and conduction band edges [5].

$$E_{fb} = E_{fb}(pH0) - 0.059 \text{ pH} \quad (7)$$

With the reduction of the NiO due to the large shift in the pH, the valence and conduction band edges shift to +2.32 and -1.18 V, respectively, while for TiO_2 the calculated values for valence and conduction band edges were +2.29 and -0.9 V, respectively. The values of +2.32 and +2.29 V for valence band edge of NiO and TiO_2 , respectively, predict a considerable decrease in the over potential associated with the oxidation of water by the valence band holes and suggests an appreciable increase in the rate of water oxidation with

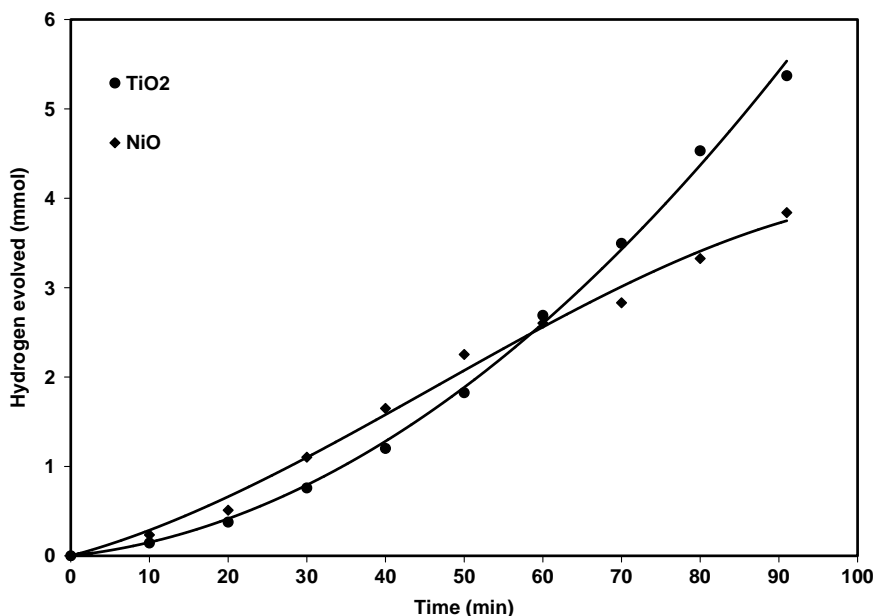
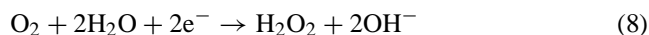


Fig. 3. Comparison of hydrogen production with time over NiO and TiO₂.

the reduction (or with the introduction of photo-induced bulk defect sites) of both NiO and TiO₂. On the other hand, with the shifting of conduction band edge towards more negative value the suitability of the conduction band edge for water reduction through dissolved oxygen along with formation of hydrogen radicals from H⁺ ions increases. Based on pH changes during illumination and the shift in the conduction band edge, i.e. from -0.5 to -1.18 V, it can be predicted that the basic reason for sharp increase in pH is the reduction of water (-0.65 V) [29] through photoexcited conduction band electrons generating high yield of hydroxyl ions over NiO as given in reaction below. These hydroxyl ions

serve as sink for photogenerated H⁺ ions thus causing a decrease in overall hydrogen yield [30]. The decrease in the rate of hydrogen and oxygen production over NiO (Fig. 5) supports the reduction of water or dissolved oxygen to give hydroxyl radicals as given below:



While for TiO₂ the extent of water reduction is relatively less compared to that of NiO as the shift in conduction band edge is lower due to the change in pH.

For NiO a sharp increase in the beginning and then a stable pH value afterwards depicts a steady state in the production

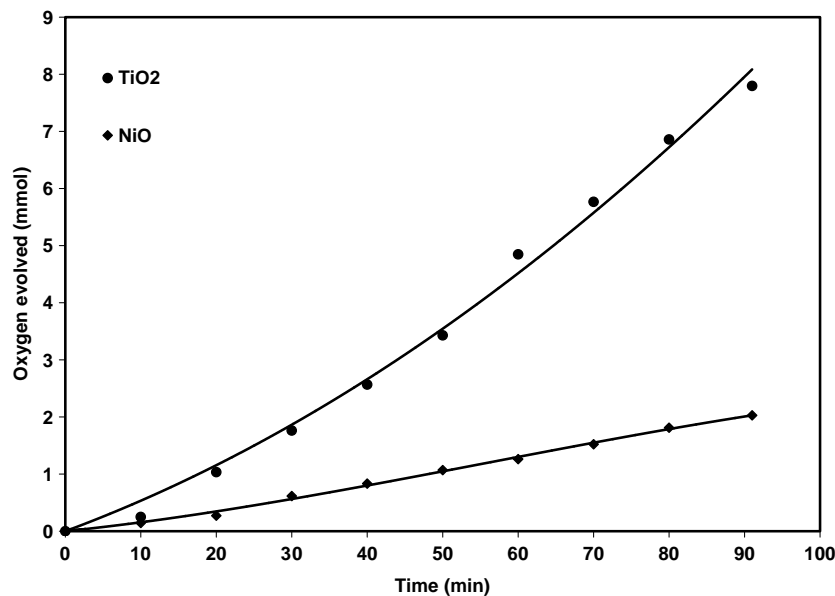


Fig. 4. Comparison of oxygen production with time over NiO and TiO₂.

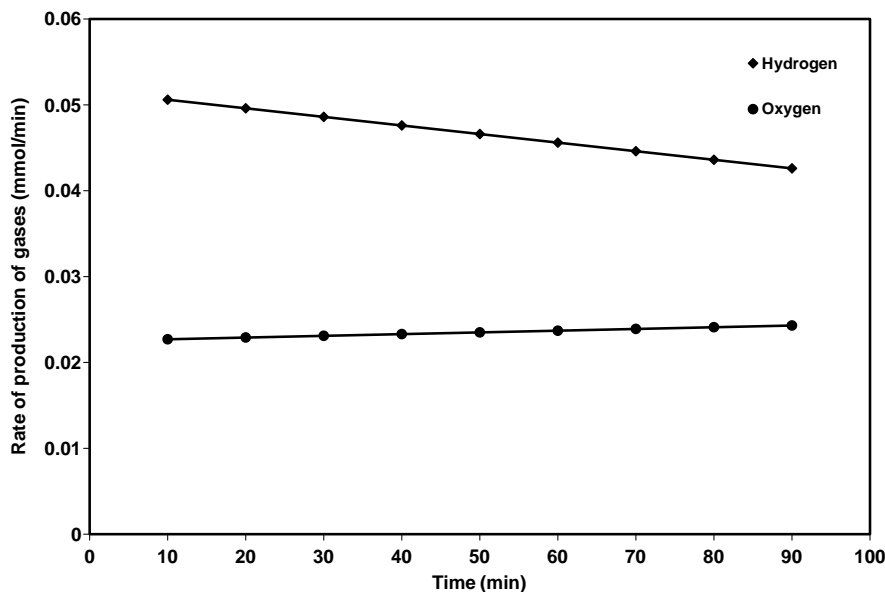


Fig. 5. Rate of hydrogen and oxygen production over NiO.

and consumption of hydroxyl ions. It is also clear from Fig. 7 that a significant fraction of H^+ ions that are produced by the donation of electrons from water molecules to photo-generated holes reacts with hydroxyl ions to give water (recombination) and leads towards the low yield of hydrogen. While for TiO_2 the above-mentioned facts does not hold due to the unsuitable edge positions.

The effect of dissolved metal ions on photocatalytic splitting of water over NiO and TiO_2 was studied by using Fe^{3+} , Ag^+ and Li^+ ions. In photocatalytic processes, metal ions are used to enhance the efficiency of the process by suppressing the non-productive electron-hole recombination and selected on the basis of redox potentials of the

couples or the reduction potentials of the ions involved. In this study two metal ions i.e. Fe^{3+} and Ag^+ were selected as electron capture agents as the redox potentials of these ions are positive than the conduction band potential of NiO while Li^+ was selected by considering the high reactivity of these ions towards hydroxyl radicals and comparable activity as compared to H^+ ions. The reduction potentials of Fe^{3+}/Fe^{2+} , Ag^+/Ag^0 and Li^+/Li^0 couples are +0.77, +0.80 and -3.05 V, respectively [24].

The effect of these metal ions on H_2 and O_2 yield for NiO is presented in Figs. 8 and 9 and for TiO_2 in Figs. 10 and 11, respectively. For NiO, in the presence of Fe^{3+} ions, instead of an expected decrease an unexpected sustained increase in

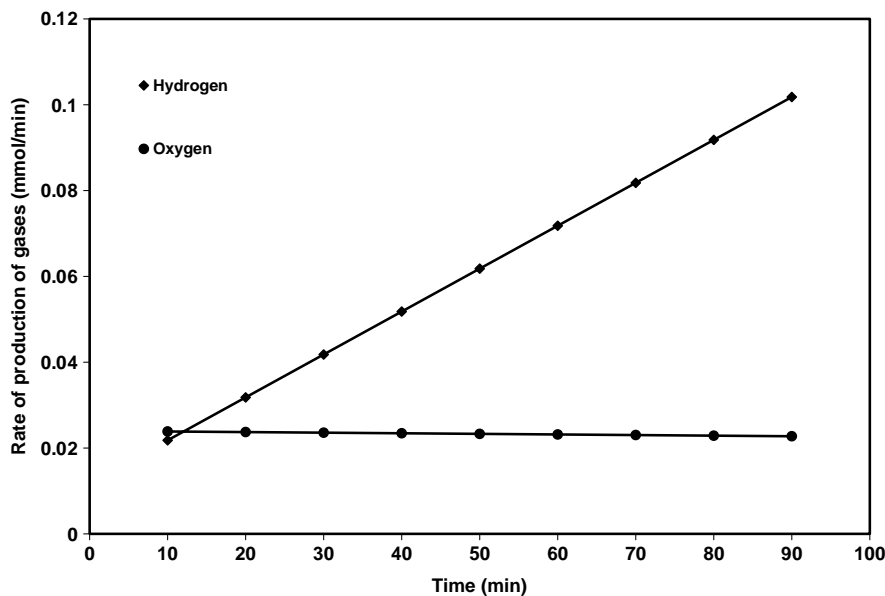


Fig. 6. Rate of hydrogen and oxygen production over TiO_2 .

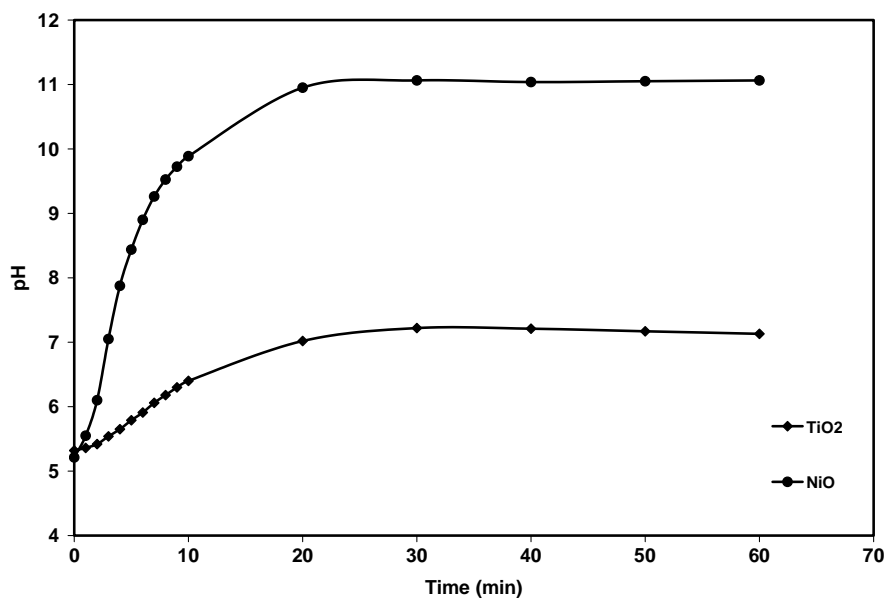


Fig. 7. pH change in argon during the course of photocatalytic splitting of water over NiO and TiO₂.

the production of hydrogen was observed (Fig. 8). This behavior indicates that in the presence of high concentration of hydroxyl ions the metal ions that were selected to work as electron capture agents act as hydroxyl ion scavengers and reduce the depletion of H⁺ ions by hydroxyl ions and forms the respective hydroxides. The unexpected decrease in oxygen yield, as shown in Fig. 9, in the presence of both Fe³⁺ and Ag⁺ indicates the decrease in the additional formation of oxygen with the decrease in the concentration of hydroxyl radicals. The initial increase in O₂ (Fig. 9) formation and then a decrease afterwards indicates the depletion of Ag⁺ with the time. This decrease is mainly due to the deposition

of Ag⁰ at the surface and formation of oxides and hydroxides.

For TiO₂, the decrease in the production of H₂ (Fig. 10) and an initial increase and then a decrease in O₂ yield (Fig. 11) in the presence of Fe³⁺ ions indicates the suitability of these ions as electron capture agents and the sustained increase indicates the regenerative behavior as given in the following equations:

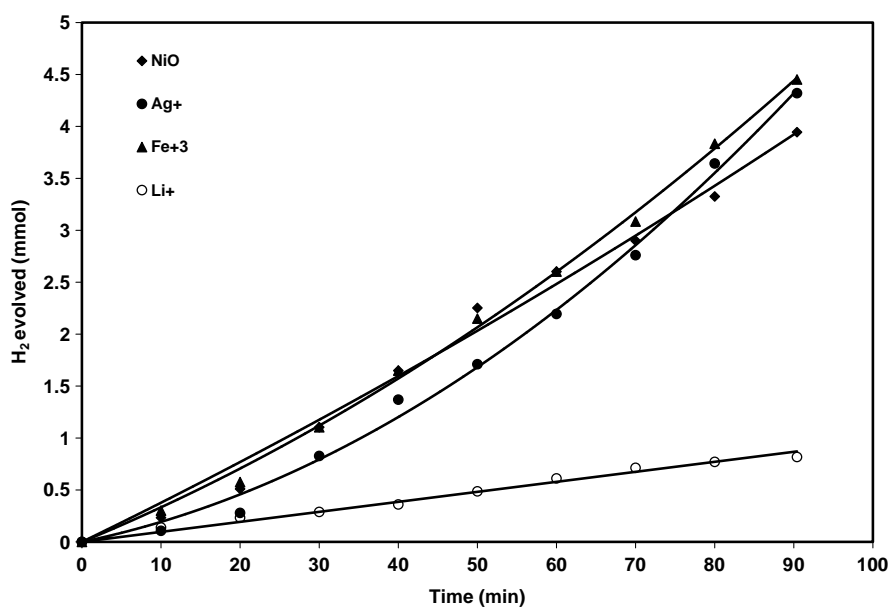
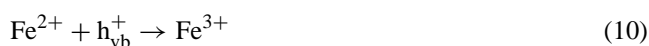


Fig. 8. Hydrogen production over NiO in the presence of metal ions.

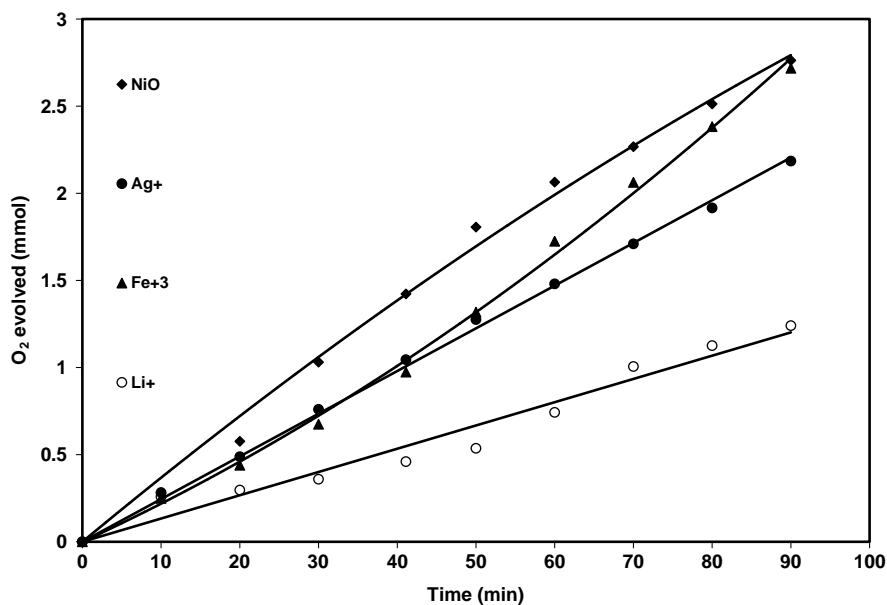


Fig. 9. Oxygen production over NiO in the presence of metal ions.

Although, Ag^+ has a favorable reduction potential of +0.80 V and qualifies for serving as an electron scavenger but in presence of Ag^+ the extent of expected decrease in H_2 hydrogen formation (Fig. 10) and an increase in O_2 yield (Fig. 11) was not comparable to that of Fe^{3+} ions. This behavior suggested the depletion of Ag^+ ions with the time. The deposition of Ag^0 at the surface of the catalyst and the possible formation of Ag_2O in the presence of O_2 are the two main contributing factors [5,6]:



The reduction potential of Li^+ is much more negative than the potential of conduction band electrons so the probability of capturing conduction band electrons is negligible. A decrease in both H_2 and O_2 production in the presence of Li^+ ions, for both the catalysts, owing to the deactivation of the catalyst by the formation and deposition of LiOH at the surface of the catalyst was observed confirming the presence of hydroxyl ions in the photocatalytic process over both the catalysts.

The ability of a photocatalytic process to convert the photons in desired products is measured in terms of “photonic efficiency” (PE). The photonic efficiency is defined

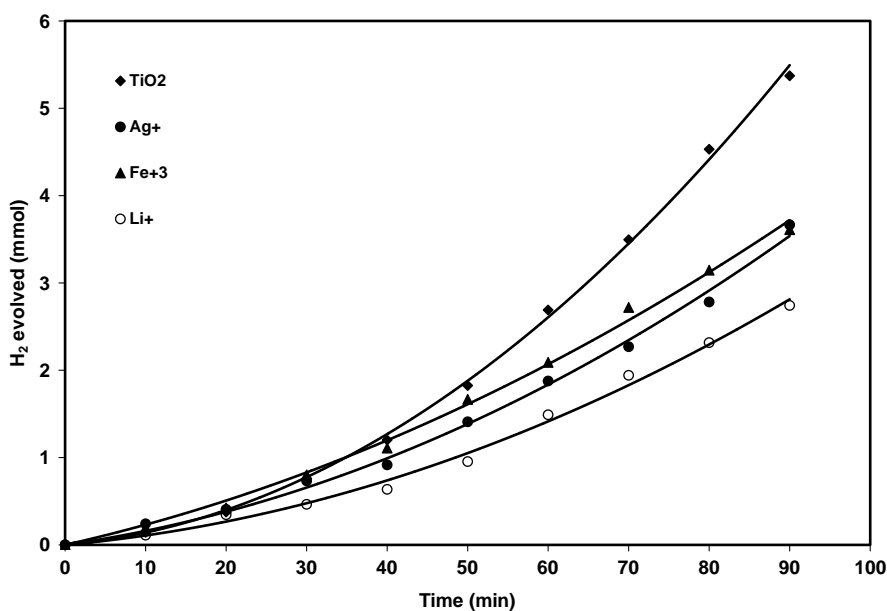


Fig. 10. Hydrogen production over TiO_2 in the presence of metal ions.

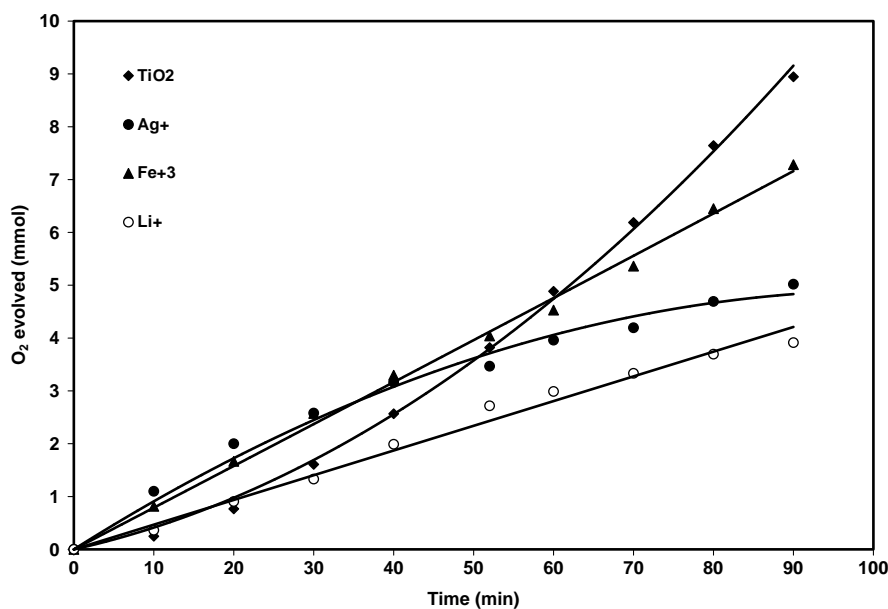


Fig. 11. Oxygen production over TiO₂ in the presence of metal ions.

as [26]:

$$\text{PE (\%)} = \frac{\text{Number of moles of product formed or consumed/time}}{\text{Number of photons of wavelength } \lambda \text{ absorbed/time}} \times 100 \quad (13)$$

In this study, the photonic efficiency for the photocatalytic splitting of water to H₂ and O₂ over both NiO and TiO₂ in both the presence and absence of metal ions was estimated. The plots of photonic efficiencies over NiO as a function of laser exposure time for H₂ and O₂ are given in Figs. 12 and 13 while for TiO₂ in Figs. 14 and 15.

It was observed that for pure NiO the photonic efficiency for H₂ production increases sharply and then decreases to a stable value indicating a low depletion of H⁺ ions in the beginning and equilibrium between generation and depletion afterwards. The reasons for the low value of ~30% for H₂ production and that of ~23% for O₂ production have been discussed in the previous section. For all the metal ions, the photonic efficiency for H₂ generation was lower than pure NiO indicating that a fraction of metal ions also works as electron capture agents and follows the order Fe³⁺ > Ag⁺ > Li⁺. While for O₂ production, approximately the same situation was observed. The observed order was

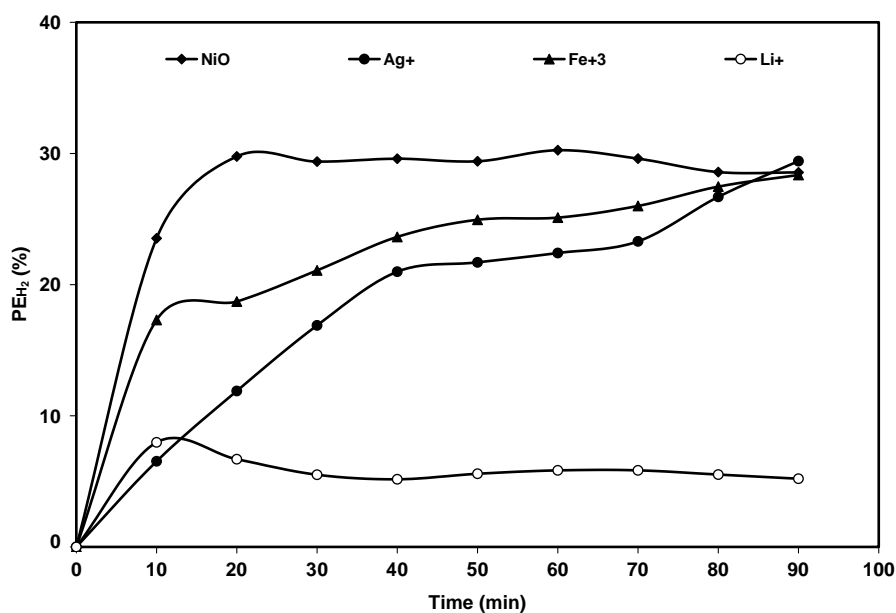


Fig. 12. Photonic efficiency of hydrogen production over NiO in the presence of metal ions.

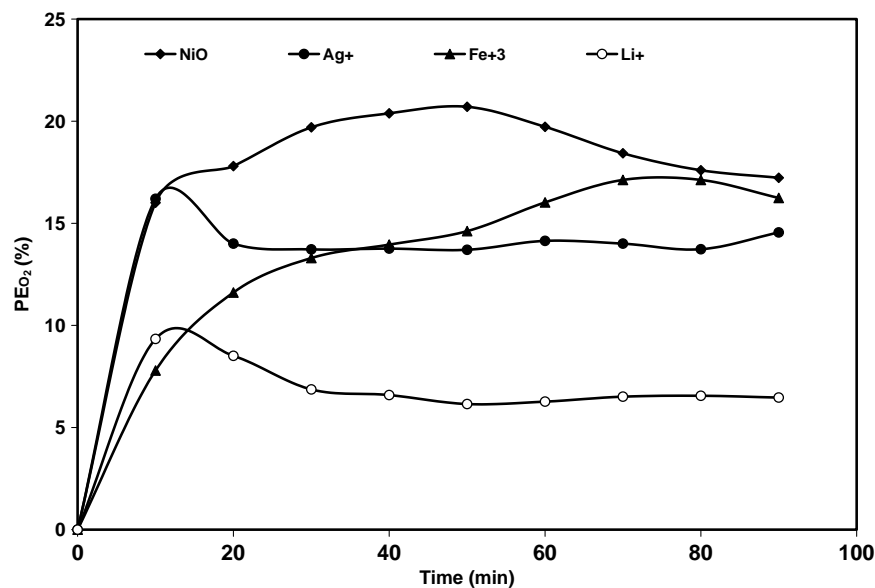


Fig. 13. Photonic efficiency of oxygen production over NiO in the presence of metal ions.

$\text{Ag}^+ > \text{Fe}^{3+} > \text{Li}^+$. While for TiO_2 the photonic efficiency for H_2 production increases slowly in the beginning and sharply afterwards owing to the fact that in the beginning the photons are consumed more in the reduction of the catalyst than hydrogen production. Once the catalyst is reduced fully, with the introduction of bulk defect sites, the photonic efficiency increase sharply. For O_2 production initially increases rapidly, reaches to a maximum value and then starts decreases sharply. The initial increase is due to the contribution from the lattice oxygen while the sharp decrease

afterwards, indicates the depletion of the oxygen through reduction as mentioned above. A photonic efficiency of $\sim 25\%$, with increasing trend was observed for pure TiO_2 while an initial increase followed by a decrease in the photonic efficiency for H_2 production in the presence of metal ions is due to the fact that these ions reduce the consumption of H^+ ions by hydroxyl ions. For O_2 production, the maximum photonic efficiency of 35% was observed for Ag^+ and the minimum photonic efficiency of less than 10% was observed for Li^+ .

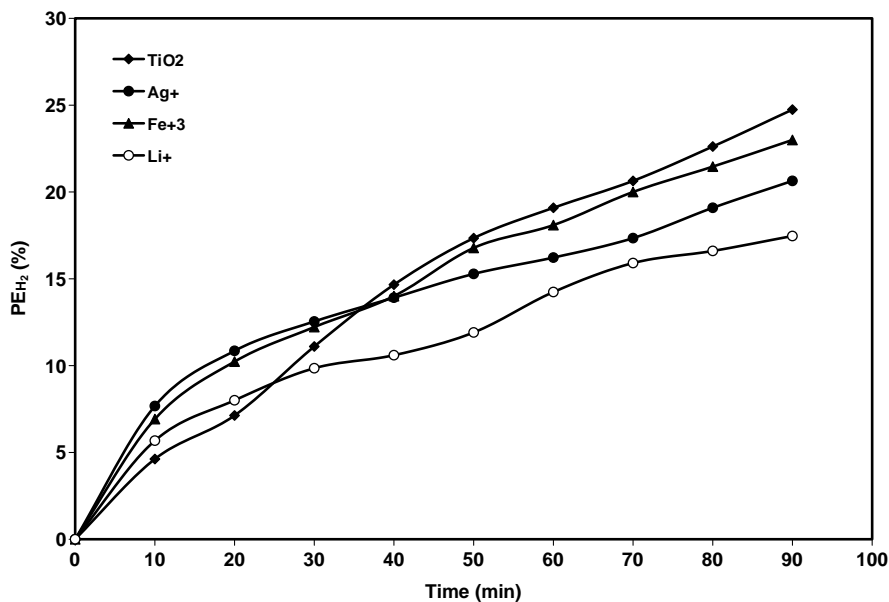


Fig. 14. Photonic efficiency of hydrogen production over TiO_2 in the presence of metal ions.

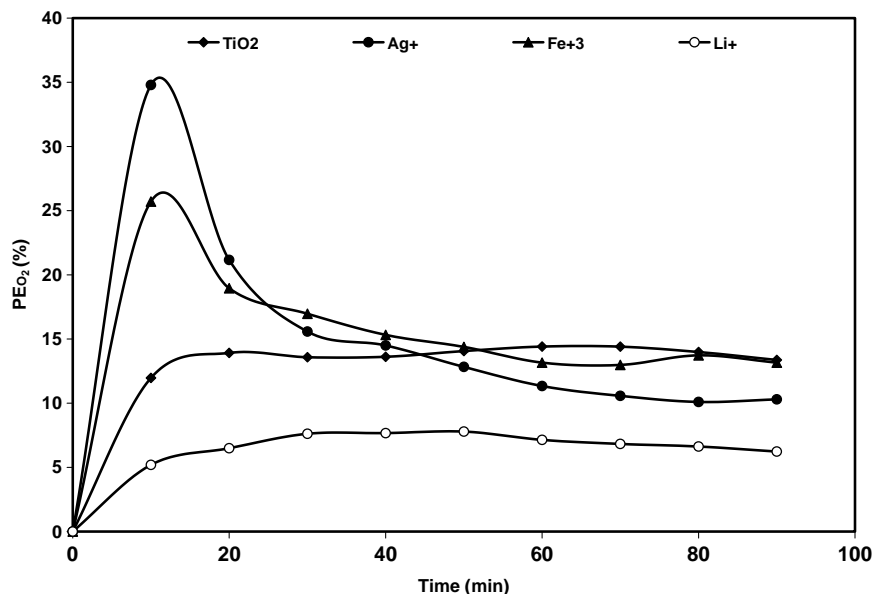


Fig. 15. Photonic efficiency of oxygen production over TiO₂ in the presence of metal ions.

4. Conclusions

It was observed that both NiO and TiO₂ undergo reduction with the absorption of 355 nm UV photons. The absorption of photons induces the release of lattice oxygen with the induction of bulk defects in both catalysts. The measurement of pH changes during illumination was found very useful in explaining the contribution of various reactions in the evolution of H₂ and O₂, with or without metal ions. Although with the reduction of the catalyst by the absorption of high UV photon flux, the stoichiometry of hydrogen and oxygen production was lost, an overall increase in the activity of NiO and TiO₂ was observed. The loss of stoichiometry could be due to the structural changes in the catalyst, which cause additional release of oxygen. Despite the creation of defect sites, both NiO and TiO₂ were found stable during the illumination and no photodecomposition either of anodic or cathodic type was observed.

Acknowledgements

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