# Photoreduction of nitrogen dissolved in water with hydrous oxides of samarium (III) and europium (III)

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The hydrous oxides of samarium (III) and europium (III) are found to catalyse photoreduction of dinitrogen dissolved in water. It is suggested that their activity depends on chemisorption of nitrogen and sufficiently negative flat band potential.

## 1. Introduction

A number of semiconductor materials in the particulate form are known to photogenerate hydrogen from water with concomitant oxygen evolution and/or formation of adsorbed oxygen [1-4]. In the presence of a sacrificial electron donor, the quantum yield of hydrogen evolution is greatly increased [1]. Few semiconductor photocatalysts are also known to have the ability to reduce dinitrogen dissolved in water [5-17]. Aqueous dispersions of TiO<sub>2</sub> are found to photogenerate less hydrogen when purged with nitrogen than argon. This was proved to result from some reduction of dinitrogen to ammonia. The photocatalytic reduction of dinitrogen to ammonia even at modest conversion efficiencies is of tremendous practical importance. If such a method is available, sunlight could be used to supplement irrigation waters with ammonia. Unfortunately, the photocatalytic nitrogen reduction is even more difficult to achieve than water photodecomposition, for the following reasons.

(1) The reduction of one molecule of dinitrogen via

$$N_{2} + 6 H^{+} + 6 e^{-} \rightarrow 2 NH_{3},$$
  

$$3 H_{2}O + 6 h^{+} \rightarrow \frac{3}{2}O_{2} + 6 H^{+},$$
(1)

involves transfer of six electrons, compared to two electrons in the reduction of water, i.e.,

$$2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^-,$$
  

$$2 OH^- + 2 h^+ \rightarrow H_2O + \frac{1}{2}O_2.$$
(2)

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Generally each photon transfers a single electron and the probability of six photons concentrating on one molecule is highly improbable.

(2) In the water photodecomposition reactions, the multi-electron transfer can be enhanced by loading the catalyst with platinum or other noble metals. In the case of nitrogen reduction, loading the catalyst with platinum interferes with nitrogen chemisorption. (In a platinum-coated catalyst, the reductions take place on platinum-coated sites. Nitrogen is poorly chemisorbed on platinum.)

(3) Photogenerated ammonia accumulates in the solution and participates in back reactions, e.g. oxidation to nitrogen, nitrite or nitrate.

(4) Unlike in water photodecomposition to hydrogen, the sacrificial electron donors generally does not increase the quantum yield. A likely reason is that the sacrificial agent interferes with nitrogen chemisorption.

(5) Dinitrogen chemisorption is a necessary requirement for catalytic activity. Most semiconductor catalysts that have sufficiently negative flat band potentials chemisorb dinitrogen poorly.

In order to increase the quantum yields of nitrogen reduction, it is necessary to search for new catalytic materials that chemisorb nitrogen strongly and at the same time having sufficiently negative flat band potentials. The spatial separation of oxidation and reduction sites in such a way that the reductions take place on nitrogen chemisorbing region would further enhance the quantum yields [16]. We have noted earlier, that the hydrous ferric oxide photocatalyst gives relatively higher yields of ammonia [10]. After examining a large number of other stable hydrous oxides we have noted that those of samarium (III) and europium (III) are also active towards photoreduction of nitrogen to ammonia. The yields are greater than those obtained with hydrous ferric oxide [10] under similar conditions.

## 2. Experimental

Hydrous samarium (III) and europium (III) oxides were prepared by gradual addition of excess 0.05M NaOH to a 0.05M solution of respective chlorides kept vigorously stirred. The semi-transparent gel of the hydrous oxide was washed and separated by centrifuging. As these catalysts denature upon drying and cannot be weighed, the volume of solution used to make the precipitate was taken as a measure of the catalyst employed. The catalyst made from 25 ml of XCl<sub>3</sub> (X = Sm or Eu) was dispersed in a thermosatted (26°C) immersion-well-type photochemical reactor of volume 300 ml. A medium pressure mercury lamp (400 W) mounted at the central axis of the reactor was the irradiation source. During photolysis the solution (275 ml) in the reactor was kept continously purged with nitrogen (99.999%) at a bubbling rate of 120 ml min<sup>-1</sup>. The solutions subject to irradiation for different intervals of time were made strongly alkaline with NaOH and distilled. Ammonia concentration in the distillate was estimated spectrophotometrically by the indophenol blue method. The residue was tested for nitrate and nitrite. All reagents used were tested for ammonia and nitrate. When the experiment was carried out in

dark with  $N_2$  purging, the level of ammonia observed was taken as the zero standard. Furthermore, the ammonia concentration obtained when the solution was irradiated while purging argon came close to the above zero standard. Hydrogen evolution during photolysis was determined by gas chromatography (Shimadzu GC-9AM gas chromatograph; carrier gas Ar). Oxygen evolution was tested by carrying out photolysis in a reaction vessel provided with a polarographic detector (Applied Photophysics) for monitoring the oxygen concentration. This method is more reliable as gas chromatography always leads to some atmospheric oxygen contamination.



Fig. 1. Time variation of the ammonia yield at pH 10 from (a)  $\text{Sm}_2O_3 \cdot [H_2O]_n$ , (b)  $\text{Eu}_2O_3 \cdot [H_2O]_n$ ; (c) nitrate yield from  $\text{Eu}_2O_3 \cdot [H_2O]_n$  (the catalyst used was made by hydrolysis 25 ml of 0.05M solutions of Sm(III) and Eu(III) chlorides).

### 3. Results and discussion

Fig. 1 shows the yield of ammonia from the catalysts  $\text{Sm}_2O_3 \cdot [H_2O]_n$  and  $\text{Eu}_2O_3 \cdot [H_2O]_n$  when the pH of the solution is ~ 10. The optimum yields were obtained at this pH. Existence of an optimum pH can be understood. Thermodynamically, the N<sub>2</sub> reduction reaction is favoured by a high concentration of H<sup>+</sup> ions (i.e., low pH). However, the flat band potential increases in the negative direction favouring N<sub>2</sub> reduction at higher pHs. These two opposing effects lead to an optimum pH.

The same behaviour is seen in nitrogen reduction with other semiconductor catalysts [10]. A feature common to both catalysts is, that the ammonia concentra-



Fig. 2. Hydrogen photogeneration from aqueous suspensions of (a)  $\text{Sm}_2O_3 \cdot [\text{H}_2O]_n$  saturated with Ar, (b)  $\text{Sm}_2O_3 \cdot [\text{H}_2O]_n$  saturated with N<sub>2</sub>, (c)  $\text{Eu}_2O_3 \cdot [\text{H}_2O]_n$  saturated with Ar, (d)  $\text{Eu}_2O_3 \cdot [\text{H}_2O]_n$  saturated with N<sub>2</sub> (the quantity of catalyst used as in given in the caption of fig. 1).



Fig. 3. Hydrogen photogeneration from 20% solution of ethanol with the catalysts (a)  $\text{Sm}_2O_3 \cdot [H_2O]_n$ , (b)  $\text{Ti}O_2$ , (c)  $\text{Eu}_2O_3 \cdot [H_2O]_n$ .

tion in the solution rapidly increases, reaches a maximum in about 4-6 h and then gradually decreases (fig. 1). The nitrate concentration in the solution shows opposite behaviour (fig. 1); in the initial phase it is negligible and then rapidly increases with a concomitant decrease in the ammonia concentration. In the experiments with the polarographic detector, a feeble oxygen signal is detectable, but the yield is far below the stoichiometry of eq. (1). This indicates that the photogenerated oxygen is preferentially adsorbed on the catalyst. Presumably, nitrate is generated via oxidation of ammonia by the adsorbed oxygen. Both catalysts liberate hydrogen from water under irradiation, argon saturated solutions give higher yields than nitrogen purged solutions as expected (fig. 2). Under sacrificial conditions (e.g., in the presence of ethanol), the hydrogen yield is drastically increased (fig. 3). In fact  $Sm_2O_3 \cdot [H_2O]_n$  is even superior to  $TiO_2$  in this respect (fig. 3). Anhydrous oxides



Fig. 4. Absorption spectra of aqueous suspensions of (a)  $\text{Sm}_2\text{O}_3 \cdot [\text{H}_2\text{O}]_n$  and (b)  $\text{Eu}_2\text{O}_3 \cdot [\text{H}_2\text{O}]_n$ .

 $Sm_2O_3$ ,  $Eu_2O_3$  are found to be almost completely inactive towards  $N_2$  reduction or  $H_2$  photogeneration. Again upon of platinization hydrous oxides loose photocatalytic activity. The absorption spectra of aqueous suspensions of the two hydrous oxides are shown in fig. 4. There is clear evidence for a absorption band edge at 330 and 290 nm, respectively, for  $Sm_2O_3 \cdot [H_2O]_n$  and  $Eu_2O_3 \cdot [H_2O]_n$ . When the electrical on-set potentials of two materials coated on platinum foil was investigated, they were found be slightly more negative than  $TiO_2$  (anatase), indicating their ability to carry out  $H_2$  photoproduction and  $N_2$  photoreduction reactions. Undoubtedly just as the hydrous ferric oxide, these two materials are also chemisorbing dinitrogen well. Hydrous oxides having layered structure are known to adsorb dinitrogen and assists its reduction [18–21]. It has been suggested that in these materials, dinitrogen is initially reduced unstable diazene ( $N_2H_2$ ). The layered structure of the hydrous oxide lattice is believed to allow entrance of  $N_2$  but not free OH that rapidly attack diazene.

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