Second Letter

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Edwards et al.[1] in their communication in essence convey the impression that the photoreduction of dinitrogen on heterogeneous photocatalysts is thermodynamically close to impossible and that the ammonia yields observed by previous workers[2, 3] may have been due to erroneous measurements of background contamination.

The authors furthermore claim to have conducted numerous experiments with promising photocatalysts under conditions identical to those used by the earlier investigators. This is actually not quite true. For example, Edwards et al. performed their experiments in quartz, rather than Pyrex vessels and employed, a medium-pressure Hg lamp; accordingly, the relative contribution of short UV light was higher than in the experiments conducted by us and most other workers in the field. Furthermore, and more seriously, the majority of the experiments seem to have been done with solids that would be expected to have little or no photocatalytic activity. Thus, Edwards et al. performed most of their experiments with "binary oxide xerogels" composed of TiO_2, Fe_2O_3, NiO, Al_2O_3, and SiO_2, which we would judge to have little chance of being photoactive in the first place. Only very few experiments were actually performed with iron-doped TiO_2 under conditions where nitrogen photoreduction could have taken place. In these experiments, the Fe–TiO_2 photocatalysts must first be heat-treated at defined temperatures and for known periods of time and subsequently stored in humid air. From the information given, it is our impression that the authors did not spend enough time and effort to optimize the photocatalyst pretreatment conditions. It should be recalled that only homogeneous samples having Fe^{3+} ions in the lattice of TiO_2 are photoactive. Heterogeneous samples, that is, those in which the surface is covered by iron oxides, or those with mixed iron–titanium oxides such as Fe_2TiO_5 on the surface, are photochemically completely inactive. The heat treatment temperature must be chosen so that the anatase–rutile conversion does not occur too rapidly. Prolonged heating at temperatures that are too high produces large crystals of low or zero photocatalytic activity. The optimal heating temperatures and times must be determined for each batch, as both vary from sample to sample, and numerous samples must be prepared and tested individually prior to the actual photoreduction experiments.

Based on the evidence provided, we can only conclude that Edwards et al. probably never had active photocatalysts at their disposal. Furthermore, we must point out that their discussion of the thermodynamics of dinitrogen photoreduction is also seriously flawed and misleading. They argue that the yields would have to be "absurdly low" (on the order of 10^{-50} M with respect to NH_3 or O_2) in view of the unfavorable thermodynamic equilibrium concentrations of the reactants. This reasoning is naive inasmuch as many thermodynamically "uphill" reactions involving TiO_2 are already well documented. Best known among these is the water splitting reaction (a).[4]

$$3\,H_2O + h\nu \rightarrow 3\,H_2 + 3/2\,O_2 \qquad \text{(a)}$$

This reaction is possible because the potential corresponding to the band gap in TiO_2 (E_{cb}) is negative vs. the normal hydrogen electrode (NHE) ($E_{cb} < E_{H^+/H_2}$), for any pH value. From the Pourbaix diagram,[5] the reduction potential E_{N_2/NH_3} is positive vs. NHE ($E_{N_2/NH_3} > E_{H^+/H_2}$). Since the formation of NH_3, according to Equation (b) is known, it follows that, irrespective of mechanism, the photoreduction of N_2, according to Equation (c) in feasible given TiO'_2 band gap energies.

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 \qquad \text{(b)}$$

$$N_2 + 3\,H_2O + h\nu \rightarrow 2\,NH_3 + 3/2\,O_2 \qquad \text{(c)}$$

Last but not least, we must reject the suggestion that our NH_3 yields were due to background contamination. This source of error was always safely eliminated by conducting blank experiments either in the absence of photocatalyst or in the dark.

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[3] J. Soria, J. C. Conesa, V. Augugliaro, L. Palmisano, M. Schiavello, A. Sclafani, *J. Phys. Chem.* **1991**, *95*, 274.

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[5] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, London, **1966**, p. 496.

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