

Second Letter

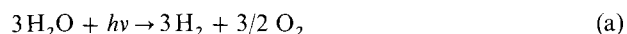
By *Leonardo Palmisano, Mario Schiavello,* and Antonino Sclafani*

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 TiO₂, Fe₂O₃, NiO, Al₂O₃, and SiO₂, 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 TiO₂ under conditions where nitrogen photoreduction could have taken place. In these experiments, the Fe–TiO₂ 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 Fe³⁺ ions in the lattice of TiO₂ 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 Fe₂TiO₅ 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.

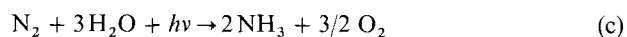
Based on the evidence provided, we can only conclude that Edwards et al. probably never had active photocatalysts at their disposal. Furthermore, we must point out that their discussion of the thermodynamics of dinitrogen photoreduction is also seriously flawed and misleading. They argue that the yields would have to be "absurdly low" (on the order of 10^{−50} M with respect to NH₃ or O₂) in view of the unfavorable thermodynamic equilibrium concentrations of the reactants. This reasoning is naive inasmuch as many thermodynamically "uphill" reactions involving TiO₂ are already well documented. Best known among these is the water splitting reaction (a).^[4]



This reaction is possible because the potential corresponding to the band gap in TiO₂ (E_{cb}) is negative vs. the normal hydrogen electrode (NHE) ($E_{\text{cb}} < E_{\text{H}^+/\text{H}_2}$), for any pH value. From the Pourbaix diagram,^[5] the reduction potential $E_{\text{N}_2/\text{NH}_3}$ is positive vs. NHE ($E_{\text{N}_2/\text{NH}_3} > E_{\text{H}^+/\text{H}_2}$). Since the formation of NH₃, according to Equation (b) is known, it fol-



lows that, irrespective of mechanism, the photoreduction of N₂, according to Equation (c) is feasible given TiO₂ band gap energies.



Last but not least, we must reject the suggestion that our NH₃ 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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