

# Visible light decomposition of ammonia to dinitrogen by a new visible light photocatalytic system composed of sensitizer ( $\text{Ru}(\text{bpy})_3^{2+}$ ), electron mediator (methylviologen) and electron acceptor (dioxygen)

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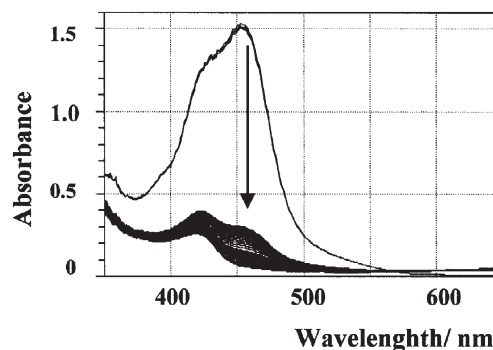
Visible light decomposition of aqueous ammonia to dinitrogen was successfully achieved by using a new photocatalytic system based on a molecular photoelectron relay composed of a sensitizer ( $\text{Ru}(\text{bpy})_3^{2+}$ ), an electron mediator (methylviologen) and an electron acceptor (dioxygen), which can be used as a visible light-driven photocatalyst instead of UV-driven semiconductors.

Because of the increasing amount of livestock waste, a number of studies have been carried out to establish an effective waste-treatment system for the protection of local and global environments from water pollution.<sup>1–3</sup> In particular, a methane fermentation system has been extensively developed to diminish the chemical and biological oxygen demand (COD and BOD) from cattle waste slurry.<sup>4</sup> Digestion gas (biomass gas) from the fermentation system has been used as fuel for the production of electricity. Thus, the methane fermentation system is regarded as one of the promising methods not only for diminution of COD and BOD but also for creation of biomass energy from waste slurry. In recent years, emission of  $\text{NO}_3^-$  from livestock waste has been recognized as a serious pollutant of ground and surface water.<sup>5,6</sup> Nitrate ions are the products from enzymatic oxidation of  $\text{NH}_3$  that originates from the urea in livestock waste by the enzymatic reaction of urease emitted from microorganisms. Removal and collection of  $\text{NH}_3$  from the cattle waste slurry before methane fermentation can contribute to the prevention of high-level nitrate pollution of surface and ground water.

In an earlier study,  $\text{TiO}_2$  was found to photoelectrochemically decompose water under UV light irradiation,<sup>7</sup> and since then many organic and inorganic compounds have been decomposed by this photocatalyst.<sup>8–10</sup> The photodecomposition of ammonia in neutral water has been reported by using  $\text{TiO}_2$ -supported Pt or Pd catalysts, and nitrogen (and nitrogen oxides) were obtained.<sup>11</sup>  $\text{TiO}_2/\text{Pt}$  decomposed aqueous ammonia into nitrogen, while pure  $\text{TiO}_2$  decomposed  $\text{NH}_3$  into nitrite and nitrate.<sup>12</sup> Some reports are found on the photodecomposition of ammonia with  $\text{TiO}_2$  in the gas phase.<sup>13,14</sup> UV light decomposition of ammonia by platinized  $\text{TiO}_2$  was achieved to produce  $\text{N}_2$ .<sup>15</sup> However, visible light conversion of ammonia into nitrogen has not been reported both in liquid and gas phases. The present authors have found that an aqueous solution of ammonia can be photochemically converted by UV irradiation into nitrogen and hydrogen with a nearly stoichiometric 1 : 3 ratio (volume) by using a platinized titanium dioxide ( $\text{TiO}_2$ ) suspension.<sup>16</sup> Many attempts at the sensitization of

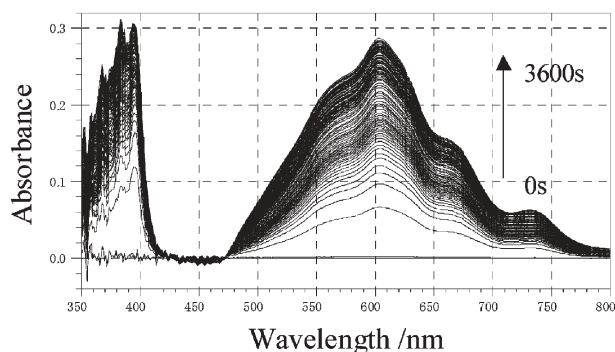
$\text{TiO}_2$  or other large bandgap semiconductors in order to use visible light which is abundant in solar irradiation have been conducted,<sup>4</sup> but a wavelength capable of being utilized and the catalytic activity have not been satisfactory enough. To create a new visible light photocatalyst based on molecules instead of semiconductors, the present authors attempted to construct a photocatalytic system using a dye sensitizer, and have had success in photodecomposing aqueous ammonia with visible light into  $\text{N}_2$  by use of a photocatalyst composed of a sensitizer ( $\text{Ru}(\text{bpy})_3^{2+}$ ), an electron mediator (methylviologen) and an electron acceptor ( $\text{O}_2$ ); the first results are reported in this paper.

A 5 ml aqueous solution of 0.1 mM  $\text{Ru}(\text{bpy})_3^{2+}$ , 10 mM  $\text{K}_2\text{S}_2\text{O}_8$ , and 3 M  $\text{NH}_3$  was prepared. The solution was put in a 10 ml cylindrical cell, and deaerated by bubbling argon gas for 30 min. The cell was irradiated in a horizontal direction with visible light either by a 500 W xenon lamp with UV cutoff (L-42) and IR cutoff filters (IRA-25S) (light intensity  $101 \text{ mW cm}^{-2}$ ) for spectral measurements (Figs. 1 and 2), or by visible light from a 100 W halogen lamp without filters (light intensity  $167 \text{ mW cm}^{-2}$ ) for gaseous product analysis (Fig. 3). During irradiation on the above mixture by the halogen lamp, gas bubbles were clearly observed, and after 1 h irradiation, 220  $\mu\text{l}$   $\text{N}_2$  was formed by the decomposition of  $\text{NH}_3$ .  $\text{H}_2$  was not formed in this system since electron accepting  $\text{K}_2\text{S}_2\text{O}_8$  was used in this mixture. It was confirmed by each blank experiment that both the Ru complex and  $\text{K}_2\text{S}_2\text{O}_8$  as well as visible light photoirradiation were needed for the  $\text{N}_2$  formation from  $\text{NH}_3$ . The gaseous products were

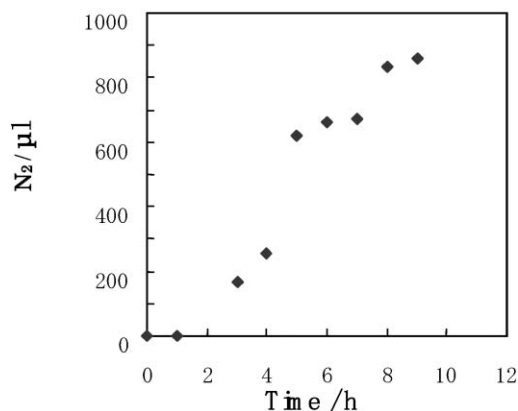


**Fig. 1** *In situ* visible absorption spectral change of the aqueous solution, 1 mM  $\text{NH}_3$ , 0.1 mM  $\text{Ru}(\text{bpy})_3^{2+}$  and 10 mM  $\text{K}_2\text{S}_2\text{O}_8$ , at pH 5.3, under visible light irradiation from a 500 W xenon lamp through a UV cutoff filter (L-42) and IR cutoff filter (IRA-25S) with a light intensity of  $101 \text{ mW cm}^{-2}$ . The spectrum was measured with a 5 s interval, total photoreaction time being 600 s after starting irradiation.

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**Fig. 2** *In situ* visible absorption spectral change of the aqueous solution, 3 M  $\text{NH}_3$ , 0.1 mM  $\text{Ru}(\text{bpy})_3^{2+}$  and 10 mM  $\text{MV}^{2+}$ , at pH 12.3, under irradiation from a 500 W xenon lamp through a UV cutoff filter (L-42) and IR cutoff filter (IRA-25S) with a light intensity of  $101 \text{ mW cm}^{-2}$ . Measured by taking the absorption of the solution before irradiation as the base line of the spectra.



**Fig. 3** Time dependent evolution of  $\text{N}_2$  for the mixture  $\text{NH}_3$  (10 M),  $\text{Ru}(\text{bpy})_3^{2+}$  (0.1 mM) and  $\text{MV}^{2+}$  (10 mM) under  $\text{O}_2$  atmosphere. Irradiated by a 100 W halogen lamp without filter, with a light intensity of  $167 \text{ mW cm}^{-2}$ .

analyzed by a gas chromatograph (Shimadzu, GC4C-PT) with a 13X-D molecular sieve column at  $80^\circ\text{C}$  using argon carrier gas. All the measurements and photochemical reactions were carried out at  $25^\circ\text{C}$ .

The irradiation of the aqueous solution of  $\text{NH}_3$  and  $\text{Ru}(\text{bpy})_3^{2+}$  by visible light in the presence of  $\text{K}_2\text{S}_2\text{O}_8$  induced the formation of  $\text{Ru}(\text{bpy})_3^{3+}$  by oxidation of the photoexcited Ru complex by  $\text{K}_2\text{S}_2\text{O}_8$ . This photochemical reaction was monitored *in situ* under irradiation by the visible absorption spectral change of the aqueous solution of  $\text{NH}_3$ ,  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{K}_2\text{S}_2\text{O}_8$  using a Shimadzu Multispeck 1500 diode array UV-Vis spectrophotometer according to our cell design<sup>17</sup> as shown in Fig. 1 where the absorption peak at 452 nm due to the  $\text{Ru}(\text{bpy})_3^{2+}$  disappeared quickly on irradiation with a simultaneous increase of the peak at 420 nm due to the formation of  $\text{Ru}(\text{bpy})_3^{3+}$ . By a separate experiment it was confirmed that  $\text{NH}_3$  does not quench the photoexcited  $\text{Ru}(\text{bpy})_3^{2+}$  at all. The following oxidation of ammonia by the photochemically formed 3+ Ru complex would not be rapid since, under steady state conditions during irradiation, the 3+ Ru complex was the predominant species. It was also confirmed by a separate experiment that  $\text{NH}_3$  decomposes into  $\text{N}_2$  by  $\text{Ru}(\text{bpy})_3^{3+}$ .

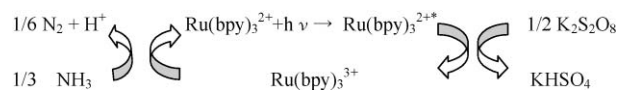
It is therefore concluded that the reaction occurs by the photochemical oxidation of the Ru(II) complex to Ru(III) by  $\text{K}_2\text{S}_2\text{O}_8$ , leading to the following degradative oxidation of  $\text{NH}_3$  by the Ru(III) complex to yield  $\text{N}_2$  (Scheme 1).

In order to develop a visible light-driven photocatalyst based on molecules instead of UV light-driven semiconductors, an electron mediator was used in combination with an  $\text{O}_2$  electron acceptor with a sensitizer (here  $\text{Ru}(\text{bpy})_3^{2+}$ ). It is interesting that methylviologen, a well-known mediator for proton reduction towards  $\text{H}_2$  evolution,<sup>8–10</sup> can work as an electron acceptor to produce  $\text{N}_2$  as follows. At first the photochemical reaction of an aqueous mixture of  $\text{NH}_3$  (3 M, ca. 5%),  $\text{Ru}(\text{bpy})_3^{2+}$  (0.1 mM) and methylviologen ( $\text{MV}^{2+}$ ) (10 mM) (at pH = 12.3) was investigated by *in situ* visible absorption spectroscopy<sup>11</sup> during photoirradiation. The *in situ* visible absorption spectrum under irradiation of the above mixture is shown in Fig. 2.

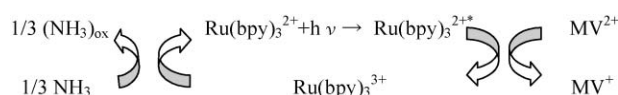
The formation of the viologen cation radical ( $\text{MV}^+$ ) having absorption maxima at 395 and 603 nm was clearly observed. However,  $\text{N}_2$  formation was not observed under this condition. Because of the fact that (1)  $\text{NH}_3$  did not quench the photoexcited  $\text{Ru}(\text{bpy})_3^{2+}$  complex, and (2) electron transfer from the photoexcited  $\text{Ru}(\text{bpy})_3^{2+}$  to  $\text{MV}^{2+}$  has been well established,<sup>8–10</sup> it can be concluded that in the above system methylviologen works as an acceptor from the photoexcited Ru complex in place of  $\text{K}_2\text{S}_2\text{O}_8$  to produce the viologen cation radical: ammonia works as an electron donor to the formed  $\text{Ru}(\text{bpy})_3^{3+}$  resulting in the accumulation of an oxidized product of ammonia ( $(\text{NH}_3)_{\text{ox}}$ , Scheme 2).

As for a candidate for  $(\text{NH}_3)_{\text{ox}}$ , hydrazine or  $\text{NH}_3^+$  might be possible. However, the mixture of hydrazine,  $\text{Ru}(\text{bpy})_3^{2+}$  and  $\text{MV}^{2+}$  produced  $\text{MV}^+$  very rapidly and  $\text{N}_2$  also was formed both under dark and illumination, so that hydrazine would not be possible as the  $(\text{NH}_3)_{\text{ox}}$  species. By stopping photoirradiation on the mixture shown in Scheme 2, about a 10% decrease of the absorbance by  $\text{MV}^+$  was observed showing that all the components in the mixture are most probably in a dynamic equilibrium state under irradiation. The structure of  $(\text{NH}_3)_{\text{ox}}$  is a subject to be investigated in the future. In the reaction of Scheme 2 the presence of Pt catalyst (a suspension of platinum black fine powder) in the solution did not induce  $\text{H}_2$  formation since the pH of the solution was basic due to the  $\text{NH}_3$ . However, Scheme 2 shows that  $\text{NH}_3$  was photochemically decomposed into an oxidized product ( $(\text{NH}_3)_{\text{ox}}$ ) by accumulating  $\text{MV}^+$ , the latter of which is capable of reducing protons to  $\text{H}_2$  by decreasing the pH to neutral or to acidic conditions.

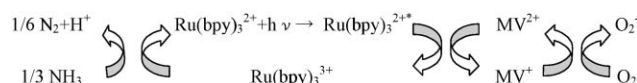
It is important that the presence of  $\text{O}_2$  in this system induced  $\text{N}_2$  evolution (Scheme 3) as a result of  $\text{MV}^+$  oxidation to  $\text{MV}^{2+}$ . For instance, irradiation of an aqueous solution of  $\text{NH}_3$  (10 M),



**Scheme 1**



**Scheme 2**



Scheme 3

$\text{Ru}(\text{bpy})_3^{2+}$  (0.1 mM) and  $\text{MV}^{2+}$  (10 mM) under  $\text{O}_2$  atmosphere ( $\text{O}_2$  was bubbled for 30 min prior to the reaction) produced 860  $\mu\text{l}$   $\text{N}_2$  after 9 h without accumulating  $\text{MV}^+$ . After the photochemical reaction in the absence of  $\text{O}_2$  (Scheme 2), the predominant species are  $\text{MV}^+$ ,  $(\text{NH}_3)_{\text{ox}}$ , and  $\text{Ru}(\text{bpy})_3^{2+}$  as evidenced by the spectra shown in Fig. 2 for which the spectrum of the mixture before irradiation was taken as a base line for the spectral change (note that if the  $\text{Ru}(\text{III})$  complex is present, the absorbance around 450 nm should be decreased to a negative level). The presence of  $\text{O}_2$  (Scheme 3) oxidizes the  $\text{MV}^+$  very quickly to  $\text{MV}^{2+}$  to accumulate the  $\text{Ru}(\text{III})$  complex which then oxidizes  $(\text{NH}_3)_{\text{ox}}$  further to  $\text{N}_2$ .

The time dependent  $\text{N}_2$  evolution by the process depicted in Scheme 3 is shown in Fig. 3. It shows an induction period for  $\text{N}_2$  evolution, which could be interpreted by either or both a slow accumulation of  $\text{Ru}(\text{bpy})_3^{3+}$  and/or slow reaction of  $(\text{NH}_3)_{\text{ox}}$  with the accumulated  $\text{Ru}(\text{bpy})_3^{3+}$ . The turnover number of  $\text{MV}^{2+}$  was calculated to be 4.2, and that for the Ru complex 420 per 9 h supporting the photocatalytic reaction of Scheme 3. The presence of suspended fine powders of  $\text{IrO}_2$  dramatically enhanced the  $\text{N}_2$  evolution rate by more than one order of magnitude.

Ammonia was thus photochemically decomposed into  $\text{N}_2$  in the presence of a strong acceptor ( $\text{K}_2\text{S}_2\text{O}_8$ ) by visible light (Scheme 1). Moreover,  $\text{NH}_3$  was photochemically converted into an oxidized product by reducing  $\text{MV}^{2+}$  to  $\text{MV}^+$  by visible light (Scheme 2). The presence of  $\text{O}_2$  in Scheme 2 induced visible light decomposition of ammonia to  $\text{N}_2$  by a photocatalytic reaction (Scheme 3). This system shown in Scheme 3 could solve the biomass waste problem by using visible light in relevance to treatment of nitrogen compounds as well as the ammonia pollutant problem in our daily life, and would lead to a solar (visible light) artificial nitrogen cycle.

Use of this kind of visible light-induced electron relay system as a photocatalyst would in principle be possible also by using solid state materials as revealed by our earlier work reporting the photoinduced solid state electron relay from EDTA via the

photoexcited  $\text{Ru}(\text{bpy})_3^{2+}$  to  $\text{MV}^{2+}$  in a cellulose matrix.<sup>18</sup> Such a molecule-based photocatalyst can exhibit the same function as semiconductor photocatalysts, working not only by UV light but also under visible light, which could promise a large variety of design and applications not only for livestock waste treatment but also for other photocleaning of the environment in the near future.

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