Semiconductor Photocatalysis:[†] Quantised CdS-catalysed Photoformation of 1-Benzyl-1,4-dihydronicotinamide (BNAH) from 1-Benzylnicotinamide (BNA⁺)

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Freshly pepared CdS suspensions (CdS-0) consisting of quantised particles and their loose aggregates catalyse the photoreduction of 1-benzylnicotinamide (BNA⁺) in water under visible-light irradiation using triethylamine (TEA) as a sacrificial electron donor. Isomeric dimers of $(BNA)_2$ are also found as one-electron reduction products from BNA⁺, whereas the photocatalysis of commercially available CdS powder (Aldrich, CdS-Ald) leads only to the formation of the dimers. The formation of cadmium metal (Cd^o) on the lattice is indispensable for the photoformation of BNAH, suggesting that the eventual two-electron reduction on irradiation of CdS-0 with TEA in water, should proceed through hydrogen atom transfer from Cd^o—H formed on the lattice of CdS-0.

Recently, we reported that a freshly prepared colloidal CdS suspension (CdS-0) catalyses the two-electron photoreduction of aromatic ketones and electron-deficient alkenes to the corresponding alcohols and alkanes,^{1,2} and that photogenerated Cd^O on the lattice acts as the catalytic site for the twoelectron transfer reduction.¹ As for the role of Cd^O on the lattice, two possibilities have been proposed: (1) Sequential electron transfer assisted by a strong interaction between Cd^O and an electron deficient carbonyl or carbon–carbon double bond. (2) The formation of Cd^O–H and hydrogen atom transfer from the Cd^O–H.

On the other hand, since the redox couple NADH/NAD⁺ represents extremely important coenzymes in biological systems, there has been a long-standing interest in the chemical reaction of NADH and NADH analogues in enzyme-free systems. In particular, the construction of the photochemical two-electron reduction of NAD⁺ to NADH has been studied as a key step to artificial photosynthesis. Although there are several reports on enzymatic systems³ or rhodium-bipyridine complexes,⁴ the two-electron reduction of NAD⁺ or NAD⁺ analogues has been tried in vain in non-enzymatic systems. This is because NAD⁺ analogues give mainly dimers in a system involving an electron-transfer process, as exemplified by the electrochemical reduction⁵ -1.1 V vs. SCE to give the dimer $[(NAD)_2]$. It is well known, however, that NAD^+ analogues are formed by attack of hydride ions.^{5c} In other words, when NAD^+ is employed as a reducing substrate, analysis of the reduction products can provide important information on the mechanism of the eventual two-electrontransfer reduction system.

With this in mind, we expanded the CdS-0-catalysed system to a study of the reduction of 1-benzylnicotinamide (BNA^+) . The present report concerns photoreduction of

[†] Part 14: N. Kanemoto, K. Isihara, Y. Wada, T. Sakata, H. Mori and S. Yanagida, *Chem. Lett.*, 1992, 835. BNA^+ to BNAH and isomeric $(BNA)_2$ as shown in Scheme 1, and also deals with the relationship between the BNAH formation and Cd^0 photoformed on the lattice of quantised CdS by two-electron reduction on a CdS-0–Cd⁰ surface.

Experimental

Materials

Very pure (99.999%) CdS powder was obtained from Aldrich (CdS-Ald). The crystal form was hexagonal, and the average particle size was 1.5 μ m. Cadmium perchlorate [Guaranteed Reagent (GR) grade] from Mitsuwa and sodium sulfide (GR grade) from Nacalai Tesque were used as supplied. 1-Benzylnicotinamide chloride (BNA⁺Cl⁻), 1-benzyl-1,4-dihydronicotinamide (BNAH) and the dimer of BNA⁺ [(BNA)₂] were prepared and purified according to the literature method.^{5d} Methyl viologen dichloride was GR grade from Nacalai Tesque. Triethylamine (TEA) was purified by fractional distillation before use.

Analysis

Determination of BNA⁺, BNAH and (BNA)₂ was carried out by liquid chromatography using a Cosmosil-ODS column (4.6 cm × 250 mm), and UV detector at 230 nm (BNA⁺) and at 355 nm [BNAH, (BNA)₂] (Toso; UV-8000). A 6:4 mixture of methanol and a buffered aqueous solution (KH₂PO₄-NaOH; pH 7) was used as eluent with an eluent rate of 0.4 ml min⁻¹. Determination of diethylamine was carried out by gas chromatography using a Shimadzu GC-7A apparatus equipped with a flame ionization detector, and a 2 m × 3 m column of ASC-L.

Preparation of the CdS-0 Photocatalyst

CdS-0 suspension was prepared *in situ* under an argon atmosphere by mixing equal amounts of aqueous solution



Scheme 1

 $(2.5 \times 10^{-2} \text{ mol dm}^{-3})$ of Cd(ClO₄)₂ and Na₂S with magnetic stirring and cooling with ice and water.

CdS-catalysed Photoreduction of BNA+

A stirred aqueous suspension containing CdS powder (70 μ mol) or CdS-0 (13 μ mol), BNA⁺ (1 mmol dm⁻³) and TEA (0.5 mol dm⁻³) was flushed with argon gas whilst cooling with ice, sealed with a rubber stopper and then irradiated with a 300 W tungsten-halogen lamp through an aqueous sodium nitrite solution filter ($\lambda > 400$ nm).

Determination of the Amount of Cd^o

The formation of Cd^O was determined by a previously reported method:^{1,6} the irradiated suspension (50 μ dm³) was added to a 1 mmol dm⁻³ aqueous solution of methyl viologen (MV²⁺) under an argon atmosphere. The blue colour of the methyl viologen radical cation (MV⁺) appears as Cd^O is reoxidised. The amount of Cd^O can be determined approximately from the absorption coefficient at 606 nm ($\varepsilon = 13700$ dm³ mol⁻¹ cm⁻¹) in the MV⁺ absorption spectrum.⁷

Results and Discussion

CdS-catalysed Photoreduction of BNA⁺: Dependence of BNAH Formation on Cd^o formation on the Lattice

We previously reported, from high-resolution transmission microscopy,^{1,8} that CdS-0 consists of quantised CdS microcrystallities (2–5 nm) and their loose aggregates and also that Cd^{O} is generated by pre-irradiation with TEA on the lattice of CdS-0.

Fig. 1 shows time-conversion plots for the photoreduction of BNA⁺ catalysed by freshly prepared CdS-0 and CdS-0-Cd where Cd⁰ was generated by pre-irradiation for 1 h in the presence of TEA. The abbreviation CdS-0-Cd means that Cd⁰ metal has already been deposited on the CdS-0 suspension before the photocatalytic reaction with BNA⁺ is carried



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Fig. 2 shows the result of CdS-Ald-catalysed photoreduction of BNA^+ . In this case, very little BNAH was formed and the main reaction is the formation of $(BNA)_2$. On continued irradiation, $(BNA)_2$ gradually disappears as observed in the CdS-0 system. In Table 1, the yields of BNAH and $(BNA)_2$ are summarised based on the conversion of BNA^+ by photolysis of CdS-0, CdS-0–Cd and CdS-Ald. Both CdS-0 and CdS-0–Cd had about fivefold the activity of CdS-Ald for the formation of BNAH.

Fig. 3 shows time-conversion plots for the formation of BNAH, $(BNA)_2$, Cd^0 and diethylamine (DEA), the oxidation product of TEA, in the photoreduction of BNA⁺ by CdS-0. Analysis of the oxidation products from TEA revealed that only DEA was detected during the photocatalysis. The formation of this compound can be explained by the hydrolysis of the iminium intermediate [$(CH_3CH=NEt_2)^+$] produced by the two-hole oxidation of TEA.^{9,10} As shown in Fig. 3, DEA was produced in parallel with the formation of reduction products, *i.e.* BNAH, (BNA)₂ and Cd⁰. However, the amount of DEA was found to be higher than that of the reduction products. A similar result was obtained for the CdS-Ald system. The discrepancy in electron balance is not



Fig. 1 Time-conversion plots for photoreduction of BNA⁺ catalysed (a) by CdS-0; (b) CdS-0-Cd for formation of (\bigcirc) BNAH, (\square) 4,4'-(BNA)₂ and (\triangle) 4,6'-(BNA)₂



Fig. 2 Time-conversion plots for photoreduction of BNA⁺ catalysed by CdS-Ald for formation of (\bigcirc) BNAH, (\square) 4,4'-(BNA)₂ and (\triangle) 4,6'-(BNA)₂

 Table 1
 CdS-catalysed photoreduction of BNA⁺ by TEA in water under visible light irradiation^a

CdS	conversion (%) BNA ⁺	yield of product (%) ^b	
		(BNA) ₂	BNAH
CdS-Ald	68	51	2
CdS-0	74	33	10
CdS-0Cd	72	48	13

^a Irradiated at >400 nm for 2 h. ^b Yields are based on BNA^+ converted.



Fig. 3 Relationship between reduction to (\bigcirc) BNAH and formation of (\bigcirc) BNAH, (\square) 4,4'-(BNA)₂, (\triangle) 4,6'-(BNA)₂, (\blacktriangle) Cd⁰ and (\bigcirc) DEA in the CdS-0 system

clear at present. Neither H_2 nor ethanol, which would be formed by the reduction of water or photoformed acetaldehyde,¹⁰ were detected. Ethylene, that may be formed by the decomposition of the intermediary iminium salt, and its reduction product, ethane, were also not detected.

The amount of Cd^o on the lattice was estimated by the formation of MV⁺ from MV²⁺ as reported previously.¹ At an early stage of the irradiation, Cd^o was formed in competition with the formation of (BNA)₂. Interestingly, the formation of Cd^o levels off after irradiation for 60 min and then the formation of BNAH was accelerated. This result demonstrates that there is a relationship between Cd^o and the formation of BNAH (cf. also Fig. 1). We have found already that the formation of Cd^{O} is inhibited on irradiation in the presence of an excess of S^{2-} . The photoreduction of ketones and alkenes by CdS-0 under such conditions does not lead to a two-electron reduction but only to a one-electron reduction.¹ Therefore, the photoreduction of BNA⁺ by CdS-0 was also carried out in the presence of excess S^{2-} (2.5 × 10⁻³ mol dm⁻³) in order to clarify the relationship between Cd^o formation and two-electron reduction of BNA⁺ (Fig. 4). As shown in Fig. 4, only a small amount of BNAH was formed without Cd^o formation, whereas the formation of (BNA)₂ shows a similar tendency in the absence of excess S^{2-} (cf. also Fig. 1). Furthermore, it was seen that BNAH was not decomposed by S^{2-} in water either with irradiation or in the dark.

These observations suggest strongly that Cd^{0} on the lattice forms a catalytic site for two-electron reduction of BNA⁺ to BNAH.

Photodecomposition of BNA Dimer Catalysed by CdS-0

The increase in the yield of BNAH accompanied by the decrease in the yield of $(BNA)_2$ cannot be ignored in the



Fig. 4 Time-conversion plots for photoreduction of BNA⁺ catalysed by CdS-0 in the presence of S^{2-} (5 mmol dm⁻³) for formation of (\bigcirc) BNAH, (\square), 4,4'-(BNA)₂ and (\triangle) 4,6'-(BNA)₂



Fig. 5 Time-conversion plots for photodecomposition of 4,4'-BNA₂ catalysed by CdS-0 for disappearance of $(\Box) 4,4'$ -(BNA)₂; isomerization to $(\triangle) 4,6'$ -(BNA)₂; reduction to (\bigcirc) BNAH

results shown in Fig. 1. In order to elucidate the relationship between the formation for BNAH and the decomposition of (BNA)₂, the CdS-0-catalysed photoreaction of 4,4'-(BNA)₂ was performed in the presence of TEA in water. As shown in Fig. 5, little BNAH is obtained in this system but the photoisomerization to 4,6'-(BNA)₂ proceeds efficiently at an early stage and the (BNA)₂ isomers are gradually decomposed on continued irradiation. Similar results were obtained in the presence of BNA⁺ alone and in the absence of TEA. CdS-Ald-catalysed photodecomposition of $4,4'-(BNA)_2$ showed similar trends to those of the CdS-0 system, although the rate of decomposition was much slower than for CdS-0. The decomposition of (BNA)₂ may be explained as an oxidation process via holes of CdS, because it was found that 4,4'-(BNA)₂ works as an effective electron donor for CdScatalysed photoreduction of MV^{2+} to MV^+ . This reaction, however, was very complex and some unidentified products were detected by high-performance liquid chromatography. Unfortunately, their structure is not clear at present. These results indicate clearly that the formation of BNAH does not occur via the decomposition of $(BNA)_2$. (See also Fig. 4.)

Mechanism of BNAH Formation on Cd^o Metal

In the electrochemical reduction of BNA^+ , the dimer $(BNA)_2$ was the major product.⁵ This fact suggests that the BNA radical (BNA⁺) formed by one-electron transfer to BNA^+ induces very rapid dimerization, leading to formation of $(BNA)_2$ isomers, and that the further electron transfer to BNA^+ cannot occur easily. Accordingly, the mechanism of BNAH formation cannot be explained by the successive two-

$$BNA^{+} \xrightarrow{e^{-}} BNA^{-} \xrightarrow{e^{-}} BNA^{-} \xrightarrow{H^{+}} BNAH$$
(1)
very fast x_{2}
(BNA)₂
CdS-Cd⁰(e⁻), CdS-Cd⁰(e⁻), H⁺ (1)

$$BNA^{*} \xrightarrow{\text{Odd Od}(2)} BNA^{*} \xrightarrow{\text{Odd Od}(2), \Pi} BNAH \qquad (2)$$

$$x_{2}$$

$$(BNA)_{2}$$

$$BNA^{\dagger} \xrightarrow{CdS(e^{\circ}) \text{ or } Cd^{0}-H} BNA^{\circ} \xrightarrow{Cd^{0}-H} BNAH \qquad (3)$$

$$| x 2$$

$$(BNA)_{2}$$
Scheme 2

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Fig. 6 Schematic diagram of CdS-0-catalysed photoreduction of BNA^+ with TEA as electron donor. VB = valence band. CB = conduction band.

electron transfer as shown in Scheme 2, eqn. (1). Since BNA^+ can easily be reduced to BNAH by hydride-forming reagents such as $NaBH_4$, it seems that BNAH formation should proceed via a reaction involving reductive species such as hydride ions or hydrogen atoms.

It has now been clarified that Cd^o carrying quantised CdS is effective for the two-electron reduction of BNA⁺, *i.e.* the formation of BNAH. There seem to be two possibilities as to how Cd^o mechanistically affects the formation of BNAH, as reported previously:¹ (1) Successive two-electron transfer through Cd^o as shown in Scheme 2, eqn. (2). (2) Hydrogenatom transfer from Cd^o-H possibly formed by a Volmer type of reaction as shown in Scheme 2, eqn. (3). As mentioned above, since eqn. (1) seems unreasonable to account for the formation of BNAH, we suggest that a two-electron reduction should proceed on Cd^o by the mechanism shown in eqn. (2). On a Cd^o surface, BNA[•] is first formed by direct electron transfer, the BNA' reacts with Cd^o-H to give BNAH, although a part of the BNA' dimerises by the coupling reaction [see Fig. 1(b)]. It has become apparent from the results of the CdS-0-catalysed photoreduction of BNA⁺ that the active species for the two-electron reduction on the CdS-0-Cd surface should be $Cd^{o}-H$.

Conclusion

As shown in Fig. 6, it has been demonstrated that photoformed electrons on quantised CdS can induce the formation of Cd^o on CdS-0 and the adsorption of a hydrogen atom on Cd^o (Cd^o—H), leading to the selective formation of BNAH from BNA⁺. CdS-0 in the presence of excess S^{2-} or bulk CdS crystallites, which never form Cd^o metal on the surface by irradiation, can induce direct one-electron transfer from the conduction band to BNA⁺, giving mainly (BNA)₂. To our knowledge, BNAH formation on a Cd^o cluster is the first example of a photochemical two-electron reducton of NAD⁺ analogues without using both an enzyme and a Rhbipyridine complex.

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