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Hybrid Technologies for an Enhanced Carbon Recycling Based on the Enzymatic Reduction of CO_2 to Methanol in Water: Chemical and Photochemical NADH Regeneration

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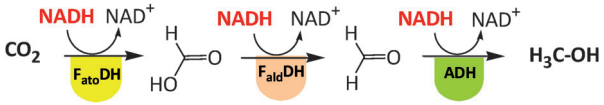
Our society lives the dilemma of the expansion of the demand for energy, while a dramatic reduction of CO_2 emission is urged for limiting the climate change. A substantial part (at least 80%) of the needed energy is obtained today from fossil carbon and, additionally, there are no alternatives available for next twenty years.[1] This is rising serious worries about the future of our Planet should the correlation of the increase of the temperature to the CO_2 emission continue. Technologies for the reduction of the immission of CO_2 into the atmosphere have been proposed. They encompass a number of possibilities, such as the improvement of the efficiency in the production (that requires large investment capitals) and use of energy,[2] the capture and storage of emitted carbon dioxide (CCS),[3] the use of perennial energy sources (solar, wind, water) and the use of renewables (biomass).[4] CCS has risen large expectations in the last ten years, but it is potentially site-related and energy intensive: it will have a net effect on expanding the extraction of fossil carbon, the intensity of which depends on the local conditions for CO_2 transportation to the disposal site and housing.

Besides such technologies, the utilisation of carbon dioxide as a carbon source for the synthesis of chemicals and fuels is under evaluation for its contribution to recycling carbon to mimic nature, with a consequent reduction of the extraction of fossil fuels.[5] Such an approach merges biological and chemical technologies for the development of new hybrid nanotechnologies.

An interesting case is the biotechnological reduction of CO_2 to methanol, which has applications as a raw chemical and fuel.[6] Such reduction occurs in water at room temperature and is promoted by three enzymes, namely formate dehydrogenase ($F_{ate}DH$), formaldehyde dehydrogenase ($F_{ald}DH$), and alcohol dehydrogenase (ADH), while the necessary energy is provided by nicotinamide adenine dinucleotide phosphate (NADH), which is oxidised to NAD^+. In nature, NAD^+ is reduced back to NADH through solar light; in a biotechnological application, such a reduction must be somehow performed by implementing the most energetically and economically convenient technologies.

Recently, we have faced the problems of: i) developing robust enzymes[7] and ii) reducing NAD^+ in situ to determine the extent to which NAD^+ can be recycled[8] to increase the ratio CH_3OH/NADH. This ratio is a key issue in defining whether a biotechnological production of methanol would be possible. In this paper, we report the preliminary result on the behaviour of some chemical and photochemical reducing systems[8] and show their potential for an effective recycling of NAD^+.

The enzymatic reduction of CO_2 in water, represented in Scheme 1, was first reported by Obert and Dave, who also reported the properties of the enzymes and showed that the three enzymes were deactivated in a short time.[9] An attempt



Scheme 1. CO_2 reduction to methanol in water promoted by $F_{ate}DH$, $F_{ald}DH$ and ADH.

to make more robust enzymes was made later[10] by encapsulating the enzymes into an hybrid matrix made of alginate and silicate obtained by reacting Ca-alginate with tetramethoxysilane (TMOS) in water. Hydrolysis of TMOS produced methanol and a cage of Ca-silicate, which blocked the enzymes without any apparent modification of their activity.[10] However, if TMOS is not completely hydrolysed before NADH is added, methanol can be formed that can be counted as methanol produced in the reduction of CO_2. We have verified that this may be the case by using $^{13}CO_2$ and $Si(O^{12}CH_3)_4$ in the encapsulation of the enzymes and measuring the amount of $^{12}CH_3OH$ and $^{13}CH_3OH$ collected after reduction of $^{13}CO_2$. Variable amounts of $^{12}CH_3OH$ (2–10% of the total) have been detected that cannot be formed from $^{13}CO_2$. To eliminate such parasitic formation of methanol, we have used $Si(OEt)_4$ (TEOS) as starting material for the formation of the encapsulating cage of the enzymes so that if incomplete hydrolysis of TEOS occurs ethanol is formed, which can be easily distinguished from methanol produced enzymatically from CO_2. Figure 1 shows the beads formed by co-encapsulation of the three enzymes.

We have also investigated, whether the co-encapsulation of the enzymes gives better results than the single encapsulation, or not. We have found that the use of singly encapsulated en-

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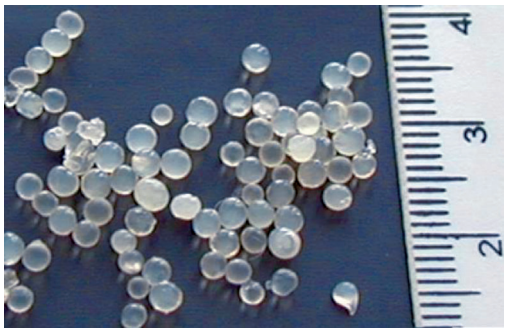


Figure 1. Beads produced from Ca-alginate and TEOS containing co-encapsulated $F_{ate}DH$, $F_{ald}DH$ and ADH.

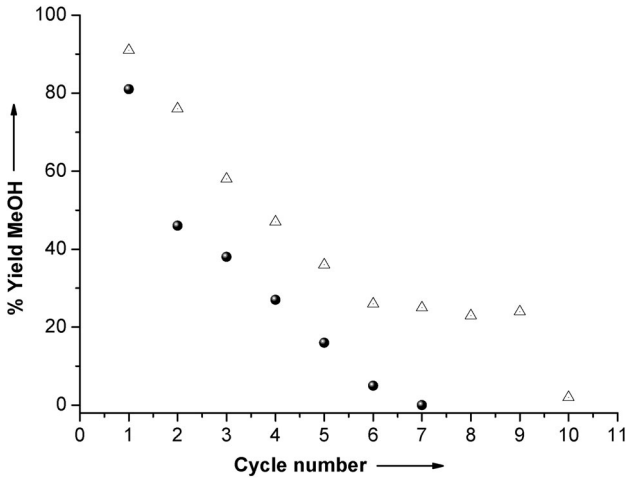
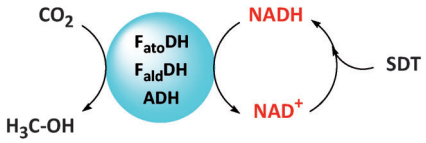


Figure 2. Methanol yield for CO_2 reduction by co-encapsulated enzymes, with NADH regeneration by NAD^+ reduction using SDT, conducting the two reactions in "one-pot" (●) and separately (△). SDT for in situ NADH regeneration was added in a 1:1 molar ratio with respect to NADH initially added. The reaction was conducted in 0.5 M TRIS·HCl [TRIS = tris(hydroxymethyl)aminomethane] buffer at pH 7 and 37 °C.

zymes reduces the rate of formation of methanol by 10–40% with respect to co-encapsulated enzymes, depending on the conditions and the amount of beads used.

Such co-encapsulated enzymes were used in experiments of the reduction of CO_2 coupled to regenerate NAD^+. The artificial reduction of NAD^+ to NADH can be performed in different ways by using: i) chemicals that act as reducing agents, ii) transition metal complexes coupled to various reducing agents including H_2, iii) semiconductors or metal systems that may use (solar) light as a source of energy for the reduction and iv) electrocatalysts that may reduce NAD^+ under electrochemical conditions.

For class (i) reagents inexpensive and easily affordable chemicals must be used. We have tested both hydrazine and sodium dithionite (SDT)[7] and have found that the latter is much more efficient than the former (Scheme 2).



Scheme 2. "One-pot" conversion of CO_2 into CH_3OH by co-encapsulated $F_{ate}DH$, $F_{ald}DH$ and ADH enzymes, with NAD^+ reduction to NADH using SDT.

Adding SDT slowly up to a stoichiometric amount [Eq. (1)] to NAD^+ after all NADH was oxidised to NAD^+ caused the reduction of NAD^+ into NADH that could reduce more CO_2. The reaction was followed by using UV-VIS at $\lambda = 344$ nm to monitor the amount of NADH and by evaluating the amount of CH_3OH formed.

$$NAD^+ + S_2O_4^{2-} + 2\,H_2O \rightarrow NADH + 3\,H^+ + 2\,SO_3^{2-} \qquad (1)$$

The conversion of CO_2 into CH_3OH after each addition of SDT to the pot, where CO_2 was bubbled through a suspension of beads in water in presence of NADH, is shown in Figure 2. After seven cycles, a total amount of 2.13 mol of CH_3OH per mol of starting NADH was formed (Figure 2, ●).

Evidently, although the addition of SDT increases the amount of CH_3OH formed per mol of NADH (the ratio CH_3OH/NADH grows from 0.33 to more than 2), the catalytic system is deactivated and after seven cycles it is dead. We have verified that the contact of SDT with the enzymes causes their rapid deactivation.

To avoid such detrimental contact, we have separated the oxidation of NADH and the reduction of NAD^+. After NAD^+ formation, the solution was separated from the beads, reacted with stoichiometric amounts of SDT and re-added to the beads: the life of the enzymes was prolonged, and CH_3OH was formed in higher amounts (Figure 2, △); more than 4.14 mol of CH_3OH per mole of NADH were formed.

In a further attempt to improve the system, we have modified the reaction apparatus and built a two-compartment reaction cell (Figure 3) so that the reduction of CO_2 occurs in compartment A, while the reduction of NAD^+ takes place in compartment B. Compartments A and B are separated by a sintered glass disc that reduces the back diffusion of the reagents

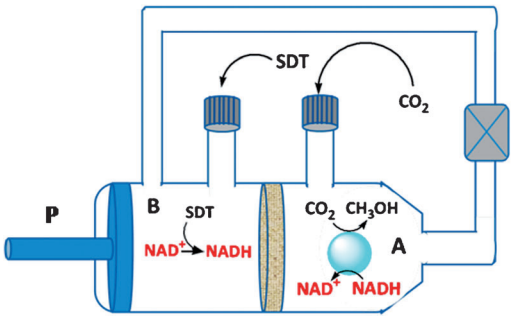


Figure 3. Two-compartment reactor for CO_2 reduction to methanol by co-encapsulated enzymes (compartment A) and NADH regeneration by SDT (compartment B). P is a plug for the transfer of the solution from B to A.

present in compartment B. A pump circulates the liquid from compartment B to A after the reduction of NAD^+ has occurred. Care must be taken in avoiding any excess of SDT in compartment B as it is brought to compartment A and may destroy the enzymes. In this way, the ratio $CH_3OH/NADH$ was further increased up to 35, which is a proof of the concept of the recyclability of NAD^+ under the operative conditions.

A further improvement may be brought to the system when transition metal systems (TMs) are used as catalysts for the reduction of NAD^+ under visible light irradiation. In this case, the electron donor has a key importance as it determines the cost of production of methanol. Phosphites have been used[11] that are of little practical application, as their cost makes the process un-economical. We have used bioglycerol as hydrogen source. Bioglycerol is the co-product of biodiesel in the conversion of natural lipids: it is accumulating at a rate that will make it a worrying waste if it is not converted into useful products or used for added-value reactions.[12] $[RuCl_2(PPh_3)_3]$[13] or $[(dppe)_2RuCl_2]$[14] (DPPE = 1,2-bis(diphenylphosphino)ethane) are able to extract hydrogen from aqueous bioglycerol that acts as a reducing agent towards CO_2 and NAD^+. The first attempts have demonstrated that the reaction is feasible. A ratio $CH_3OH/NADH = 3.2$ has been reached that can be improved considerably. Key issue is again the separation of the two processes (reduction of CO_2 and reduction of NAD^+) that require much engineering for an optimal exploitation of the reactive system. Alternatively, dihydrogen can be biotechnologically produced from glycerol and used with TM systems (Rh, Mo, Ir, W, Pd, Ni, Pt) as catalysts.[15] Such attempts are still under investigation to define the catalyst behaviour.

Here, we describe the behaviour of semiconductors such as ZnS or Ru/ZnS and show that they are interesting agents for the reduction of NAD^+ and the regeneration of NADH.

ZnS-A synthesised at room temperature has a large surface area (105 $m^2 g^{-1}$) and a maximum of light absorption at about $\lambda = 360$ nm. Therefore, it allows working at the border of UV and Visible light. It performs considerably better than ZnS-C (nanorods) or Ru-loaded ZnS-A (Figure 4). ZnS-A was tested with watery-glycerol or isopropanol, selected for its known hydrogen-transfer properties in industrial applications.

Ru-spots deposited on the surface of the photocatalyst reduce the performance of the latter most probably because it subtracts light intensity useful for ZnS-A electron excitation to the conduction band (Figure 4). It is worth to note that the energy of the conduction band edge of metallic Ru is considerably lower than that of ZnS-A, so that an electron transfer from the excited Ru to the ZnS-A conduction band cannot occur at all. For such reasons, the absorption of incident light by Ru-covered ZnS-A with respect to ZnS-A itself is less efficient, resulting in a lower catalytic activity. Concerning the lower activity of ZnS-C (nanorods), it can be ascribed to its considerably lower surface area (48 $m^2 g^{-1}$) with respect to ZnS-A.

As a source of light either a Xe-lamp was used or a lamp with an emission in the range $\lambda = 360$–440 nm. In both cases, radiation was filtered by using a common glass, which cuts off wavelengths lower than $\lambda = 350$ nm. The regeneration of

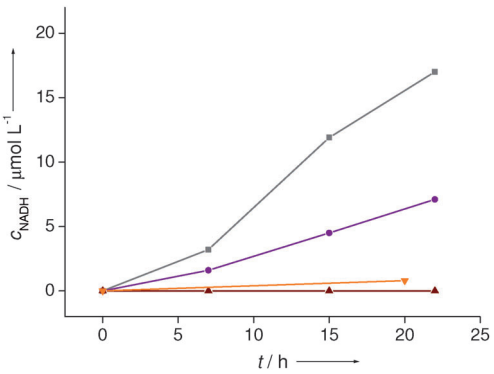


Figure 4. Comparison of the activity of ZnS-A (■) in the reduction of NAD^+ with that of Ru-loaded ZnS-A (●), ZnS-C nanorods (▼) and without a photocatalyst (▲). The NADH concentration is based on NADH absorption measured at $\lambda = 344$ nm.

NADH from NAD^+ was followed by concurrently using different techniques. The fluorescence spectrum of the NADH (Figure 5) clearly shows an increase of the peak intensity due to the reduced species upon irradiation. HPLC also showed the continuous increase of the concentration of NADH during irradiation.

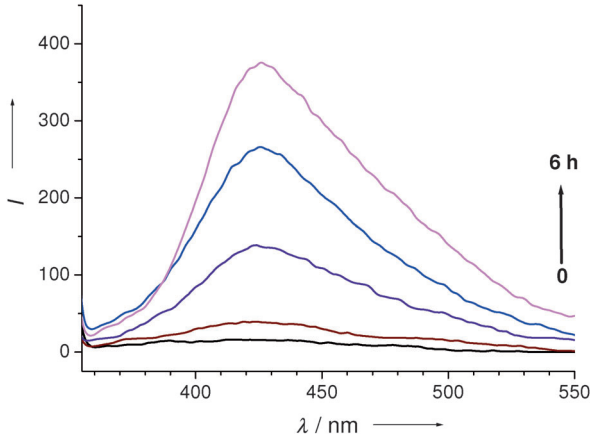


Figure 5. Photocatalytic NADH regeneration. Fluorescence spectra were measured before switching on the light and after 0.5, 1.5, 2.5 and 6 h irradiation in the presence of ZnS-A as a photocatalyst.

^1H NMR spectroscopy also shows the formation of the active isomer of monomeric NADH. Concerning the e^--donors (Figure 6), glycerol demonstrated an interesting activity, which was also better than isopropanol. This finding adds to our previous observations[13,14] and further supports the potential of bioglycerol as a reducing agent.

Thus, NADH was photochemically regenerated from NAD^+ by using bioglycerol as an e^--donor and working at the border of the visible light domain. Considering that UV light is commonly used with triethanolamine or ascorbic acid as e^--donors, our findings considerably improve the process both energetically and from the point of view of the cost of reagents. A point that still deserves investigation is the tuning of

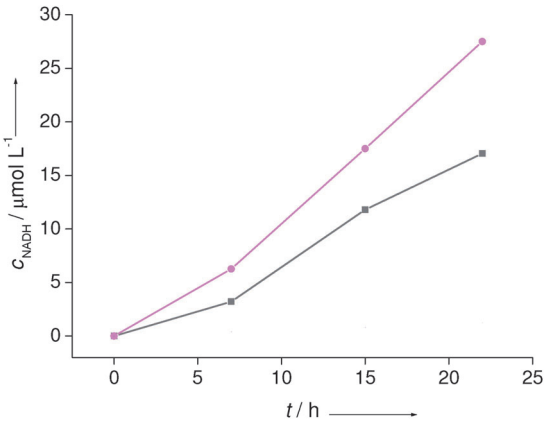
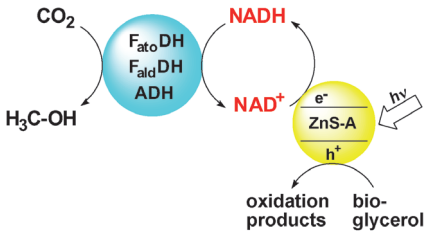


Figure 6. Comparison of the performance of different electron donors (■ isopropanol, ● glycerol) in the photocatalytic regeneration of NADH from NAD^+ in the presence of ZnS-A.

the rates of the two processes: i) formation of NAD^+, and ii) regeneration of NADH. The enzymatic reaction of reduction of CO_2 to methanol is considerably faster than the photochemical reduction of NAD^+. This issue is under investigation in our laboratory to identify more powerful photocatalysts that may improve the e^--transfer rate from the e^--donors to NAD^+.

The results reported above open a new horizon to the NAD^+ conversion into NADH using photocatalysts and to the use of watery bioglycerol as e^-- and H-donor (Scheme 3).



Scheme 3. CO_2 conversion into CH_3OH at room temperature using light to regenerate the enzyme cofactor (NADH) by ZnS-A photocatalysis, with bioglycerol as H- and e^-- donor.

In conclusion, this preliminary work done in the field of NAD^+ reduction to NADH coupled with CO_2 reduction to methanol has given interesting results that encourage searching for more reactive photo-systems that may reduce NAD^+ at a rate compatible with the CO_2 reduction by enzymes, so to feature a possible application.

Experimental Section

Materials and characterisation

All starting reagents and solvents were commercial products purchased from Aldrich. Solvents were dried, distilled,[18] and stored under N_2 atmosphere. All manipulations were performed under a dry N_2 atmosphere by means of vacuum-line techniques. N_2 and CO_2 (99.999%) were supplied by Rivoira IP.

Gas chromatography was used for both, liquid and gas sample analysis. Liquid phase samples were analysed by using a flame ionisation detector (FID), an HP-5 (5% phenyl-95% methylsiloxane) capillary column and He as a carrier.

HPLC analyses were performed by using a BIORAD Aminex HPX-87H column. During analysis, the column was kept at 60 °C. A 0.1 M aqueous solution of sulfuric acid was used as a mobile phase. The volume of the samples was 45 µL. Two kinds of detectors were used, namely a refractive index detector and a UV-Vis absorption detector.

UV-Vis absorption spectroscopy was used as a quantitative and qualitative method for NADH determination. Either full spectrum or single wavelength ($\lambda = 344$ nm) were used. All measurements were recorded in 1 cm quartz cuvettes. Fluorescence spectroscopy was used for NADH detection. Emission spectra ($\lambda = 350$–550 nm characteristic for NADH.) were measured with an excitation radiation of $\lambda = 344$ nm.

Brunauer–Emmett–Teller surface area analysis was used to determine the specific surface area of solids by using a Chemisorb Micromeritics System. The samples were flushed with N_2 for 30 min before analysis that was performed by using a mixture of 30% N_2 and 70% He.

Diffuse reflectance spectra of the photocatalysts were recorded by using a UV-VIS-NIR spectrophotometer equipped with an integrating sphere. UV-Vis diffuse reflectance spectra were measured in the wavelength range of $\lambda = 250$–800 nm. Samples were ground with $BaSO_4$ and pressed in a pellet. A $BaSO_4$ pellet was used as a reference. Reflectance (R) was converted to $F(R_\infty)$ values, where $F(R_\infty)$ is the notation for the Kubelka–Munk function and R_∞ ist the absolute reflectance of the sampled layer, by applying the Kubelka–Munk theory. The band-gap energy was accurately determined by means of transformed diffuse reflectance spectra. The extrapolation of the plots to $[F(R_\infty)E]^2 = 0$ (E is the energy of photon) allowed estimating the band-gap energy of ZnS, which is a direct semiconductor. The band-gap energies were determined by using a plot of $[F(R_\infty)E]^2$ vs. E.

Preparation of co-encapsulated enzymes

Tetraethyl orthosilicate (TEOS, 1.6 mL) was added to a solution (4 mL) of sodium alginate in water (2% w/w) while stirring the resulting mixture vigorously for several minutes. A buffer solution (1 mL) of TRIS·HCl [0.5 M, TRIS = tris(hydroxymethyl)aminomethane], degassed and neutralised at pH 7 by using HCl, contained 10.0 mg of each enzyme (F_{ate}DH, F_{ald}DH and ADH). After homogeneisation of the mixture, it was dropped by using syringe in a solution of $CaCl_2$ (0.2 M) for the formation of 1.5 mm beads. The gelification of alginate was complete after 0.5 h. The beads formed were then filtrated on paper and washed several times to eliminate the excess of calcium ions and ethanol produced by TEOS hydrolysis.

Reduction of CO_2 to methanol by co-encapsulated enzymes and NADH

The reduction of CO_2 was performed either in a batch reactor or in a flow system while bubbling CO_2 through the solution. The reaction in batch was performed in a low pressure stainless steel autoclave at 0.5 MPa of CO_2, placing a glass reactor filled with the reaction mixture in the autoclave, and flushing with CO_2 before starting. For the reaction in CO_2 flow, a sealed glass tube was used in a

thermostated bath at 37 °C with a septum through wich CO_2 was bubbled by means of a needle. The exit was connected to a 0 °C trap by using a tube to avoid loss of methanol produced. The methanol produced was collected and determined by analysis of both the reaction mixture and the condensed phase in the trap. In a typical reaction run, NADH (200 mg) was dissolved in TRIS·HCl (5 mL of the 0.5 M buffer at pH 7) and degassed. The beads prepared as above were suspended in the solution, and the system kept at 37 °C for 3 h while slowly bubbling CO_2 through the system. Afterwards, the methanol produced was determined, and the beads filtered, washed and reused in a new reaction cycle.

Test of release of methanol from beads produced from TMOS

Beads prepared from TMOS (tetramethoxysilane, prepared as reported for TEOS) were used in the reduction of $^{13}CO_2$ in a batch reactor. The formed CH_3OH was analysed by using GC–MS and shown to contain 2–10% $^{12}CH_3OH$ produced from residual TMOS hydrolysed during the reduction of CO_2.

NADH regeneration by reduction of NAD^+ with SDT

a) In a typical experiment, NAD^+ (200 mg) was dissolved in the buffer TRIS·HCl (5 mL, 0.5 M, pH 7). The solution was transferred into a glass reactor and thermostated at 37 °C in an N_2 flow. After several minutes, a water solution of SDT was slowly added (in 1:1 molar ratio with respect to NAD^+). The reaction was complete after 20–25 min as demonstrated by HPLC and spectrophotometric analysis. The yield of the reaction was determined by measuring the absorbance at $\lambda = 344$ nm using a calibration curve. The addition was repeated until no further production of CH_3OH was observed. A total molar ratio CH_3OH/NADH equal to 2.13 was observed.

b) The same reaction was performed by separating the solution from the beads after oxidation of NADH and performing the reduction of NAD^+ with SDT in a separate vessel. The solution containing NADH was added again to the beads, and CO_2 bubbled through the solution. This cycle was repeated ten times, and a ratio CH_3OH/NADH = 4.14 was observed.

c) The cycle of reactions was performed in the equipment shown in Figure 3, reaching a CH_3OH/NADH ratio higher than 35.

ZnS-A preparation

ZnS-A powder was prepared according H. Kisch's method with minor modifications.[16] All steps of this preparation were performed by using Schlenk techniques. A solution of Na_2S (4.8 g, 0.2 mol) under N_2 atmosphere in deionised and degassed water (50 mL) was added dropwise to an aqueous solution (50 mL) of $ZnSO_4 \cdot H_2O$ (3.58 g, 0.2 mol). The mixture was stirred for 24 h at room temperature. The white precipitate obtained was carefully filtrated under N_2 atmosphere by using a sintered glass filter, and then washed several times with water, until a filtrate at neutral pH (7.00) was obtained. The product was dried under vacuum for 6 h. The final product particles had dimensions in the range 10–25 nm.

ZnS-C preparation

ZnS-C nanorods were prepared according to M. Wu's method with some modifications.[17] A solution of zinc acetate (0.8 M, 0.8 L) was prepared using an aqueous solution of ethylenediamine (ratio ethylenediamine/water = 1:2). This solution was added drop by drop to a solution of thiourea (1.6 M). The mixture was transferred into a glass tube containing a magnetic stirring bar that was placed into an autoclave. The reaction was run at 200 °C for 20 h. The pink-white powder was washed three times with ethanol, six times with water and then once again with ethanol. The white powder was dried at 80 °C for 17 h. The whole procedure was performed under an N_2 atmosphere. The size of the final particles was in the range 20–45 nm.

Ruthenium-loaded ZnS catalyst preparation

ZnS-A powder (400 mg) was suspended in an aqueous solution containing the desired loading amount of $RuCl_3 \cdot 3H_2O$ (3 mL). A solution of $NaBH_4$ (excess) was added dropwise to the suspension while sonicating. After 2 h, the powder was filtered and washed a few times with water and acetone. The powder was dried at room temperature under vacuum. The dry product was stored in an N_2 atmosphere. The Ru content was determined by using atomic absorption spectroscopy and found to be 0.5%. The properties of the catalysts are reported in Table 1.

Table 1. Band gap energies of photocatalysts.

Photocatalyst	Band gap energy [eV ± 0.02]	Onset [nm]
ZnS-A	3.47	358
0.5 %Ru@ZnS-A	3.57	347
ZnS-C	3.60	344

Photocatalytic tests for the regeneration of NADH from NAD^+

Photocatalytic tests of NAD^+ regeneration were performed in a glass cylindrical reactor (Pyrex, $V = 10$ mL). The nanophotocatalyst powder was suspended in distilled, deoxygenated water. The concentration of the photocatalyst was 1 g mL^{-1}. Isopropanol or glycerol was added as a sacrificial electron donor (5 vol%). NAD^+ (1.5 mM) was added. Degassed water was used in the experiments. The suspension in the closed reactor was illuminated using a 125 W Xe lamp (full spectrum) or a 8 W lamp ($\lambda = 365$ nm) as light sources. The full light of lamps was used. During the illumination run, the mixture was stirred magnetically at constant temperature. The necessary volume of the reaction solution was sampled at given intervals of time. The samples were filtered through syringe filters (Rotilabo, 0.22 μm) and analysed by using UV-Vis absorption spectroscopy (detection at $\lambda = 344$ nm), fluorescence spectroscopy and HPLC methods.

Acknowledgements

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Keywords: carbon dioxide storage · enzymes · hybrid technologies · methanol · reduction

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