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PAPER

Urea derivatives enhance the photocatalytic activity of dye-modified titanium dioxide†

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Trace amounts of urea derivatives enhance the rate of nitrobenzene N3-sensitized TiO_2 photoreduction by catalyzing the proton transfer. The usually required addition of transition metal co-catalysts becomes dispensable for this visible light photocatalysis, facilitating its application in organic synthesis.

Introduction

Semiconductors are widely used in photocatalysis.[1] Photocatalytic water cleavage[2–5] and photodegradation of dyes,[6] phenols[7] or chlorobenzenes[8] are typical applications. More recently examples of the use in organic synthesis have been reported.[9,10,11,12,13]

Semiconductors based on TiO_2,[14] CdS or ZnO materials have been explored extensively. To extend the absorption of titanium dioxide into the visible range, metal,[15] carbon, nitrogen[16] or sulfur doping or dye surface modifications are used.[17] However, for chemically productive photocatalytic hydrogen production or reduction reactions, precious-metal species,[18–20] such as Pt and RuO_2, are required in most cases as extra co-catalysts to promote the transfer of photoinduced charge carriers from the bulk to the surface at which protons are converted to hydrogen.

The photoreduction of nitroarenes to anilines is an application of such semiconductor photocatalysis to organic synthesis.[21] We have now observed that typically required metal co-catalysts, such as Pt, Pd or Au, can be substituted by urea derivatives without loss of efficiency.

Results and discussion

Commercial TiO_2 particles (P25) were surface modified with the ruthenium complex N3 in analogy to Grätzel-type dye solar cells,[22,23] to accomplish photocatalytic activity with green light. High power LEDs with a narrow band width of their emitting wavelengths (530 ± 10 nm) and an intensity of more than 60 lumen (manufactures claim) were used to mediate the photoreduction of nitroarenes in acetonitrile solution with triethanolamine (TEOA) as sacrificial electron donor (Fig. 1). The green light irradiation

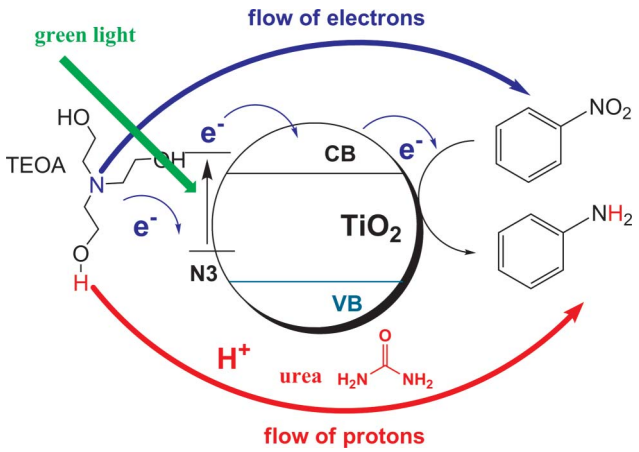

Fig. 1 Photocatalytic nitrobenzene reduction with dye-sensitized TiO_2 in the presence of urea as proton transfer mediator.

requires longer irradiation times for complete nitroarene conversion if compared to UV experiments, however, the corresponding anilines were detected as the sole products of the reduction by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Using identical experimental conditions (50 mg TiO_2 modified with 2 mol% N3, and 10 eq. TEOA in 2.5 ml of acetronitrile, see ESI† for experimental details) the co-catalyst was systematically varied and the conversion of the reaction after 24 h of irradiation was monitored by GC. Table 1 summarizes the obtained results. The use of unmodified TiO_2 and irradiation with green light gave minimal conversion (<2%) of nitrobenzene after 24 h, while the N3 dye sensitized TiO_2 without addition of any metal or non-metal co-catalyst converted 39% of the nitrobenzene into aniline. No conversion is observed in the absence of green light with any of the described systems.

The addition of small amounts of metal salts is required to achieve good conversions, as earlier reported.[21] Surprisingly, small amounts of added urea lead to a similar effect. As little as 10^{-6} mol% related to nitrobenzene causes quantitative conversion of nitrobenzene to aniline. Similar effects were observed with

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Table 1 Conversion of nitrobenzene photoreduction with N3-modified TiO_2 in the presence of different co-catalysts

Co-catalyst	Conversion of nitrobenzene to aniline [%][a]		
None	39		
Amount added[b]	**0.5 mol (%)**	**10^{-4} mol (%)**	**10^{-6} mol (%)**
$AuCl_3$[21]	49	99	44
K_2PtCl_4[21]	36	90	46
Urea	55	99	99
DMU[c]	49	99	99
TMU[d]	78	95	83
Thiourea	75	99	90
DMSO	48	48	94

[a] Reaction monitoring by gas chromatography after 24 h; the given values are the average from three independent reactions. [b] In relation to nitrobenzene. [c] *N*,*N*-Dimethylurea. [d] Tetramethylurea.

Table 2 Photoconversion of nitroarenes into their corresponding amines with N3-modified TiO_2 in the presence of 10^{-4} mol% thiourea

4-R-C_6H_4–NO_2	Conversion to 4-R-C_6H_4–NH_2 [%][a]
R = CO_2Et	99
R = CN	99
R = Br	62

Aldehyde	Conversion to corresponding alcohol [%]
C_6H_5–CHO	12
4-CHO-pyridine	85

Table 3 Photoreduction of nitrobenzene with MV^{2+}, TEOA, $Rubpy_3^{2+}$ and thiuorea

Amount thiourea [mol%]	Conversion of nitrobenzene to aniline [%][a]
—	54
10^{-3}	98
10^{-5}	92

[a] Integration of signals in GC chromatograms after 24 h of irradiation.

N,*N*-dimethylurea (DMU), tetramethylurea (TMU) and thiourea, but not with cucurbit[6]uril or cyanuric acid. 4-Substituted nitroarenes are reduced without formation of side products using 10^{-4} mol% thiourea as co-catalyst (Table 2), while aromatic aldehydes require an electron poor arene, such as in pyridine, for sufficient conversion.

Additions of thiourea, dimethylsulfoxide (DMSO) and TMU lead to a comparable acceleration of the nitrobenzene photoreduction as reported for the addition of metal salts.[21] Acceleration factors, calculated as the ratio of the reaction rate constants with added co-catalyst and the reaction rate constant without added co-catalyst, are 2.8 for 10^{-4} mol% thiourea, 10^{-4} mol% TMU and 10^{-6} mol% DMSO. A value of 2.3 was found for the addition of 10^{-4} mol% $AuCl_3$ under the same conditions (Table 3). The apparent product quantum yield[24] increased from 0.2% without additive to 1.2% with 10^{-4} mol% thiourea as additive.

Next, the reaction kinetics of nitrobenzene reductions in identical experimental setups with added 10^{-4} mol% $AuCl_3$, 10^{-4} mol% thiourea or 10^{-6} mol% DMSO were monitored over 24 h (Fig. 2) and revealed a significant difference: With the gold

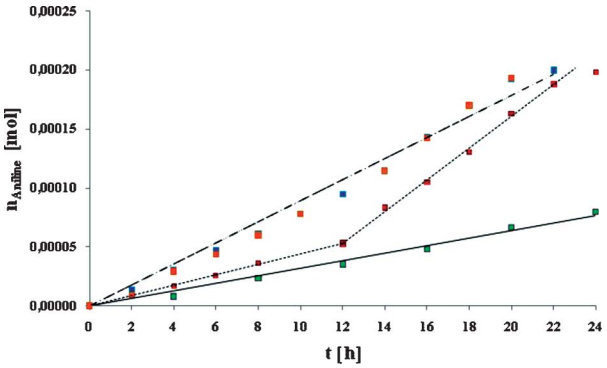

Fig. 2 Reaction kinetics of the dye-sensitized TiO_2 photoreduction of nitrobenzene in the presence of 10^{-4} mol% $AuCl_3$ (red, dotted), 10^{-4} mol% thiourea (blue, dash-dot-dot), 10^{-6} mol% DMSO (orange, dash-dot-dot) and without catalyst (green, continuous line). $n_{aniline}$ [mmol] per $n_{nitrobenzene}$ [mmol] calculated from signal integrals in gas chromatograms using an external standard.

salt, an induction period of slow conversion during 10–12 h is observed, while in the presence of thiourea and DMSO the rate of conversion is constant over the irradiation time.[25] The slow initial rate in the case of gold(III) chloride is explained by the formation of catalytically active metal clusters (Au^0_n) under the reductive conditions and the buildup of dihydrogen gas pressure.[26] No H_2 gas was detected during the photoreactions in the presence of urea derivatives or DMSO, which indicates a different mechanism of the nitrobenzene reduction. Cyclic voltammetry of nitrobenzene and spectrophotometric titrations of the N3 complex showed no effect of added thiourea on the reduction potential of the substrate and the electronic properties of the dye (see ESI† for data). A surface modification effect of the TiO_2 by urea described by Mitoraj and Kisch[27] can be also be excluded, as no accumulation of a pyrene-labeled thiourea from solution on the semiconductor surface was found using AFM and fluorescence microscopy. Recently described surface modifications of TiO_2[28] leading to visible light absorption and increased photocatalytic activity by extended heteroaromatic structures arising from pyrolysis of ureas required thermal treatment of the catalyst-urea mixtures, which was not performed in our case.

Furthermore, we investigated the effect of added thiourea to a homogeneous photocatalytic system consisting of a dye, TEOA, methylviologen, thiourea and nitrobenzene, which, without nitrobenzene and thiourea but with platinum oxide, has already been investigated for hydrogen evolution from water. $Rubpy_3Cl_2{\cdot}6H_2O$ was chosen as redox active sensitizer, because of its known redox chemistry and better solubility compared to N3 and methylviologen (MV) as the electron transfer agent (Table 3). The photocatalytic reduction of nitrobenzene to aniline upon 24 h irradiation with 440 nm proceeded in 54% without added thiourea, while 98% aniline were obtained with 10^{-3} mol% added thiourea. The rate acceleration by added thiourea in a homogeneous photoreduction excludes the role of thiourea as a surface modification agent for TiO_2.

Next, we investigated the effect of added urea derivatives on the proton transfer. The use of deuterated triethanolamine (TEOA-D3) as electron and proton source under identical reaction conditions gave (1) full deuteration of the amino group of the aniline, as confirmed by GC-MS and (2) a decreased rate of

Table 4 Photoreduction of nitrobenzene with N3-modified TiO_2 and TEOA-H3 or TEOA-D3

	Reaction rate/$\times 10^{-9}$ mol s^{-1} [b]		Acceleration factor[c]		
Co-catalyst [mol%][a]	TEOA-H3	TEOA-D3	TEOA-H3	TEOA-D3	H/D-ratio[d]
none	0.99	0.36	—	—	2.7
TU 10^{-4}	2.68	1.12	2.8	3.1	2.4
TMU 10^{-4}	2.76	1.53	2.8	4.2	1.8
DMSO 10^{-6}	2.69	1.42	2.8	3.9	1.9
Au^{3+} 10^{-1}	2.26	1.26	2.3	3.5	1.8

[a] Related to nitrobenzene. [b] Reaction monitored by GC-MS, calculated from integration from three independent reactions; reaction rate from the kinetic plots after 20 h of irradiation. [c] Acceleration rate determined by the ratios of $k[\text{TEOA-H3}]_{\text{additiv}}/k[\text{TEOA-H3}]_{\text{no-catalyst}}$ for each system. [d] Kinetic isotopic effect k[TEOA-H3]/k[TEOA-D3] for each catalytic system.

conversion of nitrobenzene to aniline. The kinetic isotope effects are 2.7 for the non-catalyzed photoreduction, 2.4 for 10^{-4} mol% thiourea, 1.8 for 10^{-4} mol% TMU and 1.9 for 10^{-6} mol% DMSO as additives (Table 4).[29] This indicates that the proton transfer or a proton coupled electron transfer is rate determining in the photoreduction reaction.

The photocatalytic nitrobenzene reduction proceeds stepwise with nitrosobenzene and phenylhydroxylamine as intermediates.[30] Our observations are in accordance with a sequential electron and rate-limiting proton transfer or a proton-coupled electron transfer. The acceleration of proton transfer by urea and DMSO has been described for other systems.[31] We therefore suggest a similar effect of the added urea and DMSO in our system leading to an overall acceleration of the photoreduction reaction. One electron oxidation and deprotonation of TEOA leads to a strongly reducing radical[32] that most likely contributes to the nitrobenzene reduction process by either electron transfer to the substrate or electron injection into the TiO_2 conducting band.

In conclusion, we have observed that the previously described photoreduction of nitrobenzene by dye-sensitized TiO_2 and green light in the presence of TEOA[21] is accelerated in the presence of urea or DMSO by catalyzing the rate-limiting proton transfer. The addition of urea or DMSO makes the use of precious metal salts, typically required for this kind of photoreduction, dispensable. This facilitates the application of TiO_2 semiconductor photocatalysis to organic synthesis.

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