Semiconductors as Heterogeneous Visible Light Photoredox Catalysts in Combined Dual Metal Catalyzed C-H Functionalizations

David C. Fabry,[a,c]* Jochen Zoller,[a] Magnus Rueping[b]*

[a]Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, Aachen D-52074, Germany

[b]King Abdullah University of Science and Technology (KAUST), KAUST Catalysis Center (KCC), Thuwal 23955-6900, Saudi Arabia

[c]Tokyo Institute of Technology, Department of Chemistry, Ookayama, 2-12-1-NE-1, Meguro-ku, Tokyo 152-8550, Japan

Abstract: The application of heterogeneous semiconductors as catalyts for C-H functionalization reactions is presented. Visible light enables electron transfer processes for transition metal catalyzed olefination reactions providing important synthesis core structures in generally good yields. The methodology provides an elegant and sustainable alternative to otherwise stoichiometrically applied transition metal additives.

1. Introduction

Heterogeneous photocatalysis has a long history mainly focussing on the activation of suitable semiconductors with UV light.[1-5] The most prominent example is titanium dioxide (TiO_2) that can be used as UV-sensitizer.[6-10] Due to its non-toxicity, its low price, and the deep knowledge of surface reactions, it is highly suitable for organic reactions, including oxidation reactions.[11-17] However, a disadvantage is the use of high energy UV light that may not be compatible with organic or highly functionalized target molecules due to UV light mediated side-reactions or decompositions.

In recent years, alternatives have been developed to shift the light excitation range towards visible light that represents an abundant and mild energy source and is often compatible with organic substrates and products. Approaches towards TiO_2 modifications with nanoparticles, antenna molecules, or dotation led to improved catalysts.[18-21] Recently we also made use of in-situ surface modifications of TiO_2, thereby allowing the visible arylation with diazonium salts,[22] both in batch and flow setups.[23, 24]. In addition the oxidation of N-tetrahydroisoquinolines and subsequent functionalization with various nucleophiles were possible.[25] In the context of more elaborate synthesis Koenig et al. reported further heterogeneous, visible light active photoredox catalysts.[22] CdS or $PbBiO_2Br$ were used in the visible light photoredox catalyzed alkylation of aldehydes with bromomalonates.

In recent years, metal catalyzed C-H functionalizations have become an important tool in organic synthesis. However, often stoichiometric amounts of metal-based oxidants such as copper or silver salts are needed for the regeneration of the active metal catalyst. Hence, we wondered if visible light active semiconductors with the appropriate band gap and reduction potential could also facilitate the regeneration of the active metal catalyst leading to more efficient and sustainable in C-H functionalization reactions. [26-32] Based on literature reports, bismuth vanadate ($BiVO_4$) [33] (band gap: 2.4 eV) and tungsten oxide (WO_3) [34] (2.6-3.0 eV) seemed to be a good starting point for investigations. Both oxides are typically used in the field of pigment and material chemistry [35-37],

absorb visible light and possess reduction potentials similar to homogeneous photoredox catalysts. [38-41]

2. Experimental
Materials and Methods

All commercially available chemicals were used as provided by the suppliers without further treatment. All solvents were dried and distilled under argon prior to use. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel ALUGRAM Xtra SIL G/UV254 aluminum plates with F-254 indicator, visualized by UV irradiation. Macherey-Nagel silica gel 60 (particle size 0.063 – 0.2 mm) was used for column chromatography. Solvent mixtures are understood as volume/volume. An 11 W fluorescent bulb, warm white, was used for irradiation with light. All reactions concerning the scope were repeated at least twice. 1H NMR, 13C NMR and 19F NMR spectra were recorded on VNMRS-400, VNMRS-600 or Mercury 300 spectrometer in CDCl3. Chemical shifts (δ) are reported in ppm and multiplicities are indicated: s (singlet), d (doublet), dd (doublet of doublet, t (triplet), dt (doublet of triplet), td (triplet of doublet), q, (quartet), quint (quintet) m (multiplet); coupling constants (J) are in Hertz (Hz). Mass spectra (MS-EI: 70 eV were conducted on a Finnigan MET SSQ 7000 system, LCMS spectra on a LTQ Orbitrap XL spectrometer and HRMS spectra on a Thermo Scientific LTQ Orbitrap XL spectrometer. IR spectra (ATR) were recorded on a Perkin Elmer spectrometer and wave numbers are given in reciprocal centimeters (cm-1). Starting materials were synthesized according to literature-known procedures and the products compared to literature known compounds. [42-44]

General procedure for the Ru-catalyzed olefination

The respective educt (1 equiv.) and acrylate (2 equiv.), Ru-catalyst (5 mol%), AgSbF6 (0.2 equiv.) and photoredox catalyst (10 mol% or 1 equiv.) were dissolved in DMA (0.1 M). A 4 mL vial equipped with a teflon-coated magnetic stirring bar served as reaction vessel. The mixture was irradiated by an 11 W lamp (distance ca. 3 cm) after placing it on an aluminium block heated at 120 °C. The reaction was quenched with 2 mL of 10% aqueous LiCl solution, after complete consumption of substrate (followed by TLC). The aqueous layer was then extracted with DCM (5x20 mL) and the combined organic layer dried over MgSO4. After removal of solvents, the crude product was purified by flash column chromatography.

General procedure for the Pd-catalyzed cyclization

In a 4 mL vial equipped with a teflon-coated magnetic stirring bar, the appropriate *N*-aryl enamide (1 equiv.), Pd(OAc)$_2$ (10 mol%), K$_2$CO$_3$ (3 equiv.) and photoredox catalyst (10 mol%, 1 equiv.) were dissolved in DMF (0.1 M) and the reaction mixture placed in front of an 11 W household lamp (distance ca. 3 cm) on an aluminium block heated at 120 °C. After complete consumption of starting material (followed by TLC), the reaction was quenched with 2 mL of 10% aqueous LiCl solution, the aqueous layer extracted with DCM (5x20 mL) and the combined organic layer dried over MgSO$_4$. After removal of solvents, the crude product was purified by flash column chromatography.

General procedure for the Rh-catalyzed olefination

A 4 mL vial was equipped with the corresponding Weinreb amide (1 equiv.), [RhCp*Cl$_2$]$_2$ (1.0/2.5 mol%) and photoredox catalyst (10 mol%, 1 equiv.) and a teflon-coated magnetic stirring bar. After addition of

AgSbF$_6$ (5/10 mol%) in chlorobenzene (0.01 mM) the corresponding electrophile (2 equiv.) was added and the reaction mixture placed in a preheated aluminum block (100 °C, actual vial temperature ~80 °C) under light irradiation from ca. 3 cm distance. After the indicated time, the reaction mixture was directly absorbed on SiO$_2$ and the product purified by flash column chromatography.

3. Results and Discussion

In order to test our hypothesis, we decided to investigation metal catalyzed C-H olefination reactions (Scheme 1).
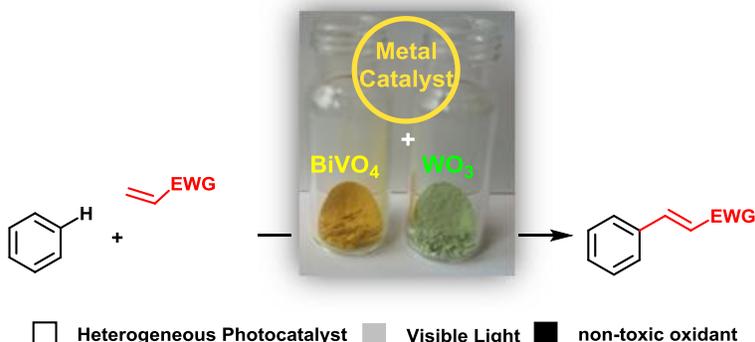
Scheme 1. Heterogeneous oxidants for C-H functionalization reactions.

Mechanistically, we assumed that the semiconductor could act as a visible light photoredox catalyst and thus would be a suitable replacement for the previously reported metal salts (Scheme 2). A catalytic cycle would begin with metal catalyst **A** that inserts into an aryl-H bond to give intermediate **B**. The following olefin insertion results in formation of **C** which upon reductive elimination provides the reduced metal catalyst **D** that needs to be oxidized in order to reenter the catalytic cycle.

We proposed that electron holes in the valence and conducting band of the semiconductor enabled by visible light irradiation, could accept those electrons coming from the reduced metal species to generate the active C-H activation catalyst. As model reaction we decided to examine the previously reported *ortho*-olefination of protected phenols [42, 45] and evaluated different visible-light absorbing heterogeneous semiconductors (Table 1, entry 1-3). We were pleased to see that in general conversion of the substrate **1a** to the corresponding product **2b** could be observed. To our delight, we found that use 1 equivalent of BiVO$_4$ provided the desired product in good yield (Table 1, entry 3). To validate if a catalytic reaction could be performed, 0.1 equivalent of BiVO$_4$ was applied as the heterogeneous photoredox catalyst and indeed, 71% yield of the product was obtained at an increased scale of 0.3 mmol (Table 1, entry 4). This shows that the reaction cannot only be performed under truly catalytic conditions, but that scaling can be accomplished without loss of performance.
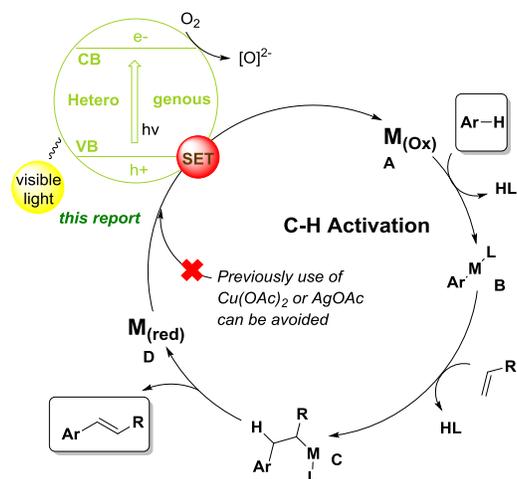
Scheme 2. Mechanistic proposal for heterogeneous C-H functionalization reactions.

Table 1. Catalyst screening and control reactions for the heterogeneous photoredox catalyzed CH olefination.

| Entry[a]	Photocatalyst	Yield[b]
1	WO_3	53%
2	TiO_2	14%
3	$BiVO_4$	84%
4	$BiVO_4$	71%[c]
5	$BiVO_4$	18%[d]
6	$BiVO_4$	49%[e]
7	$[Ir(ppy)_2(bpy)](PF_6)$	75%[f]
8	$BiVO_4$	5%[g]

[a] Standard conditions: phenol (0.1 mmol), 1.0 equiv photocatalyst under air, irradiation with 11 W CFL lamp; [b] yield of isolated product; [c] 0.3 mmol phenol, 0.1 equiv $BiVO_4$ air, 36 h, [d] 0.1 equiv $BiVO_4$ argon, 36 h, [e] 1.0 equiv $BiVO_4$ argon, [f] 3 mol% Ir-cat, 48 h; see ref. [42], [g] 1.0 equiv $BiVO_4$ under air no light.

Further control reactions were conducted regarding the role of oxygen. When 0.1 equivalents of semiconductor in presence of argon was applied, only 18% yield of the product could be isolated (entry 5), indicating oxygen plays a crucial role in the reaction. With 1 equivalent of $BiVO_4$ under the same conditions (Table 1, entry 6), stoichiometric conversion with regard to the amount of heterogeneous catalyst was observed. Please note that the regeneration of the reactive Ru catalyst is a 2-electron redox process and as such the use of 1 equivalent of $BiVO_4$ can theoretically lead to 50% yield. Thus, this results reveals that $BiVO_4$ can serve as 1-eletron transfer reagent that needs oxygen in order to regenerate its oxidized form. Interestingly, the heterogeneous system delivered the product in half the time if compared to the homogeneous system using $[Ir(ppy)_2(bpy)](PF_6)$ as photoredox catalyst (Table 1, entry 7).

A final control reaction showed that in the absence of light no catalytic reaction is observed (Table 1, entry 8). Thus, for the first time we were able to demonstrate that $BiVO_4$ can act as an efficient visible

light photoredox catalyst that can be coupled to enable a Ru-catalyzed C-H olefination. With the optimized reaction conditions for the *ortho*-olefination in hand, various substrates were tested (Table 2). We were pleased to see different substituted phenols as well as acrylates could be efficiently converted into their olefinated counterparts (**2a-e**) in good to very good yields demonstrating that this dual catalytic process can be valuable alternative to the use of stochiometric oxidants in C-H olefinations.

Table 2. Scope of the *ortho*-olefination of phenolethers by combining heterogeneous photoredox and Ru-catalysis.
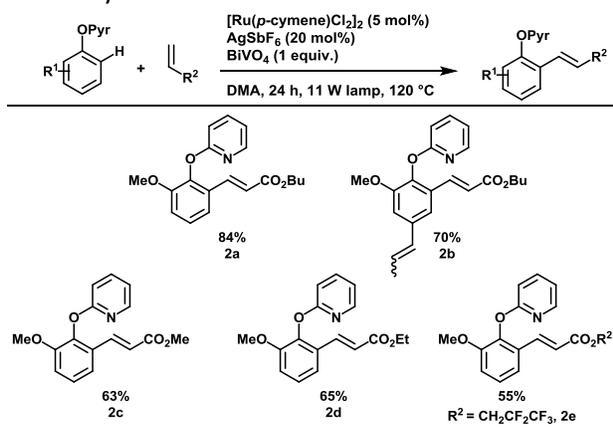
[a] Reaction conditions: substrate (0.2 mmol), 2 mL DMA, irradiation with 11 W CFL lamp.

In order to extend this combined photoredox and metal catalysis concept to other transition metals we decided to evaluate the compatibility with palladium catalyzed C-H functionalizations. Hence, the intramolecular ring-closing reaction of enamides (**3a**) to pharmaceutically interesting indole [46-51] core structures (**4**) was targeted. [44, 52] While the use of WO_3 did only provide low yields (Table 3, entry 2) we were pleased to see that also here $BiVO_4$ (Table 3, entry 1), both in catalytic and stoichiometric fashion furnished the desired indole (**4a**) in high yields of 81%/82%, respectively.

Table 3. Catalyst screening for the heterogeneous photoredox catalyzed indole synthesis.

Entry[a]	Photocatalyst	Yield[b]
1	$BiVO_4$	82%/81%[c]
2	WO_3	15%
3	TiO_2	73%

[a] Standard conditions: enamine (0.1 mmol), 1.0 equiv photocatalyst under air, irradiation with 11 W CFL lamp; [b] yield of isolated product; [c] 0.5 mmol enamine, 0.1 equiv $BiVO_4$ air.

In order to evaluated the applicability of the combined semiconductor and Pd-catalysis procedure we tested different substitution patterns at the enamide substrate (Table 4). We were pleased to see that both electron-withdrawing (**4d**) as well as donating groups (**4b-c**) are well-tolerated delivering the corresponding indole motifs in good to very good yields (Table 4). Also in the indole-9 position, electron

donating and withdrawing groups could be successfully applied in the cyclization reaction (**4e-f**). Finally, the ester part was varied yielding a tert-butyl ester in 71% yield (**4g**).

Table 4. Scope of the heterogeneous photoredox catalyzed enamine cyclization in combination with Pd-catalysis.
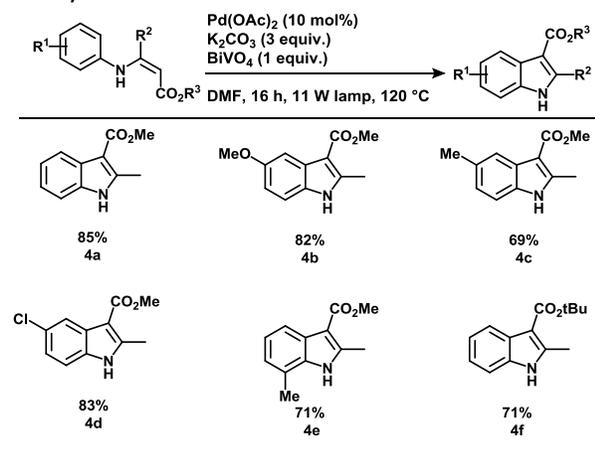
[a] Reaction conditions: substrate (0.2 mmol), 2 mL DMF, irradiation with 11 W CFL lamp.

Having successfully demonstrated that bismuth vanadate is a compatible visible light photoredox catalyst in Ru and Pd catalyzed CH-functioalizations we wondered if also Rh-catalyzed olefinations would be amenable to the dual catalysis concept. Hence, we examined the rhodium-catalyzed *ortho*-olefinations of arylamides (Table 5). [43, 53]

Table 5. Catalyst screening and control reactions for the heterogeneous photoredox catalyzed Weinreb olefination.
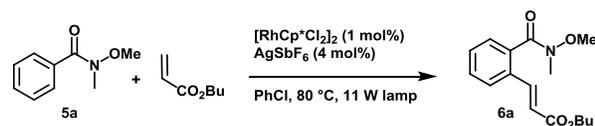

Entry[a]	Photocatalyst	Yield[b]
1	$BiVO_4$	58%
2	WO_3	84%/81%[c]

[a] Standard conditions: amide (0.1 mmol), 1.0 equiv photocatalyst under air, irradiation with 11 W CFL lamp 24 h; [b] yield of isolated product; [c] 0.5 mmol amide, 0.1 equiv WO_3 air, 36 h.

In contrast to the previous reactions, not bismuth vanadate (Table 5, entry 1, 58% yield), but WO_3 provided the highest yield of the olefination product **6a** with 84% yield for a stoichiometric reaction and 81% yield for a catalytic reaction. The latter reaction was moreover realized at gram-scale in order to guarantee enough photo-absorbing catalyst in the reaction due to the high molecular weight of the semiconductor (Table 5, entry 2). With the optimized reaction conditions, we tested the scope by varying the aryl substituents and amide groups. Similar to the previous cases, generally a good functional group tolerance was observed allowing the efficient synthesis of olefinated Weinreb (**6a-c**) and alkyl amides (**6d-g**) (Table 6).

Table 6. Scope of the heterogeneous photoredox catalyzed Weinreb and alkylamide olefination using Rh-catalysis.
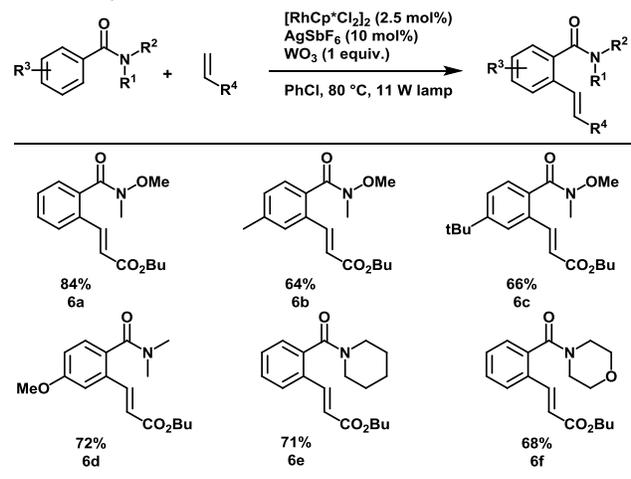
[a] Reaction conditions: substrate (0.2 mmol), 2 mL PhCl, irradiation with 11 W CFL lamp, 24 h.

4. Conclusion

In summary, we report for the first time the use of heterogeneous semiconductors as visible-light photoredox catalysts for transition metal catalysed C-H olefination reactions. The three most common metals for catalytic C-H functionalizsations, Pd, Rh, and Ru, could be successfully applied in the dual catalytic visible light driven process. Thereby, commonly applied oxidants can be avoided and replaced with heterogenous photocatalysts. Given that the semicondutors, $BiVO_4$ and WO_3, are i) cheaper as the often used homogeneous Ir oder Ru-photocatalysts, ii) stable under the different reaction conditions, iii) easily used and separated from the reaction mixture and, iv) compatible with different transition metal catalysts, we anticipate this dual catalysis concept will contribute to the development of further sustainable methodologies and procedures.

5. References

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Graphical Abstract

C-H Functionalization *Heterogeneous Photocatalysis*