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Editorial

Photoinduced bismuth vanadate-catalyzed $C(sp^2)$-H functionalization

Visible light-induced organic reactions have gained much attention in recent years due to their mild conditions and high efficiency [1,2]. In this context, many efficient photocatalysts including transition metal complexes and organic dyes have been developed for various organic transformations. However, most of them are homogeneous photocatalysts, which cannot be recycled after the reaction leading to high costs and pollution. Recently, great efforts have been devoted to the development of low-cost, efficient, and recyclable heterogeneous photocatalysts for organic reactions from the perspective of green chemistry. For example, the heterogeneous photocatalytic systems based on semiconductors like carbon nitride (C_3N_4) [3,4], perovskites ($CsPbBr_3$) [5], zinc indium sulfide ($ZnIn_2S_4$) [6], tungsten selenide (WSe_2) [7], graphene oxide [8], organic polymers [9], *etc.*, have been demonstrated to be potential photocatalysts for various organic transformations.

In a typical heterogeneous photocatalytic system, the semiconductor photocatalyst absorbs the photon of light, in which the photogenerated electrons and holes are produced. The photogenerated electrons could function as a reductant in a reduction process, while the holes could act as oxidants in an oxidation process. Therefore, it is feasible to apply these semiconductors as photocatalysts for various organic reactions, in which single electron reduction/oxidation processes are generally involved.

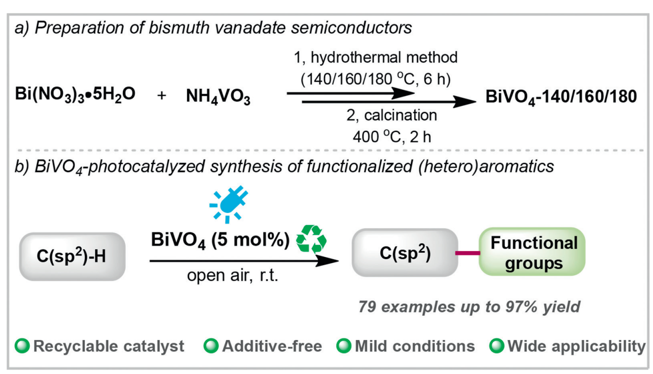
Very recently, the research group of Chen and Yu at Zhengzhou University disclosed that bismuth vanadate could be a versatile heterogeneous catalyst for photocatalytic functionalization of $C(sp^2)$–H bonds (Scheme 1) [10]. It was found that the prepared $BiVO_4$ is a universal and robust heterogeneous photocatalyst for the functionalization of $C(sp^2)$–H bonds to construct different types of arenes and heteroarenes under visible light irradiation at ambient conditions. This heterogeneous catalyst approach features the benefits involving recyclable catalysts, additive-free, mild conditions, and wide applicability.

Firstly, three bismuth vanadate semiconductors ($BiVO_4$–140/160/180) were prepared by a self-developed combined hydrothermal/calcination method. They were also characterized by XRD, UV–vis absorbance, photocurrent, photoluminescence, hydrodynamic particle size, and SEM. The results show that the $BiVO_4$–180 prepared using the 180 °C hydrothermal method has better optoelectronic properties and smaller particle sizes. Subsequently, $BiVO_4$–140/160/180 were used in complex organic synthesis, with $BiVO_4$–180 demonstrating the best photocatalytic properties.

As shown in Schemes 1 and 2, various $C(sp^2)$–H functionalized target aromatic/heteroaromatics (79 examples, up to 97% yield) such as tetrahydroquinoline-succinimide fused heterocycles, tetrahydroquinolines, 3-(*p*-(*N*,*N*-dimethyl)benzyl) indoles, α-aryl α-amino acid esters, and thiocyanation/vulcanization/selenation (hetero)aromatics were smoothly synthesized including modification of drugs and dipeptide esters. Additionally, the $BiVO_4$–180 semiconductor photocatalyst can be recycled and reused up to 8 times with no significant change in catalytic activity and structure. This strategy also applies to sunlight as a light source.

A plausible mechanism for this strategy was proposed as shown in Scheme 2. First, under visible light irradiation, an electron in the $BiVO_4$–180 valence band (VB) is excited to the conduction band (CB), leaving a hole (h^+) on VB. **1a** then undergoes a single electron transfer (SET) with the hole to produce intermediate **1aa**. At the same time, an electron in the CB undergoes a SET with O_2 in the air to form $O_2^{\bullet -}$. Next, **1aa** loses a proton to $O_2^{\bullet -}$, rendering radical **1ab** together with $HOO^{\bullet}$. The addition of **1ab** to **2a** leads to the formation of radical **4aa** which subsequently experiences an intramolecular cyclization, affording radical intermediate **4ab**. **4ab** then proceeds hydrogen abstraction by $HOO^{\bullet}$ to give the product **4a** with the release of H_2O_2.

In conclusion, Chen and Yu's group recently prepared the bismuth vanadate semiconductors ($BiVO_4$–140/160/180) and subsequently investigated their photocatalytic activities. It has been demonstrated that $BiVO_4$–180 is a universal and robust heterogeneous photocatalyst for the functionalization of $C(sp^2)$-H bonds to construct different types of arenes and heteroarenes. Significantly, the $BiVO_4$–180 can be recycled and reused up to 8 times with no significant change in catalytic activity and structure. Outstanding advantages of those developed reactions include mild conditions, recyclable catalysts, and wide applicability. Compared with commercial materials, the self-prepared semiconductor has a smaller particle size and exhibits better photocatalytic activity. Such a strategy to enhance photocatalytic activity by controlling the size of semiconductors may bring a bright future for heterogeneous photocatalytic organic synthesis.



Scheme 1. Catalyst preparation and $BiVO_4$-photocatalyzed functionalization of $C(sp^2)$–H bonds.

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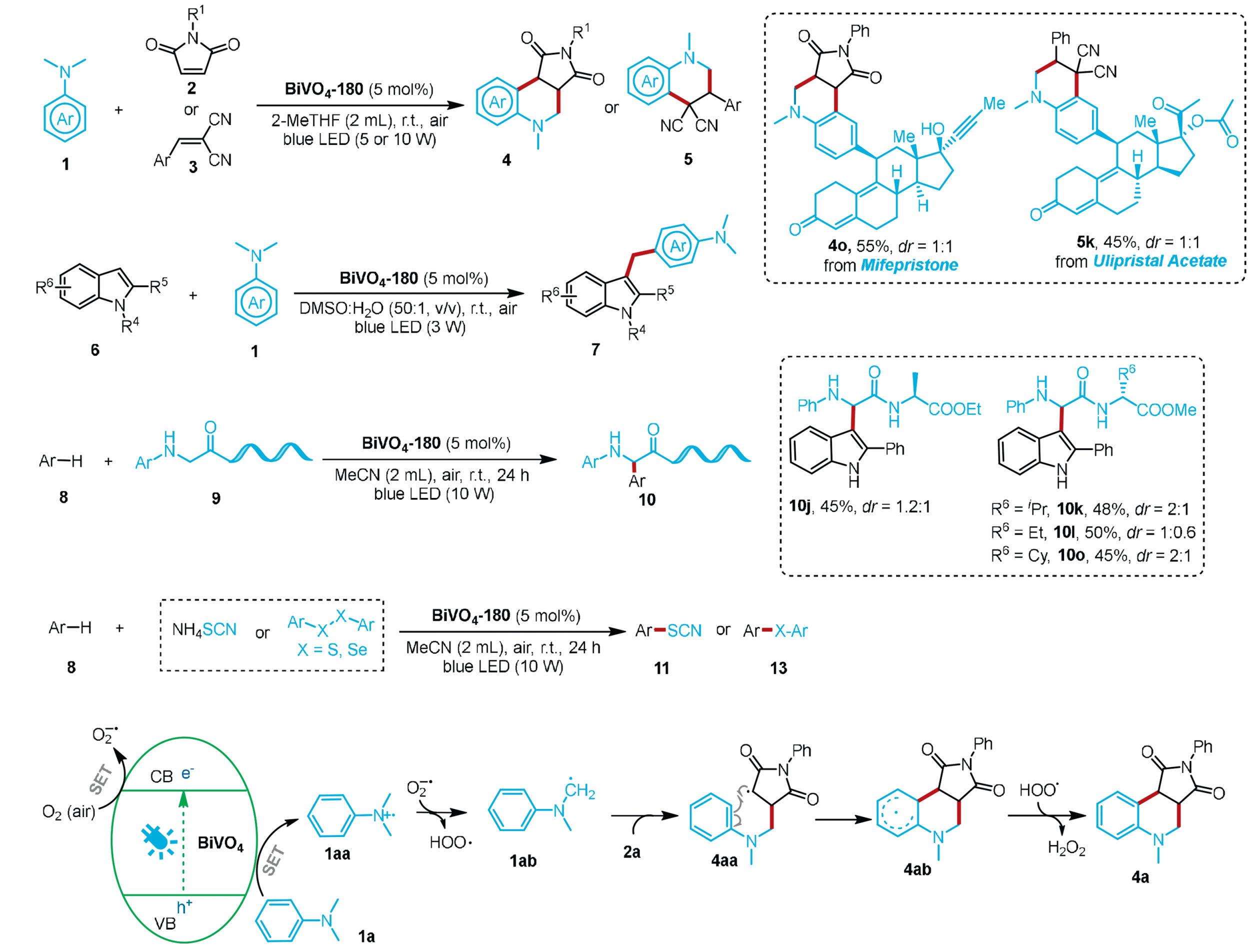

Scheme 2. $BiVO_4$-photocatalyzed reactions and plausible mechanism.

Although the results showed the potential of bismuth vanadate as a versatile photocatalyst, they were obtained under laboratory conditions. Scaling up this catalyst for industrial or large-scale production processes would require consideration of its practicality and scalability. Moreover, further studies are needed to evaluate its long-term stability and durability under various conditions.

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