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Visible Light-Driven Oxidative Coupling Reactions of Amines by Photoactive WS₂ Nanosheets

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ABSTRACT: Visible-light driven photocatalysis has been emerging as an efficient and sustainable approach for chemical transformation in organic reaction, in which photo-stable and cost-effective photosensitizers are required to trigger and promote it. Monolayer WS_2 nanosheets smaller than 120 nm were prepared by means of a modified liquid exfoliation method, and they showed strong photoluminescence in the visible range of electromagnetic spectrum from 450 to 650 nm. These photoactive WS_2 nanosheets were exploited as photocatalysts in the oxidative coupling reactions of various amines under visible light irradiation. They showed excellent photocatalytic activity and reusability without the loss of their catalytic activity in the visible light–driven oxidative coupling reactions of various amines. In addition, the mechanism responsible for WS_2 nanosheets-catalyzed imine production under visible light irradiation was fully investigated.

KEYWORDS: aerobic oxidative coupling, amines, photocatalysis, tungsten disulphide, 2D nanosheets, visible light-driven reaction

INTRODUCTION

Visible light in the solar spectrum has been employed as a sustainable driving force for various chemical transformations in organic reaction.¹ For efficient transformation to desired products under visible light irradiation, the use of photosensitizers is essential to provide electron or hole transfer to reactant chemicals.^{1e, 2} Organometallic compounds involving precious metals have been widely utilized as photosensitizers in photocatalysis due to their long excited state lifetimes.^{1a} However, the weak long-term stability of organometallic photosensitizers and the limited abundance of their constituents precious metals limit their practical applications.³ Hence, it still remains important and interesting to develop alternative photosensitizer materials that address these issues.

Tungsten disulfide (WS₂) is an emerging transition metal dichalcogenide (TMD) that has received great attention in various research fields.⁴ The optical properties of exfoliated WS₂ can be modulated by varying its thickness; decreasing the number of layer; eventually leads to a transition from indirect bandgap in bulk WS₂ to direct bandgap in monolayer WS₂.⁵ Monolayer WS₂ is able to emit photoluminescence (PL) and also strongly absorbs in the visible region of the electromagnetic spectrum. Hence, monolayer WS₂ could be a promising candidate to serve as a photosensitizer in visible light-driven organic reaction. However, to our best knowledge, there has been no report thus far regarding the chemical transformation of organic compounds photocatalyzed by monolayer WS₂. In particular, we are interested in exploring the use of WS₂ as

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a photocatalyst in light-driven conversion of amines to imines because imine derivatives are essential intermediates in the synthesis of pharmaceutical, agrochemicals, dyes, and fine chemicals.⁶ A few reports showed the photocatalytic transformation of amines to imines by several types of photosensitizers.⁷

Herein; we demonstrate the oxidative coupling reactions of various aryl amines photocatalyzed by WS₂ nanosheets under visible light irradiation. The photoactive WS₂ nanosheets prepared by simple liquid exfoliation showed great photocatalytic activity and reusability in the oxidative coupling reactions of the various amines. The mechanism responsible for WS₂-photocatalyzed transformation of the amines to the corresponding imines was also investigated.

EXPERIMENTAL METHODS

Preparation of tungsten disulfide (WS₂) nanosheets: photoactive WS₂ monolayer was prepared by modified liquid exfoliation method. Bulk WS₂ (2 mg/mL) was sonicated in NMP by a tip sonicator in an ice bath for 90 min at a power of 150 W. After more addition of 1 mL NMP to the dispersion to make the final concentration of 1 mg/mL, the mixture was sonicated further for 60 min at the same power in the ice bath. The resulting dispersion was then centrifuged at 5000 xg for 90 min, and the supernatant was obtained.

General procedure for oxidative coupling reactions of amines; a 0.1 mmol portion of amine substrate was dissolved in 7 mL of acetonitrile, followed by addition of 3 mL of a dispersion of WS₂ nanosheets (11 wt. %) in a Pyrex reactor equipped with a rubber septum in an oil bath placed on a hot plate. After purging with O₂ gas into the reaction solution, it was irradiated with 60 W white LED lamps at 50 °C (a distance between the reactor and the lamp was 7 cm) as shown in Figure S1. After reaction for a certain period of time, the product as well as the unreacted amine were extracted with diethyl ether (3×2 mL). Then, the conversion and yield of the product were quantified by Gas Chromatography (YL Instrument 6500GC) using the calibration curves prepared by bromobenzene as an internal standard and each imine product.

*Recyclability of WS*₂ *nanosheets;* after the first round of reaction, all the reactant and the product were extracted out with diethyl ether, and the remaining catalyst solution was centrifuged at 15000 rpm for 45 min by using a micro centrifuge. The WS₂ sediment was then collected, followed by addition of 3 mL NMP. The WS₂/NMP solution was sonicated with a tip sonicator for 30 min at a power of 22 W in an ice bath. The dispersed WS₂ nanosheets were used again in the next round of oxidative coupling reaction.

RESULTS AND DISCUSSION

Photoactive WS_2 nanosheets were prepared by means of a modified liquid exfoliation method based on the previously reported method,⁸ to obtain a smaller size of monolayer WS_2 nanosheets, the sequential ultrasonication of bulk WS_2 in *N*-methyl-2-pyrrolidone (NMP) was carried out in an ice bath. After centrifugation, the exfoliated WS_2 nanosheets were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM) (Figure 1).



Figure 1. Characterization of exfoliated WS₂ nanosheets: (a) AFM image; (b) height profile along the dash line in (a); (c) statistical analysis of lateral sizes; (d) TEM image; (e) lattice structure; (f) SAED pattern; and (g) FFT pattern.

The AFM image of the exfoliated WS₂ nanosheets and a corresponding height profile showed that they had a height of 1 nm, suggesting that most of the nanosheets were monolayers (Figure 1a, b). Analysis of the lateral size distribution showed that majority of the WS₂ nanosheets were laterally smaller than 120 nm (Figure 1c). TEM analysis confirms the formation of WS₂ monolayer with a clear lattice fringe of 2.5 Å (Figure 1d, e). In addition, SAED and FFT patterns clearly show the 2H hexagonal crystal structure of WS₂ monolayer (Figure 1f, g).



Figure 2. Optical properties of exfoliated WS₂ nanosheets: (a) photographs of fluorescent WS₂ solution without and with light irradiation; (b) fluorescence emission spectra for various excitation wavelengths; (c) absorption and photoluminescence excitation (PLE) spectra of exfoliated WS₂ nanosheets; (d) Raman spectra of bulk WS₂ and exfoliated WS₂ nanosheets

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Next, optical properties of the exfoliated WS₂ nanosheets were investigated. The WS₂ solution showed blue emission under ultraviolet (UV) light irradiation (Figure 2a). The PL maximum wavelength of the WS₂ nanosheets was bathochromically shifted from 435 to 575 nm as the excitation wavelengths were gradually increased (Figure 2b). This shift can be attributed to a quantum confinement effect arising from various sizes of smaller WS₂ nanosheets.⁹ The obtained WS_2 nanosheets showed a maximum excitation wavelength at 365 nm and a maximum emission wavelength at 439 nm in their PL excitation (PLE) spectra (Figure 2c). Raman spectra of the WS₂ nanosheets clearly showed a bathochromic shift in their E_{2g}^1 vibrational mode (from 348 to 352) cm⁻¹) and a hypsochromic shift in their A_{1g} vibrational mode (from 420 to 417 cm⁻¹) relative to those of bulk WS₂ (Figure 2d). A decrease was observed in the distance between the two peaks for these vibrational modes, indicating that the monolayer WS₂ nanosheets were well prepared.¹⁰ The feature for monolayer WS₂ was also observed in its absorption spectrum in which the characteristic excitonic peak of monolayer WS₂ for the direct electronic transition at K point of Brillouin zone appeared at 627 nm (1.97 eV) (Fig. 2c, black line).¹¹ Note that the monolayer WS₂ nanosheets exhibited strong absorption in the visible region of the electromagnetic spectrum.

We then examined the photocatalytic activity of the obtained WS_2 nanosheets in the oxidative coupling reaction of various amino compounds (Scheme 1). As shown in Table 1, the oxidative coupling reaction of benzylamine (0.1 mmol) as a model substrate was carried out in the presence of the WS_2 nanosheets (11 wt. %) and of molecular oxygen under irradiation by white LED light (60 W). Benzylamine was converted into the corresponding product, *N*-benzylidene benzylamine,

with high yield (94%) under very mild conditions (Table 1, entry 1). However, without addition of WS_2 nanosheets, the starting compound was hardly converted into the product (Table 1, entry 2). In addition, the reaction scarcely occurred in the absence of light (Table 1, entry 3). In particular, when 1T-phase of metallic WS₂ nanosheets, which are not photoactive, were added to the reaction (Table 1, entry 5), the oxidative coupling reaction was not promoted. As an additional control experiment, bulk WS₂ was also examined in the visible light-driven oxidative coupling reaction of benzylamine. As expected, no benzylamine was converted into the product in the presence of bulk WS_2 under visible light (Table 1, entry 6). The inactivity of bulk WS_2 in this photocatalysis can be attributed to the fact that the band edge position of its conduction band is much lower than the potential of molecular O₂ because bulk WS₂ with stacked multilayers (Figure S4a) exhibits an indirect bandgap of 1.3 eV in the near-infrared range of electromagnetic spectrum.^{11a, 11c, 11d} In addition, bulk WS₂ showed no emission in visible range despite its strong absorption of visible light (Figure S4b, and S4c). However, monolayer WS₂ nanosheets exhibited a direct band gap of 1.9 eV in visible range, and the band edge positon of their conduction band is higher than the potential of molecular O_2 ,¹² which facilitates the transfer of photo-excited electrons from WS₂ nanosheets to O₂ to produce superoxide that is an essential species in the photocatalzyed oxidative coupling reaction of amines. All control experimental results clearly indicated that semiconducting WS₂ nanosheets of 2H-phase (Figure 1d, g and S2) were the essential photoactive catalysts that promoted the oxidative coupling reaction of amines.

Page 9 of 20



Scheme 1. Photocatalytic oxidative coupling of benzylamine into imine by WS₂ nanosheets

Table 1. Photocatalytic oxidative coupling reaction of benzylamine by WS₂ nanosheets^a

| Entry | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 ^c | 9 |
|-----------------------|----|----|----|----|----|------|----|----------------|-----|
| WS_2 | + | _ | + | _ | 1T | Bulk | + | + | + |
| hv | + | + | _ | _ | + | + | + | + | + |
| O_2 | + | + | + | + | + | + | Ar | + | Air |
| Yield(%) ^b | 94 | 15 | 16 | 13 | 9 | n.r | 10 | 2 | 30 |

^{*a*}Reaction conditions: 0.1 mmol of amine, WS₂ (11 wt. %), 3 mL NMP, 7 mL CH₃CN, O₂, 60 W white LED lamp, 50 ^oC. ^{*b*}Determined by GC using bromobenzene as an internal standard. ^{*c*}0.1 mmol of *p*-benzoquinone was added as a superoxide scavenger.

Further experiments were carried out to investigate the mechanism responsible for the WS_2 photocatalyzed oxidative coupling of benzylamine. After removal of O_2 from the reaction mixture by purging with Ar gas, benzylamine was hardly converted into the product (Table 1, entry 7),

indicating that molecular O_2 is a crucial component for the oxidative coupling reactions. According to the previous reports, the molecular oxygen is converted into a superoxide radical by acquiring an excited electron from the conduction band of a photosensitizers.^{7b, 7d, 13} To confirm that a superoxide radical was involved in the WS₂-photocatalyzed oxidation of the amine pbenzoquinone (BQ) which is well known as a superoxide scavenger, was added in the reaction (Table 1, entry 8).¹⁴ The product yield decreased significantly to 2% in the presence of BQ, indicating that the formation of a superoxide radical is an essential step in WS₂ photocatalyzed oxidative coupling of amines. We further investigated the PL response of the WS₂ nanosheets to benzylamine to indirectly confirm that benzylamine could be oxidized by hole transfer from the valence band of the WS₂ nanosheets (Figure S3). The PL intensity of the WS₂ nanosheets gradually decreased as the concentration of benzylamine increased. This PL quenching of the WS_2 nanosheets can be ascribed to electron transfer from benzylamine to the valence band of the photoexcited WS₂ based on their potential energy.^{1c, 13b, 15} This reductive quenching of the WS₂ PL could induce oxidation of benzylamine to yield a benzylamine radical cat- ion as reported previously.^{7d, 13b, 16} According to the previously reported mechanism, a superoxide radical can abstract a hydrogen atom at the benzylic position of a benzylamine radical cation to produce benzylimine and hydrogen peroxide (H₂O₂) as a by-product. Therefore, we analyzed the benzylamine coupling reaction mixture during the middle of the reaction by ¹H-NMR to confirm the production of H_2O_2 ; the NMR spectrum, the peak for H_2O_2 clearly appeared at 10.95 ppm (Figure S5).

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On the basis of the above experimental results, we proposed a mechanism responsible for the oxidative coupling reactions of amines photocatalyzed by WS_2 nanosheets as shown in Scheme 2. When WS_2 nanosheets are photoexcited, their excited electrons are transferred to O_2 producing a superoxide radical while their holes are transferred to amine yielding amine radical cations. Reaction between the superoxide radical and the amine radical cation forms the intermediate imine, which can be activated by its interaction with a hole from WS_2 nanosheet to produce a desired product after addition of another amine and removal of ammonia.



Scheme 2. Proposed mechanism for the oxidative coupling of benzylamine photocatalyzed by WS₂ nanosheets.

Next, the oxidative coupling reactions of various amines photocatalyzed by WS_2 nanosheets were examined as listed in Table 2. Benzylamines bearing electron donating or withdrawing substituents were converted into their corresponding products with high yields by WS_2 photocatalysis (Table 2, entries 1-8). However, the benzylamines with electron donating groups

(Table 2, entries 1-4) underwent photocatalyzed oxidative coupling more efficiently than those with electron withdrawing groups (Table 2, entries 5-8). In addition, the benzylamine having a methyl group at ortho-position showed a slight decrease in product yield (Table 2, entry 2) compared to the para isomer (Table 2, entry 1) owing to steric hindrance. Thiophene-methylamine a heterocyclic amino compound, that is known to poison metal catalysts, was also examined (Table 2, entry 9); it was converted into the corresponding product with a high yield, that was somewhat lower than the yields for benzylamines. It was found that cyclohexylamine was not an active substrate in WS₂-photocatalyzed oxidative coupling reactions (Table 2, entry 10) as compared to benzylamines. Secondary dibenzylamine also yielded the corresponding imine with moderate yield (Table 2, entry 12). In addition to the homocoupling reactions, an oxidative cross-coupling reaction between benzylamine and heptylamine was also conducted in the presence of WS_2 nanosheets, showing moderate yield (Table 2, entry 13). These results suggest that photoactive WS₂ nanosheets are a promising photosensitizer that promotes the oxidative coupling reactions of various amines.

| R | NH ₂ <u>WS₂,</u> NMP, | O ₂ , White LED CH ₃ CN, 50 ⁰ C F | | ^ N ~ | R |
|-----------------|--|--|-----------|---|--------------------------|
| entry | amine | product | t. (h) | $\begin{array}{c} \text{conv.} \\ (\%)^b \end{array}$ | sel. (%) ^b |
| 1 | NH ₂ | N | 30 | 92 | 95 |
| 2 | NH ₂ | N N | 30 | 85 | 96 |
| 3 | NH ₂ | | <u> </u> | 95 | 98 |
| 4 | NH ₂ | | < 30 | 92 | 96 |
| 5 | NH ₂ | | > 48 | 79 | 69 |
| 6 | F NH2 | F. N. | 48 | 90 | 89 |
| 7 | Cl NH2 | | 48 | 92 | 94 |
| 8 | | | 48 | 91 | 90 |
| 9 | NH ₂ | S N S | 48 | 83 | 85 |
| 10 | | | 30 | | |
| 11 | NH ₂ | N | 30 | 77 | 86 |
| 12 | | | 36 | 63 | 93 |
| 13 ^c | NH ₂ + NH ₂ | N~~~~ | 30 | 71 | 78 |

Table 2. Photocatalytic oxidative coupling reactions of various amines by WS_2 nanosheets^{*a*}

^{*a*}Reaction conditions: 0.1 mmol of amine, WS₂ (11 wt. %), 3 mL NMP, 7 mL CH₃CN, O₂, 60 W white LED lamp, 50 ^{*o*}C. ^{*b*}Determined by GC using bromobenzene as an internal standard. ^{*c*}Added 3eq. of heptylamine

Finally, we investigated the recyclability of photoactive WS₂ nanosheets in the oxidative coupling reaction of benzylamine under visible light irradiation. After each round of reaction, some portion of WS₂ nanosheets were lost due to their incomplete recovery according to quantification of the collected catalysts using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) as shown in Table S1. However, there was no leaching of WS₂ into the solution of the product, indicating that WS₂ nanosheets are chemically stable during the reaction. We also analyzed the structure of the WS₂ nanosheets with TEM after recycling them five times in the reaction. As shown in Figure S6, WS₂ nanosheets retained the same size and morphology after reactions. In order to keep the amount of catalyst constant in every reaction cycle, we made up the lost amount of WS₂ nanosheets in the next round of reaction. As shown in Figure 3, benzylamine was converted into the corresponding product with high yields in all rounds of reaction. This result indicates that the photocatalytic activity of the WS₂ nanosheets remained almost the same throughout their use in all reaction cycles.



Figure 3. Recyclability of photoactive WS₂ nanosheets in the photocatalytic oxidative coupling of

benzylamine

CONCLUSION

In summary, we readily prepared small-sized photoactive WS₂ nanosheets by means of a simple modified liquid exfoliation method, and successfully applied them as photocatalysts in the oxidative coupling reactions of various amines. The WS₂ nanosheets exhibited excellent photocatalytic activity and recyclability in these reactions. The mechanism responsible for the WS₂-photocatalyzed oxidative coupling of the amines was also fully investigated. To the best of our knowledge, this is the first reported example for the use of WS₂ nanosheets as a photosensitizer in light-driven organic synthesis. The use of WS₂ nanosheets-based photocatalysts can be expanded to other organic reactions driven by solar energy.

ASSOCIATED CONTENT

Supporting Information.

The supporting information is available free of charge on the ACS publication website at DOI: http://pubs.acs.org. Materials, instrumentation, additional experimental procedures, XPS, PL and NMR and FT-IR analysis for all imine products.

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