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Visible light induced decomposition of sulfonyl hydrazides using Pd/ZrO₂ nanocomposite photocatalyst

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ABSTRACT

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A new approach to synthesis of thiosulfonates has been developed under mild conditions without any oxidants and promoting reagents through a Pd/ZrO₂ nanocomposite photocatalyst catalyzed decomposition of sulfonyl hydrazides. This protocol gave the products in moderate yields, comparable to the best results reported so far. Finally, a plausible reaction mechanism was proposed.

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1. Introduction

Thiosulfonate derivatives are common in antimicrobial, antiviral, bactericidal, and fungicidal¹ compounds in nature. Therefore, their synthesis has attracted the attention of chemists. In recent decades, many efficient methods of compounding thiosulfonates have been developed. Traditional methods focus on the direct oxidation of disulfides (Scheme 1a)² and mercaptans (Scheme 1b).³ However, the disadvantages of these methods include the use of volatile organic solvents and strong oxidizing agents, the severe reaction, the toxic nature of the catalysts, and adverse reactions. Tian's group,⁴ Jiang's group⁵ and the others⁶ have used sulfonyl hydrazides as reaction reagents. However, the thiosulfonate yield obtained by these methods is low. As a consequence, a convenient approach to thiosulfonate synthesis that is environmentally friendly and sustainable is highly desirable.

Palladium nanoparticles (Pd NPs) supported on zirconium oxide (ZrO₂) have been widely applied as a catalyst in organic reactions⁷ due to their advantages of high stability, reusability, and a lack of toxicity. However, they have not yet been carefully studied as a catalyst under visible light irradiation in the synthesis of thiosulfonates. It has been reported that under visible light irradiation, electrons excited by metal NPs are injected into the chemical antibonding orbital and a reaction is induced because of the chemically adsorbed molecules.^{8,9} To the best of our knowledge, researchers have repeatedly found that organic

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transformation induced by visible light is innately continuous and environmentally friendly.¹⁰ Sulfonyl hydrazides are multipurpose and readily accessible intermediates in organic synthesis. In past decades, large studies have sought to develop sulfonylation reactions using sulfonyl hydrazides due to their reducibility¹¹ and nucleophilicity. Hence, we propose a method of synthesis that differs from previous methods. We attempted to cleave S–N bonds and construct sulfur–sulfone bonds to obtain thiosulfonate in the condition of Pd/ZrO₂ in O₂ under visible light at ambient temperatures (Scheme 1c).

a) oxidising mercaptan :				
$R-SH \xrightarrow{[O]} R-SO_2$ S-R				
b) oxidizing disulphide :				
$R-S-S-R \xrightarrow{[0]} R-SO_2$ S-R				
c) This work :				
$R-SO_2NHNH_2 \xrightarrow{Pd/ZrO_2 hv O_2} \xrightarrow{R-SO_2} \xrightarrow{R-SO_2} \xrightarrow{S-R}$				
Scheme 1. Synthetic strategies for the synthesis of thiosulfonate.				

2. Results and discussion

The Pd/ZrO₂ was prepared by the reported literature¹² via a simple impregnation-reduction process using PdCl₂, lysine and NaBH₄ as starting materials (see Supplementary material). The

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as-prepared \mbox{Pd}/\mbox{ZrO}_2 was characterized by XRD, TEM, and UV–vis.

The prepared 3 wt % Pd/ZrO₂ was characterized by XRD, TEM, and UV–vis respectively. First, it is obvious that the diffraction peaks of the Pd/ZrO₂ could correspond to the pure ZrO₂ entirely from Figure 1a, indicating that the structure of ZrO₂ remained unchanged after the metal NPs were loaded, which may be account of the the metal content is inferior to the detection limit and/or the crystallinity of the surface metal NPs is poor . Moreover, as can be seen from the TEM image (Figure 1b), the Pd nanoparticles disperse equally on the surface of the ZrO₂. Finally, UV–vis spectra (Figure 1c) shows that the light absorption of Pd/ZrO₂ is stronger than ZrO₂ both in the UV and visible range, suggesting that the enhanced light absorption arises from the dispersion of Pd nanoparticles on the ZrO₂ surface.



Figure 1. (a) The X-ray diffraction patterns for pure 3 wt % Pd/ZrO_2 (blue) and ZrO_2 (black). (b) TEM image of 3 wt % Pd/ZrO_2 (c) UV-vis spectra of pure ZrO_2 (black), 3 wt % Pd/ZrO_2 (red).

First, we explored the photocatalytic activity of Pd NPs toward sulfonyl hydrazides. To optimize the reaction conditions, we chose 4-methyl benzenesulfonyl hydrazide (1a) as the substrate. The reaction was performed in the presence of 3 % wt Pd/ZrO_2 as a photoredox catalyst, O_2 as the oxidant and EtOH as the solvent at ambient temperature under irradiation of incandescent light (0.4 Wcm⁻²) for 24 h. To our delight, we obtained a 92% HPLC yield (Table 1, entry 3) of the desired thiosulfonate (2a). As shown in Table 1, the application of 4 wt % Pd provided a lower yield of 2a, and 5 wt % Pd gave only a small amount (Table 1, entries 4 and 5). Pd NPs is nanoparticles of nonplasmonic transition metals, so, we then used Au/ZrO₂, because it has been well demonstrated to have localized surface plasmon resonance (LSPR),¹³ but the result was a poor yield of 2a (Table 1, entry 1). When 3 wt % Pd/CeO₂ was used as the photoredox catalyst, no improvement in the transformation was observed (Table 1, entry 6). The use of ZrO_2 as a catalyst led to a 10% yield of product (Table 1, entry 2). It is important to note that visible light and a catalyst are essential in the reaction (Table 1, entries 15).

With these results in hand, we then explored the scope of our method by changing the aryl sulfonyl hydrazide substrate. It was possible to convert sulfonyl hydrazides bearing either electrondonating or electron-withdrawing groups to their corresponding thiosulfonates with excellent yields. It is noteworthy that the presence of neutral substituents on the aromatic groups had a significant effect on the efficiency of the conversion and furnished satisfactory yields. Unfortunately, aliphatic sulfonyl hydrazides were not adaptable substrates for this protocol, presumably because of the relative instability of the sulfonyl radicals generated in situ.

Table 1. Optimization of the reaction conditions^a

\rightarrow	$-SO_2NHNH_2$ Solv $45^{\circ}C, \gamma$	rent, 24 h visible light	s- -so ₂	
Entry	Catalyst	Solvent	Yield ^b (%)	
1	3% wt Au/ZrO ₂	EtOH	13	
2	3% wt Pd/CeO ₂	EtOH	70	
3	3% wt Pd/ZrO ₂	EtOH	92	
4	4% wt Pd/ZrO ₂	EtOH	68	
5	5% wt Pd/ZrO ₂	EtOH	25	
6	ZrO ₂	EtOH	10	
7	3% wt Pd/ZrO ₂	MeOH	70	
8	3% wt Pd/ZrO ₂	i-PrOH	75	
9	3%wt Pd/ZrO ₂	Dioxane	65	
10	3%wt Pd/ZrO ₂	DMSO	63	
11	3%wt Pd/ZrO ₂	H_2O	n.r	
12	3%wt Pd/ZrO ₂	MeCN	Trace	
13	3%wt Pd/ZrO ₂	THF	68	
14	3%wt Pd/ZrO ₂	DMF	10	
15	3% wt Pd/ZrO ₂	EtOH	n.r ^c , n.r ^d	

 a Reaction conditions: 1a (0.6 mmol), catalyst (50 mg), solvent (2 mL), O₂, irradiation under incandescent light (0.4 $Wcm^{\text{-}2})$ at 45°C for 24 h.

^bHPLC yield

° No Light

^d No Catalyst

We then screened for the sulfenylation of $TsNHNH_2$ (1a) under Pd NPs catalysis. Investigations of protic and aprotic solvents under identical catalysis conditions showed that EtOH was the best medium for thiosulfonate formation (Table 1, entry 3). A product yield of 92% was eventually obtained in HPLC with an 80% isolated yield after 24 h.

The advantages of heterogeneous catalysts exist in their good stability, easy separation and fantastic recyclability. As expected, the recycled photocatalyst showed good reusability in five cycles only with a slight decrease in its activity, which was reveled on Figure 2a.

The time course of the catalytic activities was then tested. As shown in Figure 2b, the yield of 2a increased with increasing visible light irradiation time. In the first 3 hours of the reaction, photogenerated electrons entered the conduction band of Pd and electron generation on the surface charge transfer complex improved.¹⁴ The yield of 2a increased slowly from the fourth hour. As shown in Figure 2b, the yield increased over time and the optimal visible light irradiation time was 12 h.

Table 2. Scope of Arylsulfonyl Hydrazides Using Pd/ZrO₂ as Photocatalysts

R	SO₂NHNH₂ 1	Pd/ZrO₂ EtOH, 24 h 45ºC, visible light	R	S -SO ₂ R
Entry	R	Substrate ^a	Product ^a	Yield ^b (%)
1		1a	2a	78
2		1b 13	2b	80
3	H ₃ C H ₃ C	l ₃ 1c	2c	75
4		H ₃ ^{1d}	2d	73
5	F	1e	2e	68
6	- C	1f	2f	67
7	Br	1g	2g	68
8		lh	2h	0

All reactions were run with 1 (0.6 mmol), Pd/ZrO₂ (50 mg) in EtOH (2 ml) under 1 atm O_2 at 45°C.

^a The products were characterized by their comparison with known compounds.

^b Isolated yield.



Figure 2. (a) Time course for the catalytic activities. (b) Recycling experiments.

To explore the reaction mechanism of the transformation, some control experiments were conducted. Because radical species are formed from hydrazide compounds via the generation of diazenes in the presence of transition metals or dioxygen,¹⁵ further reactivity tests were performed by introducing the radical scavenger TEMPO into the reaction mixtures of *p*-toluenesulfonyl hydrazide under standard conditions (Scheme 2). After 24 h reactions at 45°C, only a trace amount of product 2a was detected, indicating that the reactions were almost

completely inhibited by TEMPO (4 equiv). This strongly suggests that the reaction proceeds via a radical mechanism.



Scheme 2. Reactivity Tests by a Radical Scavenge

At the same time, we also speculated that this reaction is closely related to the $-NHNH_2$ group. When benzene sulfonamide was used in the standard condition, no target product was found. This indicates that the $-NHNH_2$ group is essential to the reaction (Scheme 3).

$$- SO_2 NH_2 \xrightarrow{Pd/ZrO_2 hv O_2} No \text{ Reaction}$$
1a

Scheme 3. Pd NPs promoted sulfenylation reation of N-substituted sulfonyl hydrazines.



Scheme 4. Proposed mechanism.

Based on previous reports and the findings described above, we propose a plausible reaction mechanism for the Pd catalytic reaction. In first step, sulfonated hydrazine is oxidized to form sulfonyl radical A in the presence of Pd NPs. The reaction proceeds as follows. First, the sulfonated hydrazine is adsorbed onto the surface of Pd NPs to form a surface charge transfer complex. Second, holes and electrons are generated on the surface charge transfer complex under visible light illumination.¹⁶ The photogenerated holes induce H⁺, which is abstracted from the -NHNH₂ group of sulfonated hydrazine and the photogenerated electrons transfer to the conduction band of Pd NPs. The nitrogen-centered radical -N=N·is formed by the sequential N-H abstracted by Pd NPs followed by the formation H-Pd NPs. Third, the sulfonyl radical A is generated in situ from sulfonyl hydrazides under visible light illumination with the release of N2. Next, the sulfonyl radical A is converted to intermediate B, which is reduced on H-Pd NPs to generate water and intermediate C, which is converted to D. Finally, the sulfur radical E is formed via sequential reduction on H-Pd NPs.

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Oxygen removes hydrogen from the palladium surface, leading to the catalytic cycle.

3. Conclusions

In summary, we have developed a new method to synthesize thiosulfonates through a Pd/ZrO_2 with sulfonyl hydrazides. In this work, for the first time sulfonyl hydrazides were applied to the preparation of a variety of thiosulfonates with a good yields. In contrast to previous work, this method utilizes recyclable photocatalysts and simple experimental procedure and good tolerance of substrates. Moreover, the fact that molecular water and dinitrogen are the only byproducts from the reactions which conclues this process is a rather green synthesis. Further studies on the application of recyclable photocatalysts based on earth-abundant metals for other organic transformations are in progress in our laboratory.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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Highlights

- This research was in O₂ under neutral conditions using visible-light Irradiation without any additive. •
- This reaction realizes the cleavage of S-N bond and the formation of S-S bond.
- Acceptic The product was nitrogen and water conforming to green chemistry.
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