Visible-light-driven photocatalytic activity of ZnO/g-C₃N₄ heterojunction for the green synthesis of biologically interest small molecules of thiazolidinones

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PII:	S1010-6030(20)30585-2
DOI:	https://doi.org/10.1016/j.jphotochem.2020.112786
Reference:	JPC 112786
To appear in:	Journal of Photochemistry & Photobiology, A: Chemistry
Received Date:	7 May 2020
Revised Date:	14 July 2020
Accepted Date:	15 July 2020

Please cite this article as: Mohammadi R, Alamgholiloo H, Gholipour B, Rostamnia S, Khaksar S, Farajzadeh M, Shokouhimehr M, Visible-light-driven photocatalytic activity of ZnO/g-C₃N₄ heterojunction for the green synthesis of biologically interest small molecules of thiazolidinones, *Journal of Photochemistry and amp; Photobiology, A: Chemistry* (2020), doi: https://doi.org/10.1016/j.jphotochem.2020.112786

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Graphical abstract



Highlight

- Fabrication of ZnO/g-C₃N₄ photocatalysts with exceptional activity is reported.
- ➤ A mild and green strategy for the synthesis of 1,3-thiazolidin-4-ones.
- ▶ 40 W domestic bulb is used because of nontoxicity and cost-effectiveness.
- > Operational simplicity, durability, and large-scale application.

ABSTRACT:

Designing a photocatalytic system with complementary properties including high surface area, high loading, extraordinary electronic properties, and easy separation for increases photocatalytic performance has remained a challenge in photocatalytic applications. Herein, an environmentally benign approach was developed to fabricate graphitic carbon nitride (g-C₃N₄) decorated with nanorods zinc oxide (ZnO). The photocatalytic activity of ZnO decorated on the g-C₃N₄ surface was developed in the synthesis of 1,3-thiazolidin-4-ones and bis-thiazolidinones under very mild and sustainable reaction conditions. The reaction can be carried out by utilizing visible light without the requirement of any additive and other external sources of energy. It was found that the proposed photocatalyst is a more facile, recyclable, large-scale application and provides some new insights into the stabilization of semiconductors for a variety of applications.

Keywords: Biologically interest small molecules;1,3-Thiazolidin-4-ones; Bis-thiazolidinones; ZnO/g-C₃N₄; Visible light; Photocatalyst.

1- Introduction

Graphitic carbon nitride $(g-C_3N_4)$ as a polymeric semiconductor has become a new research hotspot and increased interest in the arena of solar energy and environmental remediation [1, 2].

Additionally, these polymeric nanostructures due to semi-conductivity, chemical robustness, excellent physicochemical stability, and earth-abundant nature can be excellent candidates for visible-light mediated photocatalytic processes [3]. Due to these properties, numerous applications of these polymeric semiconductors in different fields have been explored including nanoelectronics, [4] energy storage materials, [5] biosensors, [6] supercapacitors, [7] photovoltaics, [8] photocatalytic, [9-15] and catalytic [16]. Incorporation of metal oxides in g-C₃N₄ nanosheets as semiconductor materials has been explored with TiO₂ [17], Fe₂O₃, [18] SnO₂, [19] CdS, [20] BiVO₄, [21] Ag₃PO₄, [22] NiS, [23] ZrO₂, [24] and ZnO [25] in photocatalytic arena. Among metal oxides, ZnO with bandgap energy 3.37 eV [26] has been widely immobilized on solid materials for catalytic/photocatalytic aims [27-29]. Due to its specific structure, supporting ZnO on g-C₃N₄ sheets could provide strong interaction between support and metal oxide for increase activity photocatalytic.

Thiazolidinones have been sought after by pharmacologists as an important compound in medicinal chemistry. It is also employed as the inhibition of numerous targets such as HCV NS3 protease [30], β -lactamase [31], PMT1 mannosyl transferase [32], PRL-3 and JSP-1 phosphatases [33]. Several methods have been reported for the synthesis of thiazolidinone-based heterocyclics [34-38] as shown in **Scheme 1** and previous methodologies comprised of the current study. However, they suffer from multistep processes, harsh conditions, low yields, and long reaction times. Siddiqui and co-workers reported an efficient and atom economic one-pot protocol for the synthesis of 1,3-thiazolidin-4-ones under visible-light illumination [39]. Our group's recent success is applying the catalytic application nanostructures such as HFIP/SBA-15, [40] β -cyclodextrin, [41] γ -Fe₂O₃, [42] and κ -carrageenan/Fe₃O₄ [43] for the synthesis of thiazolidinones skeletons. Thus, the development of new synthetic methods remains an attractive goal.

Generally, there is an immediate need for developing efficient and sustainable protocols for all biological molecules under milder conditions. Based on the above considerations and previous studies, [44-46] we report a simple and efficient method for the synthesis of $ZnO/g-C_3N_4$ and its catalytic potential towards the preparation of thiazolidinones under visible light irradiation and milder reaction conditions. To the best of our knowledge, the synthesis of thiazolidinone compounds under visible light irradiation and milder reaction conditions by photocatalysts has not been reported thus far.

2- Experimental

2.1. Materials and Methods

The materials and solvents used in the current work were obtained from commercial sources without further purification. The FT-IR spectra were performed using a Perkin Elmer-Spectrum Two with ATR probe. The morphologies of the samples were taken on FE-SEM, Zeiss-SIGMA VP. The TEM images were recorded on Zeiss-EM 900. The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE NMR spectrometers at 400 and 100 MHz, respectively.

2.2. Synthesis of g-C₃N₄

The nanosheets g-C₃N₄ was fabricated by thermal polymerization of melamine by terms of our previous report [47] with some modifications. In a typical synthesis, 5.0 gr of melamine was put in an alumina crucible with a cover and heated for 550 °C for 4 hours at a rate of 5 °C/min. The obtained yellow precipitate was cooled slowly at a rate of 1 °C/min to ambient condition.

2.3. Synthesis of ZnO/g-C₃N₄

0.5 g of g-C₃N₄ was dispersed in 50 mL of DI-H₂O under ultrasonic irradiation for 30 min to obtain g-C₃N₄ nanosheets. Then, 5.0 mL aqueous dispersion of g-C₃N₄ with 5.0 mL aqueous 0.1 M of ZnSO₄.7H₂O was stirred for 30 min at room temperature. For growth ZnO nanorods on the g-C₃N₄ surface, the reaction mixture was kept at 373 K for six hours in the reflux condition. The obtained white solid was purified with MeOH for several times and at dried room temperature. The loading of 15 wt % of ZnO on the surface of g-C₃N₄ was confirmed by AAS.

2.4. General Procedure for the synthesis of 1,3-thiazolidin-4-ones.

The model reaction, the mixture of aniline (1 mmol), benzaldehyde (1 mmol), thioglycolic acid (1 mmol), PhMe (5 mL) as a solvent in 100 mg of ZnO/g-C₃N₄ catalyst in a 20 mL Schlenk tube was added. The reaction mixture was exposed to visible light irradiation using 40 W domestic bulb for 12 hours. After the reaction is complete, the organic phase was extracted with ethyl acetate/diethyl ether (9:1) and then dried over sodium sulfate (Na₂SO₄), and finally, the main product identifies with ¹H and ¹³C-NMR spectroscopy.

2.5. Data NMR.

After compounds are known and are previously reported in the literature [48].

2,3-*diphenylthiazolidin-4-one:* (Table 3, 4a): White solid, Yield = 97%. ¹H NMR (400 MHz, DMSO-d₆), $\delta_{\rm H}$ (ppm) = 3.87 (dd, *J* = 15.8 Hz & 1.6 Hz 1H), 6.13 (s, 1H), 7.11-7.38 (m, 10H), ¹³C NMR (100 MHz, DMSO-d₆): $\delta_{\rm C}$ (ppm) = 33.53, 65.37, 125.61, 126.93, 127.06, 128.89, 128.91, 129.11, 137.29, 139.50, 170.94.

3-(4-hydroxyphenyl)-2-phenylthiazolidin-4-one: (Table 3, 4b): White solid, Yield = 68%. ¹H NMR (400 MHz, DMSO-d₆), $\delta_{\rm H}$ (ppm) = 3.91-4.07 (dd, *J* = 15.8 Hz & 1.6 Hz 1H), 5.94 (s, 1H), 6.36-7.11 (m, 9H) ¹³C NMR (100 MHz, DMSO-d₆): $\delta_{\rm C}$ (ppm) = 34.08, 64.89, 116.13, 123.83, 127.00, 127.23, 128.61, 136.75, 139.92, 155.57, 170.33.

2-*phenyl-3-(p-tolyl)thiazolidin-4-one:* (Table 3, 4c): White solid, Yield = 78%. ¹H NMR (400 MHz, DMSO-d₆), $\delta_{\rm H}$ (ppm) = 2.31 (s, 3H), 4.03-4.07 (dd, *J* = 14.8 & 4.2 Hz, 1H), 6.08 (s, 1H), 7.04-7.56 (m, 9H), ¹³C NMR (100 MHz, DMSO-d₆): $\delta_{\rm C}$ (ppm) = 20.65, 34.18, 65.02, 121.36, 127.02, 127.54, 128.83, 129.77, 130.85, 137.41, 140.11, 170.75.

2-*phenyl-3-(pyridin-4-yl) thiazolidin-4-one:* (Table 3, 4d): White solid, Yield = 97%. ¹H NMR (400 MHz, DMSO-d₆), $\delta_{\rm H}$ (ppm) = 3.91-4.11 (dd, *J* = 16.3 & 2.4 Hz, 1H), 6.72 (s, 1H), 7.25-7.49 (m, 7H), 8.46-8.48 (m, 2H), ¹³C NMR (100 MHz, DMSO-d₆): $\delta_{\rm C}$ (ppm)= 33.16, 62.48, 117.82, 125.59, 129.02, 129.39, 140.15, 145.17, 150.70, 171.76.

3-(2-aminoethyl)-2-(p-tolyl)thiazolidin-4-one: (Table 3, 4e): White solid, Yield = 57%. ¹H NMR (400 MHz, CDCl₃), $\delta_{\rm H}$ (ppm) = 2.39 (s, 3H), 2.55 (t, *J* = 4.8 Hz, 2H), 2.74-2.89 (m, 1H), 3.62-3.79 (m, 1H), 3.49-3.57 (dd, *J* = 12.2 Hz & 1.6 Hz 1H), 5.57 (s, 1H), 7.17-7.31 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): $\delta_{\rm C}$ (ppm)= 21.27, 32.23, 41.03, 46.69, 63.67, 127.19, 129.84, 135.85, 139.47, 171.39.

3-(*p*-tolyl)-2-(*p*-tolylamino)thiazolidin-4-one: (Table 3, 4f): White solid, Yield = 85%. ¹H NMR (400 MHz, DMSO-d₆), $\delta_{\rm H}$ (ppm) = 2.26 (s, 3H), 3.60-3.69 (dd, *J* = 16.6 Hz & 2.6 Hz, 1H), 7.13 (d, *J* = 10.9 Hz, 2H), 7.48 (d, *J* = 11.2 Hz 2H). ¹³C NMR (100 MHz, DMSO-d₆): $\delta_{\rm C}$ (ppm)= 20.93, 43.65, 119.75, 129.63, 132.99, 136.74, 166.91.

3-(4-chlorophenyl)-2-phenylthiazolidin-4-one: (Table 3, 4g): White solid, Yield= 88%. ¹H NMR (400 MHz, CDCL₃), $\delta_{\rm H}$ (ppm) = 3.70-3.74 (dd, *J* = 14.8 Hz & 1.4 Hz, 1H), 6.11 (s, 1H), 7.35-7.63 (m, 9H). ¹³C NMR (100 MHz, DMSO): $\delta_{\rm C}$ (ppm) = 43.65, 121.25, 127.58, 129.16, 138.17, 167.32.

3-benzyl-2-phenylthiazolidin-4-one: (Table 3, 4h): White solid, Yield= 93%. ¹H NMR (400 MHz, DMSO-d₆), $\delta_{\rm H}$ (ppm) = 3.35-3.38 (dd, J = 10.28 Hz & 1.2 Hz, 1H), 3.95-4.01 (m, 2H), 5.57 (s, 1H), 7.09-7.38 (m, 10H). ¹³C NMR (100 MHz, DMSO-d₆): $\delta_{\rm C}$ (ppm)= 32.2, 46.11, 62.29, 127.43, 127.94, 129.15, 129.09, 129.27, 129.39, 136.23, 140.36, 171.37.

3-(4-chlorophenyl)-2-phenylthiazolidin-4-one: (Table 4, 4i): White solid, Yield = 95%. ¹H NMR (400 MHz, DMSO-d₆), $\delta_{\rm H}$ (ppm) = 3.81-3.92 (dd, *J* = 16.4 Hz, 1H), 6.61 (s, 1H), 7.14-7.48 (m, 14H). ¹³C NMR (100 MHz, DMSO-d₆): $\delta_{\rm C}$ (ppm) = 34.27, 65.11, 123.26, 126.42, 127.38, 129.11, 139.04, 139.57, 170.70.

2,2 '(1,4-phenylene)bis(3-(p-tolyl)thiazolidin-4-one): (Table 4, 4j): White solid, Yield = 94%. ¹H NMR (400 MHz, DMSO-d₆), $\delta_{\rm H}$ (ppm) = 2.22 (s, 3H), 3.80-3.92 (dd, *J* = 16.4 Hz, 1H), 6.39 (s, 1H), 7.04-7.21 (m, 8H), 7.29 (s, 4H). ¹³C NMR (100 MHz, DMSO-d₆): $\delta_{\rm C}$ (ppm)= 20.98, 33.01, 63.54, 125.90, 127.73, 129.66, 135.40, 136.31, 140.96, 170.83.

2,2'-(*1*,2-*phenylene*)*bis*(3-(*p*-*tolyl*)*thiazolidin*-4-*one*): (Table 4, 4k): White solid, Yield = 85%. ¹H NMR (400 MHz, DMSO-d₆), $\delta_{\rm H}$ (ppm) = 2.26 (s, 3H) 4.01-4.08 (dd, *J* = 14.2 Hz & 4.7 Hz, 1H), 7.11-7.49 (m, 12H), 10.10 (s, 1H). ¹³C NMR (100 MHz, DMSO-d₆): $\delta_{\rm C}$ (ppm)= 20.93, 43.65, 119.75, 129.63, 132.99, 136.73, 166.92.

3- Results and Discussion

In the current study, we synthesized ZnO/g-C₃N₄ as an excellent semiconductor under the thermal polymerization of melamine. Meanwhile, by embedding ZnO metal oxide in the g-C₃N₄ surface, the photocatalytic properties of these nanosheets are well increased. The salient advantages of the proposed photocatalyst are demonstrated in the stabilization of ZnO and synergistic effect with visible-light illumination for enhancing the photocatalytic activity in the synthesis of thiazolidinones under very mild and sustainable reaction conditions.

The chemical groups of the ZnO/g-C₃N₄ were analyzed by FT-IR spectra. As depicted in **Figure 2a**, several absorption bands in 1242, 1326, 1424, and 1580 cm⁻¹ can be ascribed to aromatic C– N stretching [49]. The absorption band assigned to the C=N stretching at 1644 cm⁻¹ is observed [50]. Also, the peak at 812 cm⁻¹ indicates the out-of-plane bending vibration of triazine units [51]. The signal appears in 491 and 2178 cm⁻¹ are attributed to Zn–O mode which suggesting the successful preparation of ZnO/g-C₃N₄ [52]. Furthermore, the phase structure of the ZnO/g-C₃N₄ was characterized by powder XRD, shown in **Figure 2b**. The XRD pattern of composite material indicates the diffraction peaks at 31.91, 34.59, 36.44, 47.67, 56.63, 62.90, 66.56, 68.19 and 69.26° which were attributed to the (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal

planes of hexagonal Wurtzite structure of ZnO (JCPDS Card No. 36–1451) [53]. The presence of g-C₃N₄ diffraction peak at 2 θ of 27.60° confirms (002) lattice plane of g-C₃N₄, also appears which demonstrate the existence of ZnO on g-C₃N₄ surface.

The surface morphology of the obtained nanocomposite was investigated by FE-SEM analysis, and corresponding images at different magnifications (2μ m to 500 nm) are depicted in **Figure 3**. The irregular and randomly sheets with micron-sized comprised over the entire surface of the sample **Figure 3a**. The magnified images from the FE-SEM (scale of 1 µm and 500 nm) depict the formation of planar sheets having a few stacked layers of g-C₃N₄ (**Figure 3b, c**). The FE-SEM analysis demonstrates that the interaction of ZnSO₄ with triazine units led to the formation of the ZnO/g-C₃N₄ with irregular nanorods. The SEM-mapping images in **Figure 5d** proved the existence of all constituent elements (i.e., C, N, O, Zn) in the ZnO/g-C₃N₄ structure.

Further topography of the ZnO/g-C₃N₄ composite was investigated using TEM analysis as depicted in **Figure 4a, b.** TEM images of the ZnO/g-C₃N₄ indicating embed and distribution ZnO nanorods among the g-C₃N₄ surface, which results in forming a ZnO/g-C₃N₄ heterojunction. Furthermore, the STEM micrograph can provide more detailed information that morphology ZnO/g-C₃N₄ composite. As shown in the dark-field STEM image confirms the nanorods of ZnO well anchoring on wrinkled sheets of g-C₃N₄ (**Figure 4**). The collected data from energy-dispersive X-ray spectroscopy (EDS) analysis further reveals that all the elements (i.e., C, N, O, and Zn) in structures of ZnO/g-C₃N₄, which exhibit purity and the perfect combination of metal oxide on g-C₃N₄ sheets **Figure 4g**.

The importance of the multi-component reaction for forming structural chiral thiazolidinones in the medicinal arena and materials science has led to wide research by chemists [54-57]. For

exploring catalytic activity synthetic conditions were initially employed for the synthesis of thiazolidinone scaffolds using benzaldehyde, aniline, and thioglycolic acid (TGA). The reaction in the presence of the ZnO/g-C₃N₄ catalyst and 40 W domestic bulb lead to the formation of 1,3-thiazolidin-4-ones with 97% yield (**Scheme 2**).

Control experiments indicated in absence ZnO/g-C₃N₄ catalyst negligible conversion (Table 1, entry 1). When the amount of the catalyst increased from 50 mg to 100 mg, the yield reaction was also increased from 68 to 97% (Table 1, entries 2 and 3). For the exploration of the reaction progress, we screened different solvents in optimized conditions. Solvents polar such as EtOH, DMF, and H₂O, the reaction underwent a sluggish conversion (Table 1, entries 4-6). Toluene as a nonpolar solvent improved the reaction yield up to 97% suggesting that PhMe can be an excellent solvent in such a reaction (Table 1, entry 3). The desired result with PhMe solvent encouraged to use nonpolar solvents such as cyclohexane and *n*-hexane. The results indicated that these solvents had a moderate effect on reaction progress (Table 1, entries 7 and 8). The activity of the $ZnO/g-C_3N_4$ composite was enhanced under irradiation of visible light and the proposed catalyst produces a large amount of product in comparison with a high-speed stirrer (HSS), Microwave, and ultrasonic irradiation (Table 1, entries 10-12). Despite decrease time reaction over Microwave and ultrasonic irradiation, based on the importance irradiation of visible light in photochemical processes and energy issues, we continued our studies in under 40 W domestic bulb. On the other hand, the increase in bulb power from 40 W to 100 W had no significant effect on reaction progress (Table 1, entry 13). Moreover, pristine g-C₃N₄ sheets and ZnO results in a low product yield (<49%) under optimized conditions (Table 1, entries 13 and 14). When ZnO anchored on $g-C_3N_4$ sheets yield reaction increase to 97% which demonstrates that the synergetic effect of metal oxide in the ZnO/g-C₃N₄ structure (Table 1, entry 3).

The catalytic activity of ZnO/g-C₃N₄ was also compared with that of homogeneous and heterogeneous catalysts and results present in **Table 2**. To highlight the advantages of using this proposed catalyst, it was compared with semiconductor-based photocatalysts. The reaction in the presence of 100 mg of ZnO/g-C₃N₄ gave a >97% conversion after 60 min under visible light irradiation. The other semiconductor-based photocatalysts such as P25, ZnO, CdS exhibited poorer catalytic activity in this transformation (Table 2, entries 1-3). The catalytic performance of ZnO/g-C₃N₄ was also compared with that of homogeneous catalysts including ZnCl₂, Zn(NO₃)₂, ZnSO₄, and Zn(OAc)₂ in optimize condition reaction. The results of the reaction demonstrated that ZnSO₄ used for preparing ZnO/g-C₃N₄, higher catalytic activity in comparison with other homogeneous catalysts (71% yield), but lower than that of ZnO/g-C₃N₄ (Table 2, entry 6).

To further verify the generality of the ZnO/g-C₃N₄ catalyst in the synthesis of thiazolidinones, we explored different substituted substrates, using various types of aldehydes and amines (**Table 3**). Treatment of benzaldehyde with a series of amines substituents furnished the corresponding rhodanine in good conversion (**4a**, **4c**, **4d**, and **4h**). However, ethylene diamine as aliphatic amine gave a lower yield (57%, **4e**).

Among the 1,3-thiazolidin-4-one derivatives, bis-thiazolidinones indicate a broad spectrum of biological activities and diverse pharmacological properties [58, 59]. In a continuation of these efforts, we expanded the synthesis of bis-thiazolidinones by selecting various dialdehydes. This reaction in the presence of the proposed catalyst and 40 W domestic bulb lead to the formation of

three series of symmetrical bis-thiazolidinone derivatives in superb yields (**Table 4**). The results demonstrated 1,4-aryl linked bis-thiazolidinone derivatives (**4i** and **4j**) formed in better yields as compared to the 1,2-disubstituted derivatives (**4k**). The low yield of the **4k** derivative as compared to **4j** and **4i** derivatives could be attributed to the steric repulsion formed at the adjacent position.

Differential rates of the reaction for substrates with the varying electronic environment would offer a handle for the selective production of the 1,3-thiazolidin-4-ones. Deploying an equimolar mixture of benzaldehyde (**1a**), amine derivatives (2b-d), TGA (3) in optimized conditions are used for the chemoselectivity study (**Scheme 3**). These results demonstrate that the 1,3-thiazolidin-4ones production is dependent on the better nucleophilicity of the amine nitrogen and electrophilic nature of the carbonyl carbon.

In addition to catalytic activity, a plausible mechanism for synthesis of 1,3-thiazolidin-4-ones is shown in **Scheme 4**. Firstly, the aldehyde has to protonated in the presence of ZnO/g-C₃N₄, and in the next step, condensation reaction of amine and aldehyde forming imine as intermediate (**A**). The TGA under visible light (40 W bulb) became thiol-substituted acyl radical via homolysis of CO–OH bond. Then, nucleophilic attack of TGA on Intermediate (**A**) generated intermediate (**B**) via remove water. Finally, it intermediate (**B**) proceeded for cyclization followed by dehydration to giving the final product. The proposed catalyst with having ZnO as Lewis acid and tri-s-triazine framework connected by ZnO makes this nanostructure to excellent bifunctional photocatalyst for protonation aldehyde. The photonic effect on the catalyst promoted the formation of 1,3-thiazolidin-4-ones with high conversion. Recently, Kaur and co-worker [60] explored photonic

effect $Cu_2ONPs/g-C_3N_4$ in the synthesis of aminoindolizines, pyrrolo[1, 2-a]quinoline, and Ynones. Besides, the reaction was carried out under dark conditions but low conversion (38%>) of 1,3-thiazolidin-4-ones was obtained in 12 h.

In addition to catalytic activity, and stability, reusability is a key factor for heterogeneous catalysts. To examine the reusability, the ZnO/g-C₃N₄ was isolated from the reaction mixture and reused in the next cycle. It can be observed in **Table 5** that the proposed catalyst recycled reactions up to four successive runs. The ICP-AES analysis of the multi-component reaction demonstrates that negligible ZnO leaching occurred. Also, the FE-SEM and TEM images of the recovered proposed catalyst after the 4th run affirmed the overall structural integrity of the material which remains intact after the catalytic experiment, demonstrating that the ZnO/g-C₃N₄ is stable under visible light irradiation (**Figure 5**). Ultimately, a large-scale reaction was indicated with the 5 mmol scale reaction under optimizing condition with 91% yield.

4. Conclusion

In conclusion, we presented an ingenious strategy to the synthesis of thiazolidinones under visiblelight illumination. We have deployed a preparation of g-C₃N₄ by thermal polymerization as excellent support for anchoring and stabilization of ZnO nanorods. The proposed methodology is efficient, simple, high scale, and easily recyclable for the synthesis of thiazolidinone scaffolds at room temperature. Moreover, modifying these nanosheets with the various semiconductors can be

developed to prepare versatile heterogeneous photocatalysts for organic transformations under

visible-light illumination and other photocatalytic applications.

Notes

The authors declare no competing financial interest.

Competing interests

The author(s) declare no competing interests.

CRediT authorship contribution statement

Robabeh Mohammadi: Investigation, Conceptualization, Methodology,

- H. Alamgholiloo: Investigation, Conceptualization, Methodology, Writing Original Draft
- S. Rostamnia: Supervision, Writing Review & Editing, Funding acquisition
- B. Gholipour: Investigation, Conceptualization, Methodology,
- S. Khaksar: Review & Editing
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Figure 1. Synthetic pathway of ZnO/g-C₃N₄ composite.







Figure 3. FE-SEM images of $ZnO/g-C_3N_4$ in different magnifications (a, b, c), SEM mapping of $ZnO/g-C_3N_4$ composites.



Figure 4. TEM images of ZnO/g-C₃N₄ in different magnifications (a, b) STEM image (c) and EDS analysis (d) of ZnO/g-C₃N₄ composites.



Figure 5. FE-SEM and TEM images after the 4^{th} recycling of the ZnO/g-C₃N₄ catalyst.



previously reported methods.





a) Aniline with benzylamine:



Scheme 3. The influence of the electronic and steric effect of the amine for selective 1,3-thiazolidin-4ones production during intermolecular competition.



Scheme 4. Plausible mechanism for the formation of 1,3-thiazolidin-4-ones.

Table 1: Optimization of the reaction condition in the formation of rhodanine.^a

Entry	Cat.	Solvent	Time (min)	Condition Reaction	Yield (%) ^b
1	-	PhMe	360	40 W bulb	17>
2	$ZnO/g-C_3N_4$	PhMe	90	40 W bulb	68 ^{<i>c</i>}
3	$ZnO/g-C_3N_4$	PhMe	60	40 W bulb	97
4	$ZnO/g-C_3N_4$	EtOH	60	40 W bulb	51
5	$ZnO/g-C_3N_4$	DMF	60	40 W bulb	39
6	$ZnO/g-C_3N_4$	water	60	40 W bulb	74
7	$ZnO/g-C_3N_4$	Cyclohexane	60	40 W bulb	69
8	$ZnO/g-C_3N_4$	<i>n</i> -hexane	60	40 W bulb	57
9	$ZnO/g-C_3N_4$	Solvent-free	150	40 W bulb	52
10	$ZnO/g-C_3N_4$	PhMe	360	Stirrer ^d	65
11	$ZnO/g-C_3N_4$	PhMe	30	Microwave	89
12	$ZnO/g-C_3N_4$	PhMe	20	Ultrasonic	95
13	$ZnO/g-C_3N_4$	PhMe	90	100 W bulb	98
14	$g-C_3N_4$	PhMe	60	40 W bulb ^e	49
15	ZnO	PhMe	60	40 W bulb	46

^{*a*} Reaction conditions: benzaldehyde (1 mmol), aniline (1 mmol), TGA (1 mmol), PhMe (5 mL) in 100 mg of catalyst.

^{*b*} Isolated yield of rhodanine.

^c 50 mg of catalyst was applied.

^d Progress of reaction with a high-speed stirrer in PhMe solvent under reflux condition.

^e Progress of reaction with an ultrasonic generator (50-60 Hz/305 W) in PhMe solvent at the ambient condition.

formation. ^a						
Entry	Cat	Time (min)	Condition Reaction	Yield (%) ^{<i>b</i>}		
1	P25	60	40 W bulb	79		
2	ZnO	60	40 W bulb	46		
3	CdS	60	40 W bulb	52		
4	$ZnCl_2$	60	40 W bulb	43		
5	$Zn(NO_3)_2$	60	40 W bulb	35		
6	$ZnSO_4$	60	40 W bulb	71		
7	Zn(OAc) ₂	60	40 W bulb	59		

Table 2. The comparison of the homogeneous and heterogeneous catalysts during the rhodanine

^{*a*} Aldehyde (1 mmol) was treated with amine (1 mmol) and TGA (1 mmol) in presence of homogeneous and heterogeneous catalysts (100 mg) in PhMe (5 mL) under visible light irradiation.

Table 3. Substrates scope for the synthesis of 1,3-thiazolidin-4-ones with the variation of the amine and aldehyde components.



^{*a*} Reaction condition: **1a** (1 mmol), **2a** (1 mmol), **3a** (1 mmol), and catalyst (100 mg) under 40 W bulb. The yields were isolated after column chromatography.

Table 4. Substrates scope for the synthesis of bis-thiazolidinones with the variation of the dialdehyde and amine components.



^{*a*} Reaction condition: dialdehyde **1** (1 mmol), **2a** (2 mmol), **3a** (2 mmol), and catalyst (100 mg) under 40 W bulb. The yields were isolated after column chromatography.

Run	Scale	ZnO/g-C ₃ N ₄		Leaching	Yield
	(mmol)	used (g) reco	very(%)	(ppm)	(%)
1^{st}	5	0.50	96	1.2	96
2 nd	4.81	0.48	91	1.3	93
3 rd	4.56	0.45	84	1.9	92
4^{th}	4.21	0.42	53	2.4	89

Table 5. The catalyst recovery and reuse during the formation of rhodanine.^a

^a Reaction conditions: benzaldehyde (1 eq.), aniline (1 eq.), thioglycolic acid (1 eq.), PhMe (5mL per 1 mmol), 40 W bulb in 1 h.
^b Isolated yield of rhodanine.