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# ARTICLE

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Photocatalytic synthesis of unsymmetrical thiourea derivatives via visible-light irradiation using nitrogen-doped ZnO nanorods

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An efficient, mild, and environmentally friendly route has been developed for the synthesis of unsymmetrical thiourea derivatives in moderate yields from the reaction of tertiary aromatic and aliphatic amines with phenyl-*iso*-thiocyanate in the presence of N-ZnO as a photocatalyst under visible-light irradiation. This method provides a pathway to actives the tertiary aromatic and aliphatic amines via C-N bond cleavage.

### Introduction

Sunlight is an unparalleled natural resource. It is a cheap, nonpolluting, numerous, and unlimited renewable source of clean energy. Since society has become increasingly aware of the harmful strike of human industry on the surroundings, the booming of ways to effectively harness the energy of solar irradiation has appeared as one of the main scientific challenges of the twenty-first century. The junction between solar energy and environmental sustainability, however, is a much older idea that dates to the turn of the last century.<sup>1-3</sup> The observation that light alone could effect unique chemical changes in organic compounds led early twentieth-century photochemists to recognize that the sun might represent a stable source of clean chemical potential. One basic barrier that has finite the use of photochemical reactions on industrial scales is the weakness of most organic molecules to absorb visible wavelengths of light. Normally, the ultraviolet (UV) wavelengths commonly needed to excite conventional organic compounds during the photochemical process. As UV irradiation makes divergent pathways that resulted in unwanted products as well as UV is not abundant in the solar spectrum, the design and fabrication of photocatalysts with highly effective solar energy utilization have attracted considerable attention recently. 4-6 Among different kinds of photocatalysts, semiconductor solids such as TiO<sub>2</sub>, ZnO, etc. as photocatalysts, have been extensively studied.<sup>7, 8</sup> Nowadays in the field of semiconductor photocatalyst materials, ZnO has appeared as the prominent candidate and also as an effective and promising candidate in green photocatalysis processes because of its excellent properties, including low cost, high redox potential, nontoxicity, and environmentally friendly features.9-11 ZnO has a good Electrical and optical properties, such as a direct band-gap of 3.28 eV and a large exciton binding energy of 60 meV at room temperature and the ntype ZnO semiconductor has higher electron mobility, high breakdown voltages, and higher breakdown field strength.<sup>12-16</sup> The Mechanism of ZnO photocatalysis pathways is shown in Figure 1.

Electronic Supplementary Information (ESI) available: [experimental section and spectroscopy data of all compounds are included]. See DOI: 10.1039/x0xx00000x Photocatalytic processes in ZnO happen with the absorption of light irradiation with enough energy ( $h\nu \ge Eg$ ). Photon absorption causes excitation and transfer of electrons (e<sup>-</sup>) from the valence band (VB) to the conduction band (e<sup>-</sup><sub>CB</sub>), which leads to holes (h<sup>+</sup>) generation in the valence band (h<sup>+</sup><sub>VB</sub>). The second steps are separation and migration of charge-carriers (e<sup>-</sup> and h<sup>+</sup>) to the ZnO surface. The extremely reactive electrons and holes at the surface of ZnO photocatalyst tend to carry out reduction and oxidation reactions to generate reactive radical species (A<sup>--</sup>, B<sup>+</sup>) The photocatalytic process continues with the participation of these reactive radical species to operate the chemical reactions over the oxidation and reduction.<sup>17-19</sup>



Figure 1 The Mechanism of ZnO photocatalysis pathways

Because of the broadband structure of ZnO, (UV) light should be applied as the photoinitiation source. This is the important limiting factor in the usage of ZnO photocatalysts because the solar spectrum makes only a small fraction of UV light (~4%). Accordingly, ZnO photocatalysts show poor efficiency under solar irradiation. To usage solar irradiation, it is needed to change the electronic property of ZnO. Several strategies have been engaged to better the photocatalytic efficiency of ZnO under visible light. <sup>20-22</sup>

Doping with metals and nonmetals is being extensively considered to develop the absorption wavelength range of ZnO via modifying the electronic bandgap in the visible-light region.

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Previous works

CS<sub>2</sub>, NaOH

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CS<sub>2</sub>, EtOH

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Exclusively, because of the commonly smaller atomic size of nonmetal elements, nonmetal doping into ZnO lattice is usually much easier to be performed experimentally than metal doping and also nonmetal elements as a doping agent are cheaper and available than metal elements. In contrast, metal doping is more likely to induce the formation of vacancies or defect states that can serve as the recombination center for photogenerated electrons and holes.

Till now, among all non-metal dopants, nitrogen has attracted the most attention. This is due to its advantages, including the similarity of nitrogen and oxygen ionic radii, N 2p and O 2p energy states, high solubility, and also low formation energy. Hybridization of N 2p and O 2p states raises the valence band upper edge and thus, bandgap narrowing occurs.

So far, visible light photocatalysis processes of N-ZnO such as water treatment and air purification are extensively investigated for the removal of pollutants. However, no usage for this photocatalyst in visible-light-driven organic synthesis, selective oxidation, and reduction process has been reported in recent years.

Thiourea comprising compounds have been offered to have a plethora of biological virtues such as molecules anti-bacterial, antifungal, anti-inflammatory and anti-cancer.<sup>23-26</sup> Moreover, they are applied as supramolecular assemblies, and anion sensing.<sup>27-29</sup>On the other hand, the field of organocatalysts has been prevailed by the cinchona-thiourea based catalysts for a variety of organocatalytic transformations.<sup>30</sup> These inherent qualities of thioureas, in combination with the widespread research on their application in the synthesis of diverse heterocyclic compounds, make them prominent building blocks for synthetic chemists.<sup>31-36</sup> consequently, a great deal of effort has been focused on the development of newer synthetic strategies for this important building block. Up to now, one of the most common methods for the synthesis of thiourea has been the reaction of primary or secondary amines with isothiocyanates.<sup>37-45</sup> These reported methods have their disadvantages including the use of toxic reagents (thiophosgene & hydrogen sulfide), harsh reaction conditions, and/or are limited to the synthesis of symmetrical thiourea derivatives. So far, no procedure has been reported to use inactive tertiary amines for the synthesis of thiourea. In this work, the tertiary amines as a precursor were activated in an optical pathway, and then by a nucleophilic attack to the highly electrophilic carbon of the isothiocyanate resulted in the formation of unsymmetrical thiourea (Scheme 1).

# **Results and Discussion**

The first step in this study was the selection of a method for the preparation of ZnO NRs. The ZnO NRs were achieved by a hydrothermal method.<sup>46</sup> After that, nitrogen-doped ZnO NRs were prepared by heating mixture a ZnO NRs and urea as nitrogen source at 600 °C for 4 h.47 The pink-colored product was then obtained and denoted as N-ZnO NRs. As can be seen, the color of the ZnO changed after the doping process, and this change in color confirms the doping process. Corresponding colors of undoped ZnO and nitrogendoped ZnO are presented in (Figure 2). We also decided to evaluate the effect of the weight of urea as a source of nitrogen on visiblelight responsive of N-ZnO NRs. Therefore, we prepared a series of catalysts by heating 0.5 g ZnO with different amounts of urea (2, 4 and 8g). The color change was observed from white to pink every time after the doping process (Figure 2)



Figure 2 (a) Undoped ZnO, (b) 0.30%, (c) 0.32%, (d) 0.38%, (e) 0.45% N-ZnO NRs

To evaluate the nitrogen content, each of the synthesized catalysts was analyzed by CHNS analysis. The data obtained by CHNS analysis of nano N-ZnO powder are given in Table 1. To describe the reproducibility of the CHNS analysis for the percentages of N incorporated in ZnO, this analysis was replicated three times.

Table 1. CHNS analysis of nano N-ZnO NRs

Catalyst ZnO/urea g ( weight ratio)	Percentage % of nitrogen
0.5/1	0.30
0.5/2	0.32
0.5/4	0.38
0.5/8	0.45

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The UV–vis diffuse reflectance spectra of five samples are displayed in Figure 3. All prepared N-ZnO NRs could be excited by visible light, whereas undoped ZnO exhibited the absorption at the ultraviolet light range. As can be seen, from figure 3 three types of N-ZnO NRs (0.30%, 0.32%, 0.38%), does not show any significant difference in the absorption intensity in the visible region. However, the catalyst containing 0.45% doped nitrogen has the highest absorption intensity in the visible region. So, this N-ZnO NRs were chosen for more characterizations.



Figure 3 UV-vis diffuse reflection absorption spectra of five type synthesized samples.

The band gaps can be determined by UV–vis diffuse reflectance spectroscopy.<sup>48</sup> Figure 3 shows the UV–vis diffuse reflectance spectra of the pure and 0.45% N-ZnO NRs. The pure ZnO had no absorption above the wavelength of 400 nm. But, the nitrogendoped ZnO showed the absorption in the visible region, indicating that the bandgap was greatly narrowed owing to the impurity N 2p states isolated above the valence-band of ZnO.<sup>49</sup>

The optical bandgap of the semiconductors can be calculated by using the absorption spectrum and the following equation to draw the Tauc plot.  $^{50, 51}$ 

# Eq.1: $(\alpha hv)^{1/n} = A(hv - Eg)$

**h**: Planck's constant, v: frequency of vibration,  $\alpha$ : absorption (extinction) coefficient, **Eg**: bandgap, **A**: proportionality constant, **n**: the value of the exponent *n* denotes the nature of the transition. In this study, this method was applied to estimate the band gap energy value of the photocatalyst which obtained from UV–Vis spectra of the corresponding semiconductors<sup>52, 53</sup>. Fig. 4 depicts the plot of band-gap energy for 0.45% N-ZnO NRs, obtained by Tauc's equation (1). <sup>54</sup>

The calculated band-gap energy found to be 2.5 eV for 0.45% N-ZnO NRs. Noticeably, by treatment of nitrogen with ZnO, the band-gap of 0.45% N-ZnO was significantly reduced.



Figure 4 The plot for the bandgap calculation of 0.45% N-ZnO NRs.

#### XRD

The diffractogram of the pure ZnO and 0.45% N-ZnO NRs are shown in Figure 5. It is observed that ZnO is having the wurtzite phase (JCPDF: 891397) in both samples. No significant peak for nitrogen is observed in N-ZnO NRs which suggests the possibility of introduction of nitrogen into the ZnO lattice without affecting the ZnO crystal structure. Hence the lattice parameter (a=3.15 Å, c=5.05 Å) decreases in comparison to the pristine ZnO (a=3.17 Å, c=5.08 Å). Oxygen and nitrogen have similar atomic radii and the introduction of nitrogen into the ZnO lattice does not make too much difference in the XRD pattern. However, it has been reported that the bond length of Zn-N is smaller than Zn-O in O-Zn-N after N doping in the ZnO lattice which is the main reason for the shifting of XRD peak (higher  $\theta$  values) and lattice parameter in N-ZnO.55 The particle size of N-ZnO as evaluated by the Scherrer formula is 48.63 nm while that of the pure ZnO is 49.5 nm. The reduction of particle size may be attributed to the incorporation of nitrogen in ZnO.



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#### FT-IR

The FT-IR Spectrum of the catalyst in the region of 400-4000 cm<sup>-1</sup> is shown in Figure. 6.<sup>56</sup> There is a broad band at 3410 cm<sup>-1</sup> indicates the presence of –OH groups of absorbed water during the preparation process. The band arising from the bonding between ZnO (473 cm<sup>-1</sup>, 532 cm<sup>-1</sup>) is clearly represented. FT-IR spectrum reveals the presence of stretching vibrational bond C–O (1650 cm<sup>-1</sup>), C–H (1381 cm<sup>-1</sup>).



Figure 6 FT-IR spectrum of undoped ZnO (a) and 0.45% N-ZnO NRs (b).

#### SEM and TEM

SEM and TEM of the synthesized 0.45% N-ZnO NRs are represented in Figure 7. The SEM images of catalyst show that the surface morphologies are in the form of a nano-rod, with a wide range of sizes. The size is approximately 46.8 nm in TEM, and also after the doping process, despite the changes occurring at the surface, the nano-rod is confirmed. The TEM image of the catalyst shows that the catalyst has a nano-rod-shaped morphology.

#### BET

The data obtained by BET measurements of nano 0.45% N-ZnO NRs have been given in Table 2. The BET surface area was found to be 7.823 m<sup>2</sup>/g, whereas the BJH adsorption surface area of pores was 9.554 m<sup>2</sup>/g. The single point total pore volume was found to be 0.072 cc/g and pore diameter was 1.29 nm.

a)

b)

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Figure 7 SEM (a and b), and TEM (c,d) images of 0.45% Nr ZaQ Baine DOI: 10.1039/DONJ02197K





 Table 2 Results of BET surface area measurements for 0.45% N-ZnO

 NRs

	BJH adsorption summary	
Surface area		9.554 m²/g
Pore volume		0.072 cc/g
Pore Diameter Dv(d)		1.29 nm
	BET summary	
Surface Area		7.823 m²/g

Synthesis of thiourea derivatives using N-ZnO NRs as visible light photocatalyst

In our effort to exploit the photocatalytic activity of N-ZnO NRs, herein we report the simple, and efficient synthesis of thiourea derivatives at room temperature from *N*,*N*-dimethylaniline and pheny-*iso*-thiocyanate under visible light irradiation. Various parameters including the solvent, light, atmosphere, and the kind of catalyst were investigated for the reaction of *N*,*N*-dimethyl-*p*-toluidine **1a**, and phenyl-*iso*-thiocyanate **2a** as the model substrates (Scheme 2).



Scheme 2 A model reaction for the synthesis of thiourea 3a.

At first, different types of solvents were examined. As shown in Table 3, among all tested solvents, EtOH gave the best result in terms of the yield (entry 1), as ethanol is a polar protic solvent and according to the proposed mechanism (Figure 8), we hypothesize intermediate B (iminium ion) is solvated by ethanol so makes B more stable,

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consequently results in an acceleration in the reaction process. So, was chosen EtOH as a standard solvent to optimize the other reaction parameters.

Entry	Solvent (2mL)	Yield of 3a (%)
1	EtOH	81
2	DMSO	61
3	CH <sub>3</sub> CN	51
4	DMF	49
5	CHCl <sub>3</sub>	48
6	CH <sub>2</sub> Cl <sub>2</sub>	43
7	Acetone	39
8	EtOAc	28
9	THF	10
10	None	0

*Reaction conditions*: (0.5 mmol) of **2a** and (1.5 mmol) of **1a** in the presence of 0.005 g N-ZnO NRs (0.45%) at room temperature, 24 h, and CFL White (15 W) under air.

In the following, the optimization of the catalyst was evaluated. Consequently, 0.003 g of the catalyst was found to be the best amount. The results are summarized in Table 4. By using undoped ZnO, the desired product was generated in only a 32% yield (entry 5).

Next, the effect of light was investigated. According to data **Table 4.** Optimization of catalyst.

Entry	Catalyst (g)	Yield of 3a
(%)		
1	(0.45%) N-ZnO (0.005g)	81
2	(0.38%) N-ZnO (0.005g)	72
3	(0.32%) N-ZnO (0.005g)	71
4	(0.30%) N-ZnO (0.005g)	63
5	ZnO (0.005g)	32
6	(0.45%) N-ZnO (0.010g)	82
7	(0.45%) N-ZnO (0.005g)	81
8	(0.45%) N-ZnO (0.003g)	83
9	(0.45%) N-ZnO (0.001g)	59
10	None	trace

Reaction conditions: (0.5 mmol) of **2a** and (1.5 mmol) of **1a** in EtOH (2 mL), under CFL White (15 W), 24 h, in air.

represented in Table 5, CFL white 15 W power was shown the best results. The reaction afforded no product in a dark condition which this result might support the photo-induced electron transfer pathway. Also, under natural sunlight, the desired product was obtained in good yield (61%) (entry 6). This observation shows that the N-ZnO NRs can efficiently absorb solar irradiation to handle this organic synthesis. As the reaction was performed in the balcony of Shiraz University (December. 18-19, 2019, 29°59' north latitude and 52°58' east longitude, 1500 m above the sea level), we supposed the light intensity and light angle of sunlight was not suitable enough to accelerate reaction as much as LED lamps.



*Reaction conditions:* (0.5 mmol) of **2a** and (1.5 mmol) of **1a**, in the presence of N-ZnO NRs (0.45%, 0.003 g) in EtOH (2mL), 24 h, in air. CFL 15W White (0.9 W cm  $^{-2}$ , 400-700 nm), Blue LED 12w (0.7 W cm  $^{-2}$ , 450-460 nm), Green LED 12w (0.7 W cm  $^{-2}$ , 535-545 nm), Blue LED 12w (0.7 W cm  $^{-2}$ , 640-650 nm).

According to observations (Table 6), the desired product was found in lower yield under argon atmosphere rather than the air atmosphere. So, this indicates that the presence of  $O_2$  is necessary for the reaction.

Table 6. The optimization of the atmosphere.				
Entry	Atmosphere	Yield of 3a (%)		
1	O <sub>2</sub> Air	83		
2	O <sub>2</sub> balloon	83		
3	Argone	29		

*Reaction conditions:* (0.5 mmol) of **2a** and (1.5 mmol) of **1a**, in the presence of N-ZnO NRs (0.45%, 0.003 g) in EtOH (2ml), under CFL white 15w, 24 h, under open air condition.

The N-ZnO NRs photocatalyst could be also separated and recovered conveniently by centrifugation from the reaction mixture and reused in the next runs. Accordingly, the catalyst was recycled and reused effectively four times without a significant decrease in photocatalytic activities. Besides, the XRD pattern and FT-IR spectrum of the recovered catalyst after the last cycle were compared to the fresh catalyst and revealed no significant changes (Figure 8).

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**Figure. 8** (a) Recyclability of recovered N-ZnO NRs for thiourea synthesis, (b) FT-IR spectrum, (c) XRD pattern of the N-ZnO NRs after four-cycle.

Finally to show the scope and generality of the N-ZnO NRs, a variety of structurally diverse of tertiary aromatic and aliphatic amines were employed as the reaction substrates. The results are summarized in Table 7. The results indicated that either tertiary aromatic or aliphatic amines with phenyl-*iso*-thiocyanate were transformed to the corresponding thiourea in moderate yields.

The proposed mechanism is shown in Figure 9. Under visible light irradiation, electron and hole pairs are generated between N 2p states and conduction band of Zn 3d. The excited electrons  $e_{CB}$  in the conduction band will move to the surface and further transfer to surface-adsorb oxygen-producing  $O_2$ .<sup>-</sup> superoxide anion. A single electron transfer between *N*,*N*-dimethyl-*para*-toluidine **1a** and hole affords an amine radical cation **A**.  $O_2$ .<sup>-</sup> superoxide anion abstracts a hydrogen atom from **A** to form  $HO_2$ .<sup>-</sup> and iminium ion **B**. Because intermediate **B** is unstable, it is easily hydrolyzed to give a secondary amine **C** in  $O_2$  and water. Then the secondary amine **C**, nucleophilic attacks phenyl-*iso*-thiocyanate **2a** to afford target product **3a**.



*Reaction conditions:* (0.5 mmol) of 2a and (1.5 mmol) of 1a, in the presence of 0.45% N-ZnO NRs (0.003 g) in EtOH (2mL), under CFL white 15w, 24 h, in air.

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Figure 9 Proposed mechanism of synthesis of thiourea

To clarify this proposed mechanism of the reaction we set a series of control experiments (Scheme 3). When the radical-trapping agent TEMPO (2 equiv.) was added to reaction mixtures of 1a and 2a under the relevant standard conditions for the formation of **3a**, product **7a** was not observed in the presence of TEMPO (Scheme 3, eq. 1). Under the optimized conditions, we also investigated the effect of triethanolamine (TEA) as a scavenger to trap the holes. According to observation, we found that the reaction afforded no desired product in the presence of TEA (scheme 3, eq. 2). These results suggested that our reaction is likely to involve a radical process.

To prove the nucleophilic attacks between secondary amine C and phenyl-iso-thiocyanate, we surveyed three conditions in a model reaction using N-methyl aniline 4 and phenyl-iso-thiocyanate 2a (Scheme 3, eq. 3-5). According to this, we found that in each every three conditions the same product 5 was formed. To prove the structure of desired product 5, we characterized the product with <sup>1</sup>H-NMR analysis (See SI).

To confirm that secondary amine C, is produced in an optical pathway, we synthesized N-methyl aniline 7 from N,Ndimethylaniline 6, in the presence (0.45%) N-ZnO in EtOH, under visible-light irradiation (Scheme 3, eq. 6). To prove the structure of desired product 7, we characterized the product with <sup>1</sup>H-NMR analysis (See SI).

# Conclusions

In conclusion, we report the preparation of visible-light to activate Ndoped ZnO nanostructure using the combustion reaction method then we have shown that the nitrogen as a non-metal dopant has a positive effect on the N-ZnO as a visible-light-driven photocatalyst. For the first time, we successfully introduced a new procedure for the synthesis of unsymmetrical thiourea derivatives through a reaction between tertiary aliphatic and aromatic amines and phenyliso-thiocyanate as precursors over N-ZnO as an activated photocatalyst in the visible-light region. The method proceeds via straightforward formation of N-C bond through the nucleophilic attack of amine to highly electrophilic carbon of phenyl-isothiocyanate to generate thiourea in EtOH as a green solvent.

# Acknowledgments

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# Photocatalytic synthesis of unsymmetrical thiourea derivatives via visible-light irradiation using nitrogen-doped ZnO nanorods

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N-ZnO as a photocatalyst under visible-light irradiation promoted for environmentally friendly route for the synthesis of unsymmetrical thiourea derivatives