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Visible light thiocyanation of *N*-bearing aromatic and heteroaromatic compounds using Ag/TiO_2 nanotube photocatalyst†

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In this study, Ag/TiO_2 nanotubes (Ag/TNT) were synthesized *via* simple hydrothermal process, and this photocatalyst was successfully exploited in thiocyanation reactions at room temperature under visible light irradiation. Four classes of important heterocyclic compounds including indole, aniline, pyrrole and 2-amino thiazole derivatives *via* Ag/TNT treated with ammonium thiocyanate formed the corresponding thiocyano compounds in moderate to excellent yields. Plasmonic property and catalytic performance of Ag nanoparticles (which mainly deposited on the surface of TNT) in absorbing species containing sulfur atoms were key components for the reactions to proceed. This potent, simple and versatile protocol reported for the first time afforded thiocyanation reactions of aniline, pyrrole and 2-amino thiazole derivatives under visible light. The reactions proceeded through a radical pathway by applying air molecular oxygen as a low-cost and environmentally friendly terminal oxidant.

Introduction

It is believed that visible light photoredox catalysis is one of the most important technologies in solving the environmental problems and energy tension of the present century.[1] In this regard, it is important to find an efficient photocatalyst that can perform well under solar light.[2,3] Ru and Ir complexes are commonly used as impressive visible-light photocatalysts. Although they show excellent photocatalytic activity in many reactions, they are very toxic and expensive.[4] Organic dyes such as Eosin Y, Rose Bengal, and rhodamine B are also used as they supersede the transition-metal complexes in photocatalytic processes.[5–9] Although these are less toxic, less expensive, and easy to handle, they cannot be recycled.

Titanium dioxide (TiO_2) has attracted much attention of scientists as a heterogeneous photocatalyst because it is cheap, stable and nontoxic. Nevertheless, this effective photocatalyst has two main disadvantages: its high band gap energy (3.2 eV)[10,11] and high recombination rate of photoinduced charge carriers.[12] However, in recent years, enhancing photocatalytic activity and bypassing these drawbacks are great challenges. Loading nanoparticles of noble metals such as Ag, Au, Pt and Pd by the assistance of the surface plasmon resonance (SPR) effect has attracted much attention.[13] Because of their ability to strongly absorb visible light and improve the separation efficiency of electron–hole pairs in addition to low cost, antibacterial activity and easy preparation, Ag nanoparticles have attracted enormous interest.[14,15]

Aryl thiocyanates are valuable compounds in organic chemistry. Thiocyano compounds are widely used in drugs and biological compounds owing to their antiviral and antimicrobial properties.[16] These compounds are also very useful for either the synthesis of heterocyclic compounds[17,18] or conversion to various sulfur functional groups.[19,20] Due to the importance of aryl thiocyanates, several methods were used to synthesize thiocyano compounds, but the main challenge is applying mild and green reaction conditions as well as using easily available reagents. Generally, thiocyano compounds are obtained *via* direct electrophilic thiocyanation or nucleophilic substitution reactions of aromatic compounds. Although these methods are useful, using toxic transition metal, corrosive halogen reagents, strong oxidants, stoichiometric amounts of these reagents and high temperature are actual drawbacks.[21–30] In addition, most of the methods are centralized on some electron-rich indoles, and other *N*-bearing heterocycles with high reactivity have been unexplored. To the best of our knowledge, only four researches have been published on thiocyanation of indoles, imidazoheterocycle and tertiary amines using visible-light photocatalysts.[16,31–33] However, these protocols are not general and have been performed only on activated given heterocycles and have also not supported thiocyanation of aromatic amines.

Ag/TNT with low amount loading of Ag has shown great photocatalytic activity.[34] Although the photocatalytic activity of Ag/TiO_2 has been successfully applied in the degradation

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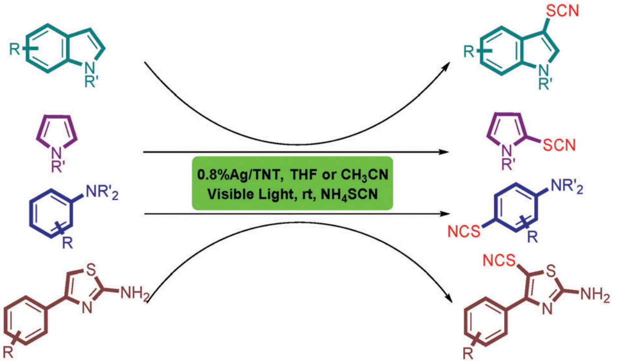


Scheme 1 Visible light methods for thiocyanation of aromatics and heteroaromatics.

of methylene blue, methylene orange and other dyes and pollutants,[35–37] there are only few reports on using Ag/TiO_2 in organic reactions.[38] Herein, we envisioned that Ag/TNT can show the merit of an effective heterogeneous photocatalyst in organic reactions. Silver nanoparticle surface has high potency to absorb molecules containing sulfur atoms. Therefore, thiocyanates as anionic species are readily absorbed on silver nanoparticles.[39–41] Hence, in this study, we synthesized an Ag/TNT photocatalyst and applied it in the thiocyanation of indole, aniline, pyrrole and 2-phenylamino-thiazole derivatives under visible-light irradiation and ambient air at room temperature (Scheme 1). This sustainable protocol exhibits the following advantages compared to non-visible-light-driven previous methods: (1) external oxidant-free, (2) milder and greener reaction condition, (3) catalytic amount of metals instead of stoichiometric amount as well as recyclability and reusability of Ag/TNT as a heterogeneous photocatalyst.

Results and discussion

At first, TiO_2 nanotubes (TiO_2-NTs) and Ag/TiO_2 nanotubes (Ag/TNT, 0.8% and 2%) were prepared through a modified solvothermal method.[34,37,42] Then, the catalyst was characterized by several methods such as Fourier-transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), UV-visible absorbance (UV-vis), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The content of Ag on TiO_2-NTs was determined by inductively coupled plasma (ICP) and atomic absorption spectroscopy; 2.0 wt% and 0.8 wt% of Ag loadings were demonstrated. Notably, 0.8% Ag/TNT showed high photocatalytic activity, which was as good as that of 2.0% Ag/TNT; thus, all characterizations were based on less percentage of silver (0.8% Ag/TNT).

FT-IR spectra of Ag/TNT are shown in Fig. 1. Accordingly, absorption peaks of O–H stretching appear at 3413 cm^{-1} and 1631 cm^{-1} and at 2920 cm^{-1} and 2912 cm^{-1}, which are related to water and Ti–OH bands, respectively. The bands appearing at 551 and 493 cm^{-1} can be due to the characteristic vibrations of Ti–O–Ti.

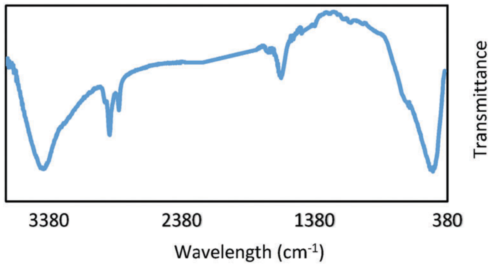


Fig. 1 FT-IR spectrum of Ag/TNT.

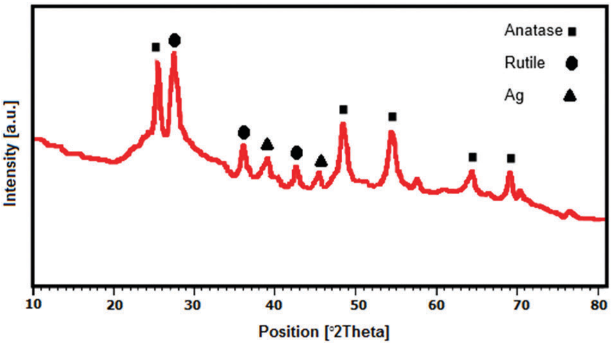


Fig. 2 X-ray diffraction patterns of Ag/TNT.

The X-ray diffraction (XRD) patterns of the vapor-thermally treated Ag/TNT are shown in Fig. 2; they indicate the presence of anatase (101) and rutile (110) phases, which are demonstrated at 2θ values of 25.26° and 27.66°, respectively.[43,44] The diffraction peaks of Ag were observed at 2θ values of 38.68°(111) and 44.18°(200).[34,37] However, due to the amount of silver that is less than 1% (0.8% determined by ICP), low intensity of Ag peaks was observed. The average sizes of crystalline TiO_2 and Ag were determined to be about 11 nm and 19 nm, respectively (the (101) and (111) peaks using the Scherrer equation).

Fig. 3 shows SEM and TEM of Ag/TNT. We clearly observed the shape of nanotubes with internal cavities. The diameter of nanotubes ranged from 10 to 12 nm. Ag NPs were observed on the surfaces of TiO_2 crystals with mean sizes of 10–50 nm, as determined by TEM.

The UV-visible absorption spectra of P25, TiO_2-NTs and Ag/TNT are illustrated in Fig. 4. Absorbed ultraviolet light below 390 nm is related to the band gap of TiO_2, which is about 3.2 eV. The peaks arise from the charge-transfer absorption from 2p orbital of oxide anions (valence band) to the 3d orbital of Ti^{4+}

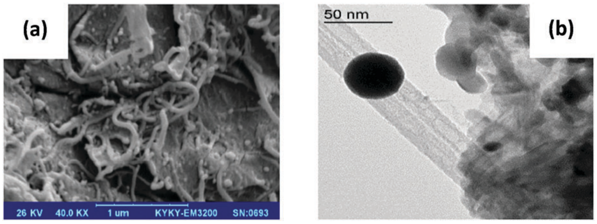


Fig. 3 SEM image of Ag/TNT (a). TEM image of Ag/TNT (b).

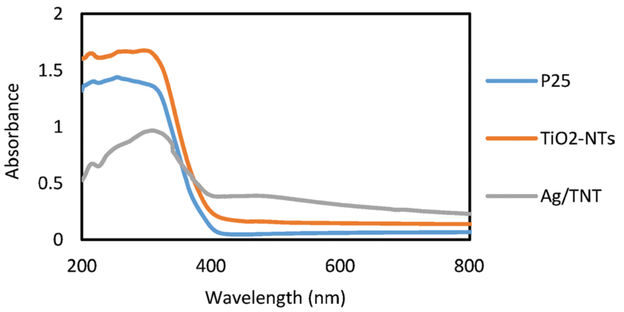


Fig. 4 UV-vis spectra of P25, TiO$_2$-NTs and Ag/TNT.

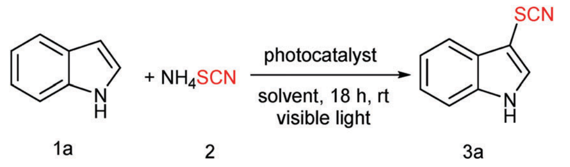
cations (conduction band) in titanium dioxide.[45–47] However, absorption in the visible area for TiO$_2$-NTs is more effective than for P25. Also, the broad absorption peak at 470 nm is related to Ag-NPs doped on TiO$_2$-NTs. Ag/TNT showed the best absorption in the visible area, which indicated surface plasmon resonance (SPR) of Ag-NPs.[13,48]

The survey XPS spectrum of Ag/TNT demonstrated the presence of C, O, Ti, and Ag; the high-resolution XPS spectra of Ag 3d and Ti 2p are shown in Fig. 5.[14] According to Fig. 5b, the orbitals of Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ appeared at 367.9 and 373.9 eV, respectively. It is noteworthy that the difference between the doublet peaks is 6 eV, which demonstrates the presence of Ag^0 in the Ag/TNT photocatalyst. Indeed, in comparison with the results of bulk Ag^0 materials (about 374.3 eV for Ag 3d$_{3/2}$ and 368.3 eV for Ag 3d$_{5/2}$), these peaks showed slight negative shifts.[14] As revealed in Fig. 5c, Ti 2p$_{1/2}$ and Ti 2p$_{3/2}$ orbitals were related to two peaks at 464.5 and 458.8 eV, respectively, in XPS spectra. Also, the spectra demonstrated an energy shift of about 0.4 higher than that of pure anatase TiO$_2$: about 464.1 eV for Ti 2p$_{1/2}$ and 458.4 eV for Ti 2p$_{3/2}$. These results are probably related to the interaction between Ag 3d and Ti 2p (Fig. 5c).[14]

After preparation and characterization of Ag/TNT, we applied it as a photocatalyst in thiocyanation of indoles, anilines, pyrroles and 2-amino thiazoles. For this purpose, we chose 1*H*-indole (**1a**) as the model substrate, and the optimization results are shown in Table 1.

At first, we examined the effect of solvents. Different solvents were used and finally, lower and higher yields were obtained by using CHCl$_3$ and THF, respectively (Table 1, entries 1 and 4). Next, the effects of different lights on the reactions were investigated; the reaction efficiency improved *via* decreasing wavelength. As shown from the results for entries 1 and 6, compact fluorescent lamp (CFL) and blue LED were the best light sources for the reactions that afforded 83% target product yield. Notably, the reaction yielded some amount of the product **3a** in dark condition (entry 9). Furthermore, we noticed that the yield of the corresponding product correlated with the size, shape, type and the amount of photocatalyst (entries 10–17). Accordingly, lower yield of the corresponding product was obtained by using bulky TiO$_2$, P25 and TiO$_2$-NTs. On the other hand, 0.8% Ag/TNT with high surface area showed good efficiency (BJH desorption summary: 221.096 m^2 g^{-1}). Up to 92% yield of product **3a** was obtained by using both 0.8% Ag/TNT

Table 1 Optimized reaction conditions^{a}



Entry	Catalyst [mg]	Solvent	Light^{g}	Yield of **3a**^{b} [%]
1	0.8% Ag/TNT [6]	THF	CFL, white	83
2	0.8% Ag/TNT [6]	CH$_3$CN	CFL, white	72
3	0.8% Ag/TNT [6]	EtOH	CFL, white	38
4	0.8% Ag/TNT [6]	CHCl$_3$	CFL, white	30
5	0.8% Ag/TNT [6]	EtOAc	CFL, white	68
6	0.8% Ag/TNT [6]	THF	Blue LED	83
7	0.8% Ag/TNT [6]	THF	Green LED	42
8	0.8% Ag/TNT [6]	THF	Red LED	28
9	0.8% Ag/TNT [12]	THF	Dark	14
10	No catalyst	THF	CFL, white	0
11	0.8% Ag/TNT [3]	THF	CFL, white	71
12	0.8% Ag/TNT [12]	THF	CFL, white	42^{c}, 64^{d}, 92, 96^{e}, trace^{f}
13	0.8% Ag/TNT [24]	THF	CFL, white	92
14	TiO$_2$-bulk [12]	THF	CFL, white	13
15	P25 [12]	THF	CFL, white	35
16	TiO$_2$-NTs [12]	THF	CFL, white	46
17	2.0% Ag/TNT [12]	THF	CFL, white	92
18	0.8% Ag/TNT [12]	THF	CFL, white	42^{h},38^{i}

[a] Reaction conditions: 1*H*-Indole (1 mmol), ammonium thiocyanate (3 mmol), solvent (6.0 mL), open to air, at room temperature, 18 h. [b] Isolated yield. [c] 1 mmol of ammonium thiocyanate was used. [d] 2 mmol of ammonium thiocyanate was used. [e] O$_2$ atmosphere. [f] N$_2$ atmosphere. [g] 12 W. [h] KSCN (3 mmol). [i] NaSCN (3 mmol).

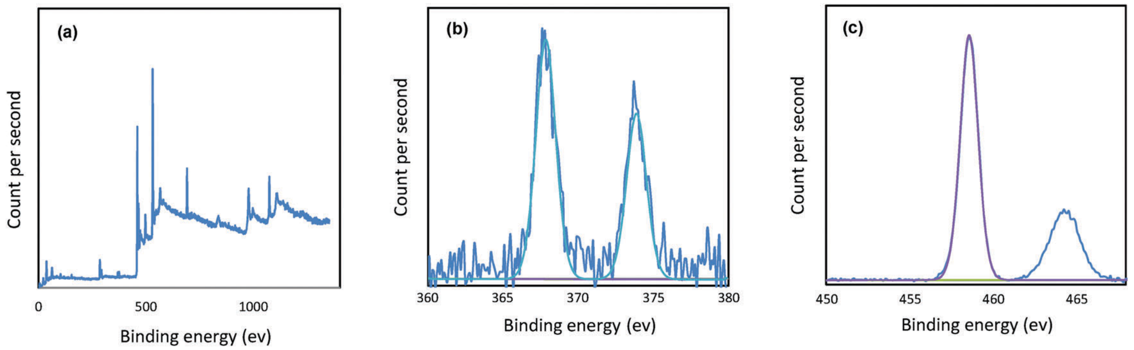
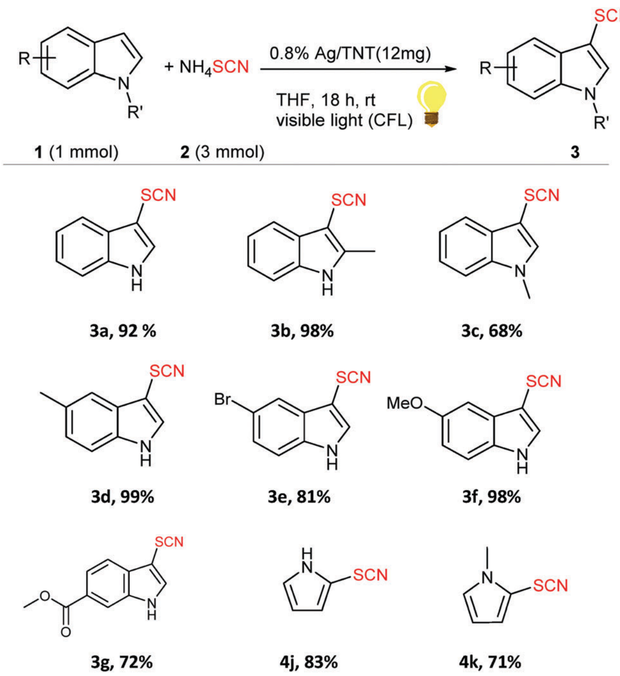


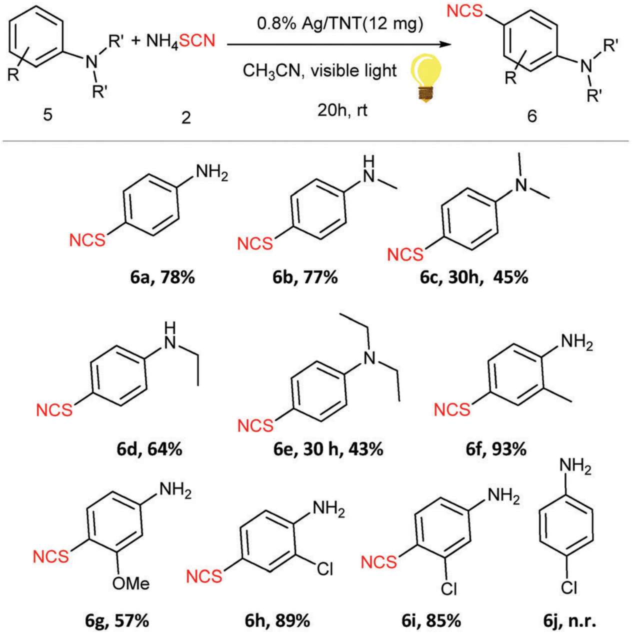
Fig. 5 XPS spectra of Ag/TNT: survey of Ag/TNT (a), high resolution XPS for Ag 3d (b), high resolution XPS for Ti 2P (c).

and 2% Ag/TNT (entries 12 and 17) as photocatalysts. These results imply that Ag-loaded TiO_2-NTs show significant increase in visible absorption capacity of the catalyst. The reaction condition did not afford any product without the addition of the photocatalyst (entry 10). Moreover, the amount of ammonium thiocyanate was controlled, and the best result was obtained *via* 3 equiv. It is noteworthy that by decreasing the amount of ammonium thiocyanate, the yield of the product **3a** decreased (entries 12^{c} and 12^{d}). This is probably due to a side reaction, which turned out to be the generation of $(NH_4)_2SO_4$; our group and Li's group identified this byproduct during the reaction.[31] Also, the reaction was investigated under O_2 and N_2 atmospheres. As expected, the reaction efficiency increased slightly under O_2 atmosphere (entry 12^{e}) and under inert atmosphere, the reaction yield decreased to trace amounts of target indole (entry 12^{f}). Finally, other thiocyanate salts such as KSCN and NaSCN were tested and the best result was obtained using ammonium thiocyanate (entry $18^{h,i}$).

With this optimized condition in hand, the scope of the reaction was investigated. Also, we turned our attention to other heterocycles. In this context, pyrrole and *N*-methylpyrrole were examined by using the present protocol. The results are summarized in Scheme 2. Accordingly, the reactions of indole with electron-donating and electron-withdrawing substituents efficiently proceeded to form thiocyanated products. It should also be pointed out that indoles bearing electron-donating groups gave higher yields.



Scheme 2 Scope of thiocyanation of indole and pyrrole derivatives using Ag/TNT[a,b]. [a] Reaction conditions: **1** (1 mmol), **2** (3 mmol), THF (6.0 mL), 0.8% Ag/TNT (12 mg), open to air, at room temperature, under irradiation of 12 W CFL, 18 h. [b] Isolated yield.



Scheme 3 Scope of the thiocyanation of aniline derivatives[a,b]. [a] Reaction conditions: **5** (1 mmol), **2** (3 mmol), CH_3CN (6.0 mL), 0.8% Ag/TNT (12 mg), open to air, at room temperature, under irradiation of 12 W CFL, 20 h. [b] Isolated yield.

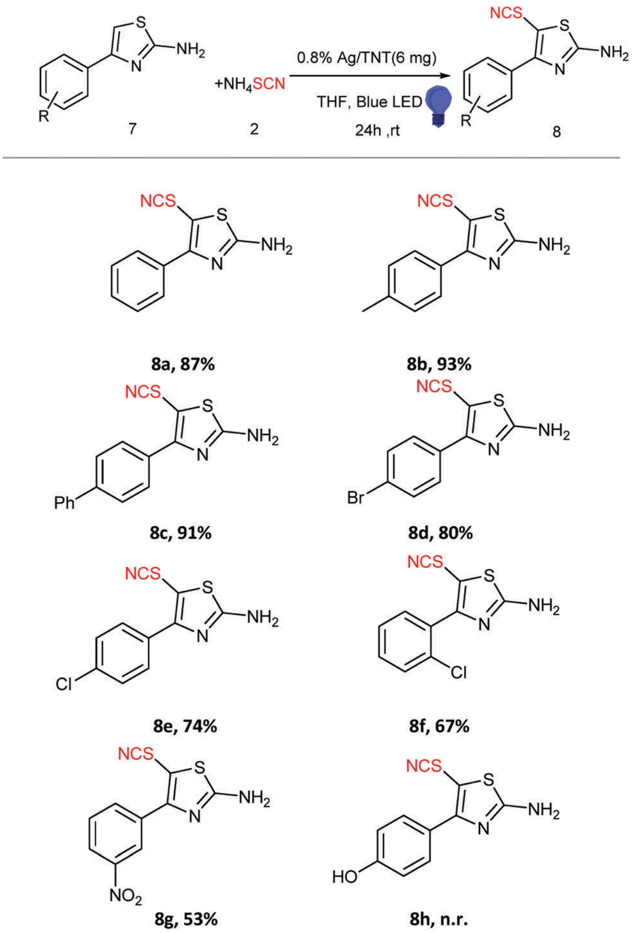
Then, we explored the thiocyanation reaction of aniline derivatives under visible light for the first time. In the case of aniline, we found that THF as a solvent was not as effective as it was for indole and pyrrole derivatives. Thus, we tested other solvents, as shown in ESI† (Scheme S1). Accordingly, CH_3CN was found to be the best solvent for aniline derivatives. However, other factors in the previous protocol were also applicable to thiocyanation of aniline. Next, the scope of thiocyanation reaction of various substituted anilines was investigated. The generality and the scope of the reactions are shown in Scheme 3. Notably, between tertiary amines such as *N*,*N*-dimethylaniline (E_{ox} = +0.96 V *vs.* NHE)[49,50] and thiocyanate anion (E_{ox} = +0.64 V *vs.* NHE),[32,50] *N*,*N*-dimethylaniline is a better electron sacrificer to quench the photoexcited state of Ag/TNT. Hence, the isolated yields of **6c** and **6e** showed significant decrease and extended reaction times rather than other substrates.

Notably, thiocyanation reaction of anilines afforded products of high *para*-selectivity. Hence, the reaction did not afford any product in the presence of a *para*-substituent (**6j**). Moreover, the presence of a substituent in the *meta* position reduced the yield of the reaction (**6g**, **6i**). Also, this reaction exhibited good diversity in the presence of electron-donating and electron-withdrawing substituents, but we noticed that electron-donating substituents were slightly better (**6f**).

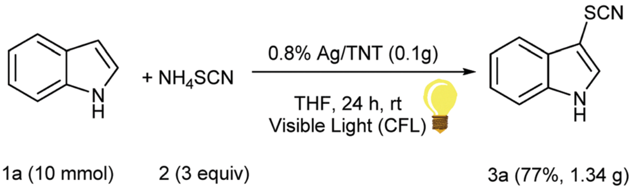
Next, encouraged by these results, we decided to study this photocatalyst in thiocyanation of 2-amino-4-phenylthiazole derivatives. 2-Amino thiazoles, especially C-5 substituted derivatives, exhibited biological activity.[31] In particular, the target product of thiocyanation reaction of 2-amino thiazole not only exhibited biological activity but also could be easily converted to other sulfur-containing compounds such as sulfides,[51] thioethers disulfides,[52] and trifluoromethyl sulfides.[51] Previously reported methods for the synthesis of thiocyanated 2-amino-4-phenylthiazole derivatives mainly suffer from one of the following drawbacks: toxic or harsh reaction conditions and intractable precursors.[53–55] Therefore, these unfavorable reaction conditions restrict their application for commercial-scale productions. Hence, an inexpensive, easy to handle and environmentally benign method for the thiocyanation reaction of this important class of heterocyclic compounds still remains unexplored. To the best of our knowledge, so far, no method has been reported for direct thiocyanation of 2-amino thiazole using visible light. To address this issue, first, we synthesized the starting material 2-amino-4-phenylthiazole derivative, which was prepared from acetophenone, iodine, and thiourea *via* a modified procedure reported by Dodson[56] and Woodbridge.[57] Next, the thiocyanation reaction of 4-phenylthiazol-2-amine was investigated using Ag/TNT with two different percent contents of silver metal (0.8% and 2.0%) and no significant difference was observed between them. Thus, to increase the reaction efficiency, we examined several reaction conditions along with 0.8% Ag/TNT. We also performed the optimization reaction of 2-amino-4-phenylthiazole in the thiocyanation reaction and found that the best efficiency was obtained when we used THF, blue LED, and 6.0 mg Ag/TNT as solvent, light source and amount of catalyst, respectively (ESI,† Scheme S2). The scope and generality were surveyed, and the results are shown in Scheme 4. A wide range of 2-amino-4-phenylthiazole derivatives containing electron-withdrawing and electron-donating groups were achieved in good to excellent yields upon isolation. Meanwhile, electron-donating substituents on 4-phenylthiazol-2-amine resulted in target products in good yields (**8b**, **8c**). 4-Phenylthiazol-2-amine bearing substituents such as $-NO_2$, –Cl and –Br (**8g**, **8e**, **8f** and **8d**) afforded thiocyanate products in moderate yields and the substrate containing –OH substituent did not produce the desired product (**8h**).

Next, to show the merits of this photocatalyst system, we conducted several experiments including a Gram-scale reaction (10 mmol indole) and catalyst recycling experiments using our protocol for thiocyanation of indole (Scheme 5 and Fig. 6). As shown in Scheme 5, the reaction afforded the desired product in excellent yield (77%, 1.34 g) after 24 hours at room temperature.

The main advantage of the heterogeneous catalyst system compared to that of the homogenous system is the ability of catalyst recycling. Having established the efficacy of Ag/TNT in thiocyanation of indoles, pyrroles, anilines and 2-amino thiazoles, we investigated the recyclability of the photocatalyst in the thiocyanation reaction of indole (Fig. 6). After completing the reaction, the reaction mixture was centrifuged to separate the photocatalyst and the corresponding product was isolated according to the procedure given in the experimental section. Then, the catalyst was washed several times with distilled water and ethanol to be applied again. Ag/TNT (0.8%) was successfully applied for 9 runs without remarkable loss of yield or extended reaction time. Similarly, each run of the reaction was conducted according to the typical procedure. In addition, ICP-AES measurement exhibited that only 8.0 wt% Ag leached out from this photocatalyst after 9 runs.



Scheme 4 Screening the scope of thiocyanation of 2-amino-4-phenylthiazole derivatives[a,b]. [a] Reaction conditions: **7** (1 mmol), **2** (3 mmol), THF (6.0 mL), 0.8% Ag/TNT (6 mg), open to air, at room temperature, under irradiation of 12 W blue LED, 24 h. [b] Isolated yield.



Scheme 5 Gram-scale thiocyanation of indole.

To gain further evidences about the reaction mechanism, we contrived some control experiments using radical and hole scavengers under the optimized reaction conditions and performed the thiocyanation reaction in the absence of visible light irradiation. In this context, thiocyanation reactions of indole, pyrrole, aniline and 2-amino-4-phenylthiazole were performed by adding 3.0 mmol of 2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO). As shown in Scheme 6(a), the yield of the reaction of 2-amino-4-phenylthiazole decreased from 87 to trace amount of target product; also, the reaction of pyrrole, indole and aniline did not result in any corresponding product after 18 and 20 h (ESI†). Afterward, we surveyed the effect of trimethylamine (TEA) as an electron sacrificer in comparison with that of SCN^- (Scheme 6(b)). Considering the redox potential

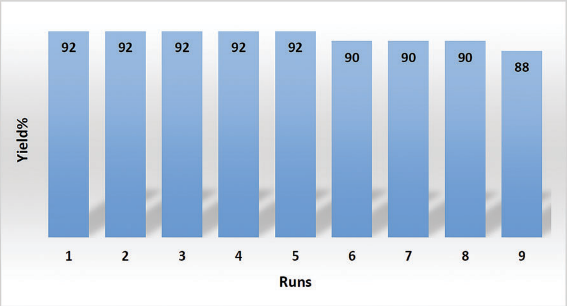
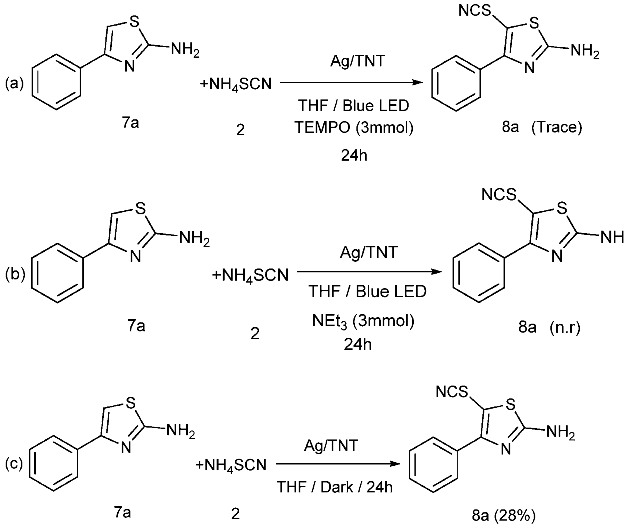


Fig. 6 Recycling of the catalyst in the thiocyanation reaction of indole. Reaction conditions: 1*H*-indole (1 mmol), ammonium thiocyanate (3 mmol), 0.8% Ag/TNT (12 mg), THF (6.0 mL), open to the air, irradiation under a 12 W CFL at room temperature, 18 h. Isolated yield.



Scheme 6 Control experiments.

value of TEA ($E^0_{1/2}$ = 1.08 *vs.* NHE),[50,58] after addition of 3.0 mmol TEA, no product of **8a** was found in this condition and the path of target product was quenched to yield trace amounts of **3a**. We also investigated the progress of thiocyanation reactions of 2-amino-4-phenylthiazole and indole under dark conditions (ESI†). As illustrated in Scheme 6(c), the reaction proceeded to give only 28% target product in dark condition. According to the aforementioned control experiments, it can be strongly deduced that the reactions proceed through a radical mechanism.

It is well-known that the deposition of noble metal nanoparticles such as Au, Ag and Cu onto TiO_2 not only enhances the absorption of visible light, because of localized surface plasmon resonance (LSPR), but also improves the separation of electron–hole pairs in a semiconductor.[59–62] A Schottky barrier at the interjunction point of Ag nanoparticles and TiO_2 accelerates electron and hole movement in opposite directions. Thus, these synergic effects improve the photocatalytic activity of Ag/TNT. On the basis of our experimental investigation and literature review,[32,63] we proposed a plausible mechanism, as illustrated in Fig. 7. Ag nanoparticles are desirable electron acceptors (Fermi level, E_r = 0.4 V).[64] First, under irradiation of

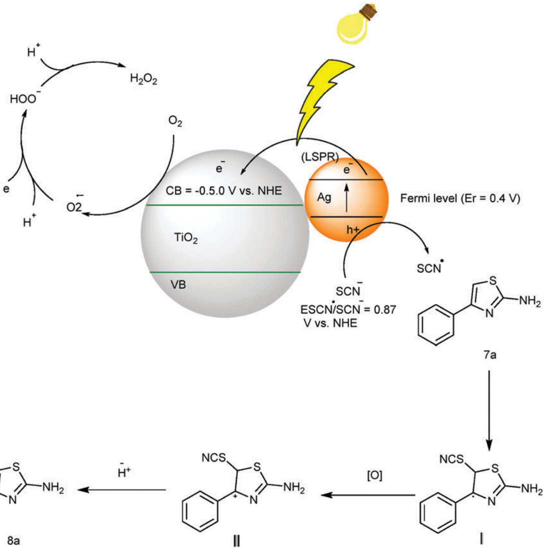


Fig. 7 The proposed mechanism of thiocyanation reaction.

visible light, due to the level of conductive band in Ag, electrons moved from Ag-NPs to the conduction band of TiO_2 and left holes on Ag-NPs. The resulting holes acquired electrons form thiocyanate anions and generated thiocyanate radicals ($E_{\mathrm{SCN^\bullet/SCN^-}}$ = 0.87 V *vs.* NHE).[32,50] Subsequently, the 2-amino-4-phenylthiazole molecule (**7a**) was attacked by the photogenerated thiocyanate radical and yielded a radical intermediate I. Then, the cation intermediate II was obtained from the oxidation of the intermediate I, which yielded the target product *via* deprotonation. Simultaneously, electron transfer from CB of TiO_2 (E_{cb} = −0.5 V *vs.* NHE)[65] to oxygen generated a superoxide anion radical ($E^0_{O_2/O_2^{\bullet-}}$ = −0.15 V *vs.* NHE).[66] Notably, generation of hydrogen peroxide was detected after the completion of the reaction by using an H_2O_2 paper indicator and ^{1}HNMR spectroscopy (ESI†).

Experimental

General procedure for the preparation of TiO_2-NTs

TiO_2-NTs were prepared by a modified hydrothermal method. At first, 0.5 g P25 was immersed into 25 mL of NaOH (10 M) solution and refluxed for 24 h in an oil bath at 108 °C. After 2 h, the mixture was cooled down to room temperature and separated by centrifugation. The obtained product was washed with 1 M HCl and deionized water until the pH reached less than 7. After that, TiO_2-NTs were dried at room temperature and then calcined for 1 h at 300 °C.[34]

General procedure for the preparation of Ag/TNT

First, 0.5 g TiO_2-NTs was mixed into 250 mL $AgNO_3$ and ethanol solutions with concentrations of 0.25 mM and 0.50 mM, respectively; then, the mixture was refluxed for 24 h at 83 °C. After 2 h, the cold mixture was centrifuged and washed with ethanol and deionized water 4 times.[42]

Typical procedure for thiocyanation

To a mixture of heterocyclic aromatic compounds (1 mmol), ammonium thiocyanate (3 mmol) in appropriate solvent, 0.8% Ag/TNT as the catalyst was added and the mixture was irradiated with visible light (irradiation light was under 12 W compact fluorescent lamp (CFL), 12 W blue LED, 12 W green LED and 12 W red LED) and was open to air at room temperature. The progress of the reactions was screened by TLC. After completion of the reactions, we separated the catalyst from reaction solvent by centrifugation and then, 20 mL H_2O was added to the reaction solvent and the mixture was extracted by CH_2Cl_2 in a decanter. The organic layer was further cleaned with distilled water (2 × 15 mL) and dried over Na_2SO_4. Then, the solvent was removed from the mixture under reduced pressure and the resulting crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (20 : 1) to give the desired thiocyanation products in good to excellent isolated yields. Furthermore, 2-amino-4-phenylthiazole derivatives were purified by recrystallization in acetone.

Conclusions

In conclusion, Ag/TNT heterojunctions exhibit much higher photocatalytic performance than pure TiO_2-NTs and P25 under visible light, which is due to the LSPR effect and the restraining effect for recombination of photogenerated electrons and holes. Considering sulfur affinity of silver metals, we exploited Ag/TNT photocatalyst in thiocyanation reactions. This easily prepared, nontoxic and cheap photocatalyst exhibited high activity toward thiocyanation of indoles, anilines, pyrroles and 2-amino thiazoles for the first time under visible light (except indoles). These photoinduced reactions have been developed using Ag/TNT as a photoredox catalyst at room temperature without an external oxidant. Simple work-up, good to excellent yields, mild reaction conditions and reusability of the catalyst are the major advantages of this unprecedented procedure.

Conflicts of interest

There are no conflicts to declare.

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