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#### Applied Organometallic Chemistry

# Deep eutectic solvent-assisted synthesis of highly efficient nanocatalyst (n-TiO<sub>2</sub>@TDI@DES (ZnCl<sub>2</sub>:urea)) for chemoselective oxidation of sulfides to sulfoxides

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**Funding information** Semnan University This study proposed a straightforward process to synthesize 2,4-toluene diisocyanate (TDI)-functionalized TiO<sub>2</sub> nanoparticles in which a cost-effective linker (TDI) with high reactivity was employed to couple nano-TiO<sub>2</sub> through covalent bonding to a deep eutectic solvent (DES). By this method, DES was successfully immobilized on the TiO2@TDI surface as an adsorbent and stabilizer. The structural, morphological, and physicochemical characteristics of the synthesized nanocatalysts were evaluated using various analytical methods including Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy equipped with energy-dispersive X-ray spectroscopy (SEM-EDX), and elemental analysis. The heterogeneity of the catalyst was also examined by a hot filtration test. The obtained TiO2@TDI@DES nanoparticles offered superior catalytic behavior and excellent yield as well as recyclability for the chemoselective oxidation of sulfide into sulfoxide using a green oxidant (hydrogen peroxide). This catalyst exhibited excellent reusability as it can be recovered for six successive cycles with no significant leach or reduction of catalytic efficiency.

#### K E Y W O R D S

2,4-toluene diisocyanate, deep eutectic solvent, nanocatalyst, nano-TiO<sub>2</sub>, oxidation of sulfide

#### **1** | INTRODUCTION

Modern chemistry nowadays is facing with crucial challenges such as developing practical routes, reaction environments, conditions, and materials in favor of green chemistry to achieve an environmentally friendly procedure.<sup>[1]</sup> In this regard, the chemists are now focusing on the development of recoverable, easily separable, nontoxic, and cost-effective catalysts.<sup>[2]</sup>

Deep eutectic solvents (DESs) have been widely employed as the neoteric ionic solvents in industrial reactions. In addition to their physical and chemical similarities with the conventional ionic liquids (ILs), DESs encompass other benefits including cost-effectiveness, convenient synthesis, green chemistry, and high atomic economy.<sup>[3,4]</sup> Due to outstanding features (e.g., broad liquid range, biodegradability, superior thermal stability, low vapor pressure, and high accessibility), DESs have been introduced as promising candidates for catalyst and reaction media.<sup>[5,6]</sup> During the DES synthesis, its physico-chemical characteristics could be easily tuned by altering the types of hydrogen-bond donors and acceptors. Lewis acidic DESs (LADESs) are homogeneous catalysts, which are capable of offering an efficient medium for organic synthesis processes. Owing to their superior stability and selectivity (compared with conventional metal halide

catalysts), LADESs have received extensive attention of academic communities.<sup>[7–9]</sup> Despite their high potency, industrialization of LADESs has been hindered by several issues including the application of relatively large amounts of LADESs, their homogeneity and difficulty in their separation, and poor reusability, which can result in serious economical and environmental consequences. Considering the mentioned problems along with the industrial preference for employing heterogeneous catalysts, DESs have been immobilized onto solid supports.<sup>[10,11]</sup>

Over the last decade, the green chemistry concerns have preferred to perform the reactions with recyclable catalyst and under solvent-free conditions. For these reasons, wide attentions were paid to the use of heterogeneous catalysts due to their recyclability and ease of separation.<sup>[12,13]</sup> On the other hand, nanoparticles (NPs) have more active sites due to their high surface/volume ratio. Therefore, the study of heterogeneous nanocatalysts is considered as a progressive research that leads to the introduction of many modified catalysts.<sup>[14]</sup>

The insoluble nature of solid acids has resulted in their proper stability, superior reusability, moderate reaction condition, environmental friendliness, ease of separation, and facile operation.<sup>[15]</sup> A well-defined grafted solid catalyst can improve the dispersion status and prevent the formation of aggregates in the solvent through steric hindrance.<sup>[16-18]</sup> In this regard, transition metal oxide nanocatalysts undoubtedly play a remarkable role in the organic reactions due to their superior aspect ratio and coordination sites, which lead to their excellent catalytic activities.<sup>[19,20]</sup> Heterogeneous catalysts were superior to homogeneous catalysts due to their effortless isolation, easy handling, and reusability. To increase the efficiency and stability of homogeneous catalysts, several approaches of immobilization have been proposed on various heterogeneous supports.<sup>[21-23]</sup> Nanocatalysts can be considered as a mediator between the homogeneous and heterogeneous catalysts. They can provide efficient, accessible, and extraordinary stable heterogeneous supports with high catalyst loading capacity. Owing to their availability, nontoxicity, superior activity, recoverability, strong oxidizing behavior, and long-term stability, titanium dioxide NPs (nano-TiO<sub>2</sub>) have attracted the attention of scientists in this field. Nano-TiO<sub>2</sub> has been widely employed as the photocatalyst for environmental decontamination and technological purposes due to its remarkable features. Furthermore, it has been long employed in photo-electrochemical cells, water or air purification, and degradation of organic pollutants.<sup>[24-27]</sup>

The organic sulfides oxidation into their corresponding sulfoxides has been recognized as one of the prominent functional group transformations in organic chemistry.<sup>[28,29]</sup> Organic sulfoxides are also significant intermediates in the asymmetric synthesis of bioactive substances.<sup>[30]</sup> They also play a pivotal role in the pharmaceutical industry or other delicate chemical procedures.<sup>[31-33]</sup> Omeprazole and fipronil pesticides are two typical instances of the widespread use of the mentioned intermediates.<sup>[34]</sup> The sulfides oxidation into their corresponding sulfoxides and sulfones has been extensively explored, and plenty of synthetic routes have been already proposed. For this purpose, some oxidants (such as concentrated HNO<sub>3</sub>, high-valence metal salts,<sup>[35]</sup> sodium metaperiodate, *m*-chloroperoxybenzoic acid,<sup>[36]</sup> halogens, and nitrogen pentoxide<sup>[37,38]</sup>) have been widely used. The majorities of these procedures are complex processes depending on dangerous and high-toxicity reagents<sup>[39]</sup> or are accompanied by overoxidation of sulfoxides<sup>[40]</sup> resulting in the formation of unpredicted sulfones or unwanted by-products.<sup>[41,42]</sup> In addition to molecular oxygen, hydrogen peroxide is one of the most powerful green oxidants. It is a cost-effective and accessible oxidant with high atom efficiency with water as the only by-product.<sup>[43–45]</sup> In this context, numerous studies have proposed a method for oxidizing sulfides into their corresponding sulfoxides by the use of  $H_2O_2$  at the presence of NiFe<sub>2</sub>O<sub>4</sub>,  $^{[46]}$  Ti(IV) complex,  $^{[47]}$  V/TiO<sub>2</sub>,  $^{[48]}$ cerium(IV) triflate,<sup>[49]</sup> molybdate-based catalyst,<sup>[50]</sup> metalloporphyrins immobilized into montmorillonite,<sup>[51]</sup> Zn complex,<sup>[52]</sup> Cu salen-Fe<sub>3</sub>O<sub>4</sub>,<sup>[53]</sup> Cu(II) Schiff base complex,<sup>[54]</sup> complex,<sup>[55]</sup> preformed manganese tantalum(V) chloride.<sup>[56]</sup> zirconium tetrachloride.<sup>[57]</sup> polymer-supported catalysts,<sup>[58,59]</sup> protic acid,<sup>[60]</sup> and organocatalysts.<sup>[61,62]</sup>

The latest development in the surface immobilization strategies involves the covalent linkage of an organic component to a solid support. The coapplication of nanosized inorganic moieties along with organic substances could significantly contribute to the development of multifunctional materials, which are known as inorganic–organic hybrids with a wide diversity of academic or technical applications. Such hybrid materials can simultaneously offer the advantages of both organic and inorganic compounds.<sup>[63,64]</sup>

Therefore, the present research is designed to introduce a new approach for the DESs immobilization onto the surface of TiO<sub>2</sub> NPs using 2,4-toluene diisocyanate (TDI) as a bifunctional covalently bound linker. In comparison with the costly traditional coupling agents (e.g., titanate and silane coupling) used for organic surface modification of TiO<sub>2</sub> NPs, TDI has several preferences including high availability, lower cost, and high activity thanks to its highly unsaturated bonds. Moreover, the TDI–TiO<sub>2</sub> NPs reaction will be rapid and feasible with no need for a catalyst to bridge between nano-TiO<sub>2</sub> and DESs for enhancing the catalyst's lifetime and recyclability. To this end, nano-TiO<sub>2</sub>@TDI@DES were successfully synthesized and applied to improve sulfides oxidation into their corresponding sulfoxides with the help of aqueous  $H_2O_2$  (30%) oxidant. Upon the reaction termination, the catalyst can be easily separated and reused with no DES leaching or significant drop in its activity. Ultimately, these catalysts were employed for the preparation of several derivatives under the optimized condition, which showed high efficiency and simple work-up.

#### 2 | EXPERIMENTAL

#### 2.1 | Materials and instruments

Chemicals were of commercial reagent grade and purchased from Aldrich and Merck. TDI was in industrial grade with 80:20 mixture of 2,4-isomer and 2,6-isomer, and it was used as received. The purification of solvents was achieved by conventional methods. The purity of the synthesized compounds and progress of reactions were assayed by thin-layer chromatography (TLC) on commercial plates coated with silica gel 60 F254. Fourier transform infrared (FT-IR) spectroscopy was implemented on a Shimadzu FT-IR 8400 equipment using KBr pressed powder plates in the range of 400–4000 cm<sup>-1</sup>. Thermogravimetric analyses (TGAs) were performed by applying a DuPont 2000 thermal analysis apparatus under air atmosphere heated from  $30^{\circ}$ C to  $800^{\circ}$ C at a ramp rate of  $5^{\circ}$ C min<sup>-1</sup>. Field emission scanning electron microscope (FE-SEM) images were taken on a TESCAN MIRA3 scanning electron microscope instrument operating at an accelerating voltage of 10 kV. X-ray diffraction (XRD) patterns were conducted at room temperature on a Siemens D5000 diffractometer (Siemens AG, Munich, Germany) using Cu K $\alpha$  radiation of wavelength 1.54° A . Mira 3-XMU scanning electron microscope was used for energydispersive X-ray spectroscopy (EDX) spectra of the catalyst. Particles were fixed on a double-sided adhesive carbon disk and sputter coated with a thin layer of gold to evade sample charging problems.

#### 2.2 | Preparation of nano-TiO<sub>2</sub>

The hydrothermal method was utilized for the synthesis of nano-TiO<sub>2</sub>.<sup>[65]</sup> In a typical procedure, aqueous  $NH_3$  was initially added dropwise to a TiCl<sub>4</sub> solution to set its pH at 1.8. Then, it was heated to 70°C for 2 h under stirring to the balance final pH at 6. The obtained

suspension was left at room temperature for a day followed by filtration and washing by NH<sub>4</sub>OAc–HOAc to eliminate all Cl<sup>-</sup>. The final precipitates were centrifuged, washed by ethanol, and vacuum dried. TiO<sub>2</sub> NPs were attained by 2-h calcination at 650°C.

## 2.3 | TiO<sub>2</sub> NP functionalization by TDI (*n*-TiO<sub>2</sub>@NCO)

*n*-TiO<sub>2</sub>@NCO was synthesized by the previously reported procedures.<sup>[66]</sup> In summary, a dispersion of *n*-TiO<sub>2</sub> (1.0 g) and TDI (1.40 g) was prepared in 50-ml dried toluene by ultrasonication for 10–15 min. The reaction mixture underwent 6 h of stirring under the N<sub>2</sub> atmosphere. The products were centrifuged and washed by dry toluene to eliminate the physisorbed and unreacted TDI molecules followed by 24 h of vacuum drying at 80°C.

#### 2.4 | DES preparation

For DES preparation, urea (20.0 mmol, 1.200 g) and zinc chloride (5.0 mmol, 0.680 g) were mixed at  $100^{\circ}$ C to reach a clear, transparent, homogeneous liquid [urea]<sub>4</sub>[ZnCl<sub>2</sub>]. The obtained DES was then employed to the synthesis processes with no further purification.<sup>[67,68]</sup>

## 2.5 | Synthesis of DES-functionalized *n*-TiO<sub>2</sub> (*n*-TiO<sub>2</sub>@TDI@DES)

To synthesis of DES-functionalized *n*-TiO<sub>2</sub>, a dispersion containing 0.5-g TiO<sub>2</sub>@TDI NPs was prepared in which 0.5-g DES was added. The solution was then stirred at 100°C for 18 h. The resulting products were washed by ethanol (3  $\times$  20 ml) and dried at 60°C under reduced pressure for 6 h.

## 2.6 | General procedure for the oxidation of sulfides

A mixture of sulfide (1 mmol) and 30%  $H_2O_2$  (2 equiv) with 40-mg catalyst was magnetically stirred at ambient temperature for the appropriate time (monitored by TLC). After the reaction was completed, the mixture was eluted with ethanol (10 ml) and centrifuged to separate the catalyst. Then, the combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and the pure products were obtained in 87–99% yields by evaporation of diethyl ether under reduced pressure.<sup>[69]</sup>

#### 3 | RESULTS AND DISCUSSION

To develop our current programs<sup>[70–73]</sup> on the use of support-immobilized DES in different organic reactions, the preparation of LADESs was addressed on nano-TiO<sub>2</sub>. In this reaction, nano-TiO<sub>2</sub> served as a novel, high-efficiency, and recyclable nanocatalyst. The nanocatalyst preparation procedure is illustrated in Scheme 1. The hydrothermal approach was exploited for the preparation of nano-TiO<sub>2</sub>. The NPs surface was then modified by TDI such that their surface hydroxyls were preferentially reacted with a para-isocyanate group of TDI giving rise to urethane bond leaving unreacted ortho-isocyanate group. Such selectivity can be assigned to the different reactivity of these two isocyanate groups as well as the steric hindrance of TDI molecules. Subsequently, the unreacted isocyanate groups were transformed into amid through the treating with urea molecules of LADESs. The structural properties of the nanocatalyst were assessed by FT-IR, FE-SEM, XRD, TGA, and EDX techniques.

## 3.1 | Characterization of *n*-TiO<sub>2</sub>@TDI@DES

#### 3.1.1 | FT-IR spectra

FT-IR spectroscopy was employed to study the DES immobilization on the nano-TiO<sub>2</sub> surface. According to Figure 1a, the broad strong band below 1200  $\text{cm}^{-1}$  is indicative of Ti-O-Ti vibration. The absorptions at 1623 and 3355  $\text{cm}^{-1}$  could be also attributed to the hydroxyl groups.<sup>[74]</sup> Based on Figure 1b, which illustrates the FT-IR results of TDI, the major adsorption at 2243 cm<sup>-1</sup> represents the vibration of the NCO group.<sup>[75]</sup> Moreover, the absorption band at 1550 cm<sup>-1</sup> can be assigned to the presence of phenyl ring in the TDI structure. Figure 1c represents the results of TiO2@TDI. Some new peaks emerged at 2266, 1649, 1595, and 1533 cm<sup>-1</sup>. The one at 2266 cm<sup>-1</sup> can be ascribed to the unreacted orthoisocyanate groups of TDI in the attachment with the n-TiO<sub>2</sub> surface, whereas those that appeared at 1649 and 1595 cm<sup>-1</sup> are related to the C=O and C-N stretching vibrations reflecting the occurrence of TDI-titania





**FIGURE 1** The Fourier transform infrared (FT-IR) spectra of (a) *n*-TiO<sub>2</sub>, (b) 2,4-toluene diisocyanate (TDI), (c) *n*-TiO<sub>2</sub>@TDI, (d) deep eutectic solvent (DES), and (e) *n*-TiO<sub>2</sub>@TDI@DES

reaction through the formation of a urethane bond (OCONH). The peak at 1533  $\text{cm}^{-1}$  is also assigned to the phenyl ring in the TDI configuration.<sup>[76]</sup> These results show the successful anchoring of TDI on the nano-TiO<sub>2</sub> surface. Figure 1d verifies the formation of DES. Accordingly, the adsorption bands emerged at 1664, 1332, 3360, and 3473 cm<sup>-1</sup> can be attributed to the vibrations of C=O, C-N, and N-H bond in amide groups. Furthermore, the one at 485 cm<sup>-1</sup> represents the Zn-Cl stretching vibration.<sup>[77]</sup> Upon the DES immobilization on n-TiO<sub>2</sub>@TDI, the formation of the amino group can be verified through the fading of the NCO peak at 2266 cm<sup>-1</sup> and the emergence of the absorption bands related to the NH stretching vibration at 3473 and 3360  $\text{cm}^{-1}$  (overlapping with N–H band of urethane). These shifts can be assigned to the direct interaction of DESs with the NCO groups of the functionalized nano-TiO<sub>2</sub> (Figure 1e). Therefore, the IR results indicate that the DESs were successfully immobilized on nano-TiO<sub>2</sub>.



**SCHEME 1** Synthetic diagram of *n*-TiO<sub>2</sub>@TDI@DES catalyst

#### 3.1.2 | XRD spectra

The X-ray powder diffraction technique was utilized to evaluate the crystalline structure of the synthesized NPs. As suggested by Figure 2a, diffraction peaks corresponding to (101), (103), (104), (112), (200), (105), (211), (204), (116), (220), (215), and (224) planes clearly show the formation of the anatase TiO<sub>2</sub> NPs (JCPD 89-4921). The diffraction pattern and the location of the characteristic peaks were also detected in the case of n-TiO<sub>2</sub>@TDI@DES (Figure 2b). This figure also suggests the crystalline stability of TiO<sub>2</sub> NPs during DES immobilization. Its higher noise/signal ratio of n-TiO2@TDI@DES reflects the successful surface functionalization of n-TiO2. An ultraweak broadband at  $2\theta = 10-30^{\circ}$  is indicative of the amorphous DESs and the presence of ZnCl<sub>2</sub> in the structure.<sup>[78-80]</sup> The successful immobilization of DESs on n-TiO2 NPs can be confirmed due to the emergence of the other peaks, which are properly in line with the anatase phase of n-TiO<sub>2</sub>.<sup>[81]</sup> The presence of ZnCl<sub>2</sub> was further assessed by the EDX results.

#### 3.1.3 | FE-SEM analysis

FE-SEM analysis was employed to describe the surface morphology of the NPs upon their functionalization. Figure 3 presents the surface morphology and particle shape and size of the samples. Based on Figure 3b, nano-TiO<sub>2</sub>@TDI possesses spherical particles that resemble the morphology of pristine nano-TiO<sub>2</sub> (Figure 3a). It can be



**FIGURE 2** The X-ray diffraction patterns of (a) *n*-TiO<sub>2</sub> and (b) *n*-TiO<sub>2</sub>@TDI@DES. DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate



**FIGURE 3** Field emission scanning electron microscope (FE-SEM) images of (a) n-TiO<sub>2</sub>, (b) n-TiO<sub>2</sub>@TDI, and (c) n-TiO<sub>2</sub>@TDI@DES. DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate

concluded that nano- $TiO_2$  did not exhibit significant deformation upon the grafting of organic molecules. Such a spherical-shaped structure is highly favorable as it

offers plenty of active sites for anchoring other species. Compared with pristine *n*-TiO<sub>2</sub>, the SEM image of *n*-TiO<sub>2</sub>@TDI@DES displayed no evident alternation in its crystallite size. Besides, aggregation and altered morphology of *n*-TiO<sub>2</sub>@TDI@DES are observable; however, the final NPs maintained their spherical shapes at a larger size (22–34 nm). These findings indicate the modification and grafting of organic compounds on nano-TiO<sub>2</sub>.

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#### 3.1.4 | Thermogravimetric analysis

TGA can be employed to investigate the characteristic decomposition pattern of the organic compounds as well as their degradation temperature, bond formation, and thermal stability. Figure 4 depicts the TGA results in the temperature range of 30°C to 800°C. According to Figure 4a, the weight loss (7 wt.%) at  $T < 170^{\circ}$ C corresponds to the evaporation of the physisorbed moisture as



**FIGURE 4** The thermogravimetric analysis (TGA) patterns of (a) *n*-TiO<sub>2</sub>, (b) *n*-TiO<sub>2</sub>@TDI, and (c) *n*-TiO<sub>2</sub>@TDI@DES. DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate

well as hydroxyl group removal.<sup>[82]</sup> The *n*-TiO<sub>2</sub>@TDI exhibited three major weight losses (Figure 4b). The first one occurred below 170°C, which can be assigned to the elimination of trapped water. The weight losses (14 wt.%) at 170-250°C can be assigned to the TDI-modified titania, whereas the next step at  $T > 250^{\circ}$ C can be related to the thermal degradation of TDI groups.<sup>[81]</sup> Upon DES immobilization on n-TiO<sub>2</sub>@TDI surface, the weight loss in the n-TiO<sub>2</sub>@TDI@DES showed an enhancement. Similarly, the TGA findings of TiO<sub>2</sub>@TDI@DES (Figure 4c) manifested three prominent weight losses. Although the first weight (20 wt.%;  $T < 170^{\circ}$ C) loss corresponded to the adsorbed moisture and elimination of the DES moieties contributing to the ionic structure of DES and the emergence of urea, the other two ones (at 190–250°C [9 wt.%] and  $T > 250^{\circ}$ C [5 wt.%]) can be attributed to the degradation of grafted TDI. Therefore, TGA results confirmed the proper grafting of TDI and DES on the *n*-TiO<sub>2</sub> surface.

#### 3.1.5 | Energy-dispersive X-ray

EDX analysis can efficiently investigate the elemental status of the samples (Figure 5). The EDX results of n-TiO<sub>2</sub>@TDI@DES in Figure 5b suggest the existence of the anticipated elements (C, O, Zn, and Ti), hence confirming the nanocatalyst structure. A comparison between EDX results of n-TiO<sub>2</sub>@TDI@DES and n-TiO<sub>2</sub>@TDI verified that DES was successfully immobilized on the TiO<sub>2</sub> NPs.

Table 1 lists the elemental status of n-TiO<sub>2</sub>@TDI and n-TiO<sub>2</sub>@TDI@DES. Comparing CHNS analysis of n-TiO<sub>2</sub>@TDI with that of n-TiO<sub>2</sub>@TDI@DES and increment was observed in the content of C, H, and N atoms of n-TiO<sub>2</sub>@TDI@DES reflecting successful coating of n-TiO<sub>2</sub>@TDI by DES. An enhancement in Zn and Cl contents in n-TiO<sub>2</sub>@TDI@DES can be assigned to the immobilization of ZnCl<sub>2</sub>.





**FIGURE 5** The energy-dispersive X-ray spectroscopy (EDX) patterns of (a) n-TiO<sub>2</sub>@TDI and (b) n-TiO<sub>2</sub>@TDI@DES. DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate

#### TABLE 1 Elemental analysis for the catalyst

Element	Amount (wt.%) <i>n-</i> TiO <sub>2</sub> @TDI@DES	Amount (wt.%) <i>n</i> - TiO <sub>2</sub> @TDI
С	19.02	7.62
0	45.13	42.71
Ν	6.53	4.96
Ti	17.82	44.71
Zn	3.82	—
Cl	7.68	—
Total	100.00	100.00

Abbreviations: DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate.

#### 3.2 | Catalytic activity of nano-TiO<sub>2</sub>@TDI@DES for selective oxidation of sulfides to sulfoxides

For further evaluation of the environmentally friendly chemical procedures,<sup>[83–85]</sup> the synthesized  $TiO_2$ @-TDI@DES was employed as an interphase catalyst in the chemoselective oxidation of various structures of sulfides to their corresponding sulfoxides at solvent-free condition

using 30%  $H_2O_2$  at ambient temperature. Initial tests were conducted to optimize the reaction condition in which the methyl phenyl sulfide oxidation was considered as a model and the impacts of time, product yield, oxidant, and catalyst were explored (Table 2).

According to Table 2, the proper yield oxidation reaction is achievable without catalyst after 24 h (Entry 1). Then, the experiments were continued to determine the required catalyst load. The best yield was achieved using 40 mg of the catalyst, giving rise to the lowest reaction time and maximum product yield (Entry 5). Table 2 also suggests that the optimized H<sub>2</sub>O<sub>2</sub> content was 2 equiv, which maximized the product yield (Entries 5, 7, and 8). Finally, the influence of the solvent (EtOH, H<sub>2</sub>O, CH<sub>3</sub>CN, phCH<sub>3</sub>, and solvent free) on the reaction was explored (Entries 5 and 9-12). Based on the results, the highest vield in short reaction time (40 min) can be achieved under the solvent-free condition, which is in line with the principles of green chemistry. The optimal condition resulting in the best reaction yield was the solvent-free condition at room temperature using 2 equiv of H<sub>2</sub>O<sub>2</sub> and 40 mg of nano-TiO<sub>2</sub>@TDI@DES.

Motivated by these interesting findings, the generality of this approach was further examined through the facile

TABLE 2	Optimization of conditions	for synthesis of meth	yl phenyl sulfoxide <sup>a</sup>
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.s.		Cat., H <sub>2</sub> O <sub>2</sub>	
R 7.51	$R_1$	Solvent free, r.t.	R <sup>r</sup> R <sub>1</sub>

Entry	Catalyst (mg)	H <sub>2</sub> O <sub>2</sub> (equiv)	Solvent	Time (min)	Yield (%) <sup>b</sup>
1	$n-TiO_2$ @TDI@DES(0)	2	_	1440 (24 h)	90
2	n-TiO <sub>2</sub> @TDI@DES(10)	2	—	55	75
3	n-TiO <sub>2</sub> @TDI@DES(20)	2	—	55	80
4	n-TiO <sub>2</sub> @TDI@DES (30)	2	—	50	86
5	n-TiO <sub>2</sub> @TDI@DES (40)	2	_	40	98
6	n-TiO <sub>2</sub> @TDI@DES(50)	2	_	45	91
7	$n-TiO_2$ @TDI@DES (40)	1.5	_	60	89
8	n-TiO <sub>2</sub> @TDI@DES(40)	2.5	—	45	95
9	$n-TiO_2$ @TDI@DES (40)	2	H <sub>2</sub> O	120	68
10	n-TiO <sub>2</sub> @TDI@DES(40)	2	ЕТОН	130	73
11	n-TiO <sub>2</sub> @TDI@DES(40)	2	Toluene	155	62
12	n-TiO <sub>2</sub> @TDI@DES (40)	2	CH <sub>3</sub> CN	190	73
13	DES (40)	2	_	600	70

Abbreviations: DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate.

<sup>a</sup>Reaction conditions: methyl sulfide (1 mmol), room temperature.

<sup>b</sup>Isolated yield.

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#### **TABLE 3** Oxidation of sulfides to sulfoxides in the presence of nano-TiO<sub>2</sub>@TDI@DES<sup>a</sup>

Entry	Sulfide	Sulfoxide	Time (min)	Conversion (%)	Yield (%) <sup>b</sup>
1	∕s∕∕		60	100	97
2	∽ <sup>s</sup> ∽∕		45	100	99
3	≫ <sup>S</sup> √∕∕		35	100	98
4	s		40	100	91
5	S_	O S S	40	100	98
6	Br	Br S	80	100	99
7	S~		35	100	92
8	C) <sup>s</sup>	O S S	120	100	98

(Continues)

#### TABLE 3 (Continued)

Entry	Sulfide	Sulfoxide	Time (min)	Conversion (%)	Yield (%) <sup>b</sup>
9	S_s_		55	100	93
10	C) <sup>s</sup> C)		70	100	87
11	HOSTON	но ССС ОН	25	100	89
12	S S		65	100	94

Abbreviations: DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate.

<sup>a</sup>Reaction conditions: sulfide (1 mmol), nano-TiO<sub>2</sub>@TDI@DES (40 mg), H<sub>2</sub>O<sub>2</sub> (2 equiv), solvent free at room temperature. <sup>b</sup>Isolated yield.

oxidation of diverse sulfides (e.g., dialkyl sulfides [Entries 1–4], alkylary l sulfides [Entries 5–7], and sulfides with other functional groups) under the optimal reaction

conditions (Table 3). Table 3 showed the high rate production of diverse sulfoxides at superior selectivity with no overoxidation by-products like sulfones. Besides,



**SCHEME 2** Proposed mechanism for the oxidation of sulfides using  $H_2O_2$  catalyzed by *n*-TiO<sub>2</sub>@TDI@DES nanoparticles

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the steric effect was observed (Entries 10–12) and some of the products were also evaluated by  $^{1}$ H-NMR (Figures S1–S4).

#### 3.2.1 | Proposed mechanism

The proposed mechanism of the sulfides oxidation through hydrogen peroxide is illustrated in Scheme 2. The in situ formation of peroxy acid through the catalyst reaction with hydrogen peroxide and subsequent oxygen transfer to the organic substrate can be seen in Scheme 2. In particular, the catalytic activity of  $TiO_2@TDI@DES$ can be assigned to  $ZnCl_2$  groups of DES on catalyst surface, which offer efficient Lewis acidic sites.

## 3.3 | Test of recycling, leaching, and heterogeneity of catalyst

Regarding environmental concerns, industries are searching for novel approaches for pollution elimination. In this regard, the heterogeneous catalysts are promising candidates due to their facile separation, recoverability, reusability, and leaching. The stability and the reusability of nano-TiO<sub>2</sub>@TDI@DES were explored within the oxidation of the sulfide using methyl phenyl sulfide (1 mmol), H<sub>2</sub>O<sub>2</sub> (2 equiv), and catalyst (40 mg) at room temperature under solvent-free condition. Upon the reaction completion, the catalyst can be easily removed and recovered through EtOAc washing and vacuum drying. The recovered catalyst can be then reused six times with no significant loss of their



**FIGURE 6** Reusability of nano-TiO<sub>2</sub>@TDI@DES for the synthesis of methyl phenyl sulfoxide. Reaction conditions: methyl phenyl sulfide (1 mmol),  $H_2O_2$  (2 equiv), catalyst (40 mg), reaction time of 40 min at room temperature under solvent-free conditions. DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate

catalytic activity (Figure 6). In Figure 7, the FT-IR spectrum of the catalyst after six runs with that of the fresh catalyst has been compared and showed the intact structure of nanocatalyst after six runs.

The catalyst leaching was also examined in the oxidation reaction of sulfides. For this purpose, the reaction was conducted under optimal conditions and stopped



**FIGURE 7** The Fourier transform infrared (FT-IR) spectra of (a) fresh n-TiO<sub>2</sub>@TDI@DES catalyst and (b) reused n-TiO<sub>2</sub>@TDI@DES catalyst after six times. DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate



**FIGURE 8** Leaching of the *n*-TiO<sub>2</sub>@TDI@DES catalyst in the oxidation reaction of thioanisole. (a) In the presence of catalyst and (b) after separation of catalyst. DES, deep eutectic solvent; TDI, 2,4-toluene diisocyanate

after half of the required time (20 min). The catalysts were then centrifuged, and the product yield was evaluated by TLC. The remained mixture was stirred in the absence of catalyst for another half of the reaction time. The reaction progress was assessed by TLC. No significant conversion was detected in the absence of the catalyst indicating negligible catalyst leaching (Figure 8).

The hot filtration test was performed to determine the heterogeneity of catalyst. After half of the required time (20 min), the catalyst was isolated from the reaction mixture by filtration and the reaction was allowed to continue. There was no further increase in the yield, verifying the heterogeneity of the catalyst.

#### 4 | CONCLUSION

The present study introduced a novel and cost-effective industrial approach for preparing supported LADES NPs. The obtained samples exhibited high efficiency as the heterogeneous inorganic–organic hybrid catalysts. This efficient and environmentally benign Lewis acidic catalyst was successfully applied in the chemoselective oxidation of sulfides. The presented method offered several advantages including high yield, moderate and cleaner reaction conditions, and feasibility with no need for column chromatographic purification; these features offer them as a promising alternative for the conventional approaches. The catalysts were successfully recovered six times with no significant drop in their activity, which demonstrates their superior stability due to the covalent linkage.

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#### **AUTHOR CONTRIBUTIONS**

Shaghayegh Taghavi: Conceptualization; data curation. Ali Amoozadeh: Supervision. Firouzeh Nemati: Supervision.

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