Core/shell structured ZnO@SiO$_2$-TTIP composite nanoparticles as an effective catalyst for the synthesis of 2-substituted benzimidazoles and benzothiazoles

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ABSTRACT

ZnO@SiO$_2$-TTIP was synthesised as a novel heterogeneous catalyst and characterised by FT-IR, XRD, TEM, SEM and N$_2$ adsorption-desorption. In this catalytic system, TTIP acts as a dopant agent for ZnO@SiO$_2$ to decreases the recombination of photogenerated electron/hole pairs and improves the catalyst activity. The catalyst was successfully utilised for the synthesis of 2-substituted benzimidazoles and benzothiazoles from 1,2-phenylenediamine and 2-aminothiophenol with wide variety of aromatic aldehydes.

1. Introduction

In general, the synthesis of core/shell structured material has the goal of obtaining a new composite material with synergetic or complementary behaviours between the core and shell materials. Many studies on the synthesis of composites, i.e. TiO$_2$, [1] Au, [2] γ-Fe$_2$O$_3$ [3] and Ag [4] coated with SiO$_2$ shells, have been reported. SiO$_2$ is a most studied shell candidate due to its relative ease in preparation, good environmental stability and compatibility with other materials, which motivated us to prepare the core/shell
structured composite of ZnO and SiO2 and expected to achieve novel properties resulting from the synergic interaction of these two chemical components.

Transition-metal catalysed organic transformations are often carried out to follow the principles of ‘Green Chemistry’ due to minimisation of waste, cleaner auxiliaries, catalysts or reagents and minimum use of energy [5–8].

Nanocatalysts are important as a bridge between heterogeneous and homogeneous catalysts [9]. One of the interesting properties of nanomaterials is that they have a high specific surface area of the active part, leading to an increase in contact with the reactants [10]. Moreover, a higher surface area gives the nanomaterials a more active surface; they are hard to be separated. Therefore, it is attractive to design a recoverable and well-dispersed catalyst.

Recently, much effort has been devoted to study ZnO as a very promising photocatalyst for photocatalytic degradation of water pollutants, owing to its high activity, low cost and environmentally friendly feature [11,12].

Benzothiazoles and benzimidazoles moieties found in various natural products and belong to one of the most important classes of heterocycles with biologically and pharmaceutically activities [13,14].

Until now, a number of methods have been developed for the synthesis of benzimidazoles and benzothiazoles [15–20].

To the best of our knowledge, most of the procedure for the synthesis of benzimidazoles and benzothiazoles suffer from one or some disadvantages such as low yields, harsh reaction conditions, time consuming process, use of expensive catalysts and boring workups. Thus presently, the development of environmentally benign, high-yielding and fast synthesis of benzimidazole and benzothiazole derivatives remains a desired goal in organic synthesis. In this work, we have elaborated core/shell structured ZnO@SiO2-TTIP via a facile chemical route for the preparation of 2-substituted benzimidazole and benzothiazole derivatives by using of H2O2 in ethanol (EtOH) media (Scheme 1).

2. Results and discussion

2.1. Catalyst characterization

A comparison between the FTIR spectra of the ZnO nanoparticles (a), ZnO@SiO2 core-shell (b) and ZnO@SiO2-TTIP (c) are shown in Figure 1. The FTIR spectrum of the ZnO nanoparticles showed a peak at 495 cm⁻¹ that is the characteristic absorption of Zn–O bond and the peaks at 3443 and 1628 cm⁻¹ can be ascribed to the absorption of water. The band at 1069 cm⁻¹ was assigned to the asymmetric Si–O–Si stretching vibration as well as the band appeared at 797 cm⁻¹ was due to the Si-O-Si bending vibrations in ZnO@SiO2 and ZnO@SiO2-TTIP [21]. In the case of ZnO@SiO2, some bands belonged to the stretching vibrations of C–H bonds are appeared in the range 2860–2962 cm⁻¹ which confirms the presence of alkoxy or alkyl chains, directly bonded to the metal atoms. The bands typical of isopropoxy groups bonded to the surface of ZnO@SiO2 appeared at 1450 cm⁻¹ and
The band at 970 cm\(^{-1}\) attributed to the antisymmetric Ti–O–Si stretching vibration [22]. The phase and crystal structure of the samples was identified by XRD. Figure 2 shows the XRD patterns of the ZnO (a), ZnO@SiO\(_2\) (b) and ZnO@SiO\(_2\)–TTIP (c).

The diffraction peaks appearing in the vicinity of 2\(\theta\) ≈ 32°, 34.5°, 36.5°, 47.9°, 56.8°, 63.0°, 66.5°, 68°, 69.5°, 73.0° and 77.0° can be indexed to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), crystal faces of wurtzite ZnO with P6\(_3\)mc space group and hexagonal structure (JCPDS No. 80-0075). Modification of ZnO nanoparticle with a thin layer of SiO\(_2\) (Figure 2(b)) shell does not influence the crystalline structure of ZnO and consequently the characteristic peaks of ZnO nanoparticles are still in consistence with the zincite phase of ZnO. The characteristic diffraction peaks of amorphous SiO\(_2\) were not obviously detected due to the small amount of SiO\(_2\) [23]. Similar result obtained for CaCO\(_3\)@SiO\(_2\) core–shell nanoparticles that no peaks of SiO\(_2\) shell in XRD spectra was observed [24]. After grafting the TTIP on the surface of ZnO@SiO\(_2\), the XRD pattern does not change indicating that the ZnO@SiO\(_2\) was properly retained after the grafting of TTIP. Some similar results are reported for grafting the TTIP on the surface of silica and showed that the XRD of silica does not change after grafting process [25,26].

In order to investigate the particle size and morphology of ZnO@SiO\(_2\), SEM and TEM images of ZnO@SiO\(_2\) were presented in Figures 3 and 4. By SEM images some data about the morphology and size of catalyst particles were obtained (Figure 3). This results show that ZnO@SiO\(_2\) nanoparticles were obtained with an average diameter of 59–91 nm.
Figure 2. XRD patterns of the samples.

Figure 3. SEM image of ZnO@SiO$_2$. 
Textural properties of ZnO@SiO2-TTIP were evaluated by N2 sorption-desorption analysis and pore size distribution was calculated by Barret-Joyner-Halenda (BJH) method. N2 Sorption-desorption isotherm is categorised to type IV (Figure 5), representative of mesoporous materials with an H2 hyteresis loop which indicates a narrow pore-size distribution. BET surface area of ZnO@SiO2-TTIP is 122.4 m².g⁻¹. Pore size distribution curve shows a maximum pore width at 2.1 nm. The larger BET surface area enhances the activity of catalyst, which is consistent with the observed results.

In the next step, the catalytic activity of ZnO@SiO2-TTIP on the preparation of benzimidazole and benzothiazole derivatives was studied. To optimise the reaction conditions, the effect of different amounts of ZnO@SiO2, TTIP and various solvents was investigated in a model reaction between benzaldehyde and 1,2-phenylenediamine (Table 1).
The reactions were carried out in the presence of 0, 0.025 and 0.03 g of ZnO@SiO₂ and 0, 0.6 and 0.9 mmol of TTIP. As shown (entry 1), although a mixture of benzaldehyde, 1,2-phenylenediamine and 2 mmol of 30% H₂O₂ mixed together at room temperature, only trace amounts of corresponding product were formed even after 8 hours and imine intermediate was the major product. By using 0.025 g of ZnO@SiO₂, 0.6 mmol of TTIP and 2 mmol of H₂O₂ the best results regarding the reaction time and yield was obtained (entry 5). Using lower amount of catalyst resulted in lower yield (entry 4), while higher amount did not affect the reaction time and yield appreciably (entry 9). The effect of other solvents such as CH₃CN, H₂O, CH₂Cl₂ was investigated under optimum reaction conditions (entries 6–8). It was found that the nature of solvent has a considerable effect on the reaction rate and the yield. However, ethanol was found to be the best solvent and the other solvents were substantially less effective.

To emphasize that the ZnO@SiO₂-TTIP is superior over ZnO nanoparticles and ZnO-TTIP composite we performed the model reaction using ZnO nanoparticles (0.6 mmol, 0.048 g) and ZnO-TTIP composite (0.6 mmol, 0.48 g ZnO, 0.6 mmol, 0.2 mL TTIP). The desired product was obtained with the yields of 35% and 70% for ZnO nanoparticles and ZnO-TTIP respectively after 10 min. It is obvious that ZnO@SiO₂-TTIP demonstrates better catalytic activity relative to ZnO nanoparticles, TTIP and ZnO-TTIP. Encapsulation of ZnO nanoparticles into a layer of silica shell prohibit the agglomeration problem [27]. It is well documented that ZnO nanoparticles have a toxic nature [28]. ZnO nanoparticles dissolve in aqueous solutions to release Zn²⁺ ion. The influx of Zn²⁺ ion could disturb the natural function of cells [29]. Surface modification of nanoparticles in most cases alters the intrinsic properties of ZnO nanoparticles [30] rather than reduce their toxicity. Therefore, we covered the ZnO nanoparticles with a thin layer of silica to relieve the releasing of Zn²⁺ ion and decrease the toxic nature of ZnO without change in the intrinsic properties of ZnO nanoparticles owing to the fact that the silica layer is benign and inert. Since the electronegativity of Si (~1.9) is higher than that of Zn (~1.65), the valence electron density of Zn in the Zn–O–Si bond is lower than that in the Zn–O–Zn bond [31], therefore, Zn in the core of ZnO@SiO₂ demonstrates more electron affinity. ZnO is a wide band gap n-type semiconductor (E₉ = 3.37 eV) and suffers from two important drawbacks; first, with the large band gap of 3.37 eV; the wavelengths below 400 nm are necessary for excitation that are in the range of ultraviolet. Another problem of ZnO is the quick charge carrier recombination of photogenered electron/hole pairs and low

| Entry | ZnO@SiO₂ (g) | TTIP (mmol) | H₂O₂ (mmol) | Solvent  | Yield (%) b |
|-------|--------------|-------------|-------------|----------|-------------|
| 1     | 0            | 0           | 2           | EtOH     | Trace       |
| 2     | 0.025        | 0           | 2           | EtOH     | 50          |
| 3     | 0            | 0.6         | 2           | EtOH     | 60          |
| 4     | 0.015        | 0.3         | 2           | EtOH     | 90          |
| 5     | 0.025        | 0.6         | 2           | EtOH     | 97          |
| 6     | 0.025        | 0.6         | 2           | CH₃CN    | 80          |
| 7     | 0.025        | 0.6         | 2           | H₂O      | 50          |
| 8     | 0.025        | 0.6         | 2           | CH₂Cl₂   | 60          |
| 9     | 0.03         | 0.9         | 2           | EtOH     | 97          |

aReaction conditions: The reactions were performed with benzaldehyde (1 mmol) and 1,2-phenylenediamine (1 mmol).
bYields refer to pure isolated products.
photocatalytic activity [32,33]. One of the best methods to decrease the recombination of photogenerated electron/hole pairs is to modify the surface of ZnO by metal doping into the ZnO nanoparticles. By collecting the photogenerated electrons from the conduction band of semiconductor, the dopant acts as a trap, increases the charge separation and consequently hampers the electron/hole pair recombination and finally improves the photocatalytic activity in the visible light [33]. In the present work, TTIP acts as a dopant agent. Due to the smaller ionic radii of Ti$^{4+}$ (42 pm) compared to Zn$^{2+}$ (60 pm), the substitution of Zn$^{2+}$ with Ti$^{4+}$ occurs, generates the point defects and decreases the electron/hole pair recombination [34]. As a result, the doping of ZnO core in ZnO@SiO$_2$ facilitates the formation of OH radicals from H$_2$O$_2$.

After optimisation of the reaction conditions, synthesis of a variety of functionalised benzimidazoles was performed to explore the efficiency and the scope of the protocol. The corresponding results have been depicted in Table 2. As shown, both aldehydes bearing electron-donating and electron-withdrawing substituents gave desired benzimidazoles in excellent yields. In addition, heterocyclic aldehydes could also be used and worked well in this reaction (Table 2, entries 13 and 14). In order to further demonstrate the power and efficiency of this catalytic system, the synthesis of benzothiazoles was investigated in the presence of prepared catalyst. The experimental results showed, treatment of a variety of aldehydes with 2-aminothiophenol in the presence of catalytic amount of ZnO@SiO$_2$-TTIP at room temperature afforded the corresponding 2-substituted benzothiazoles in (92–97%) yields (Table 3). Also, to show the efficiency of this method, a comparison of the efficiency of this method with selected previously methods is collected in Table 4. The results show that this method is comparable to some previously reported methods in terms of reaction times, temperatures and yields.

In another step, recyclability of ZnO@SiO$_2$-TTIP was studied. For this purpose, the reaction of 1,2-phenylenediamine and benzaldehyde was selected in the optimised reaction conditions. As shown in Figure 6, catalytic activity of ZnO@SiO$_2$-TTIP was restored

### Table 2. Direct synthesis of 2-substituted benzimidazoles.$^a$

| Entry | Ar          | Time (min) | Yield (%)$^b$ | Mp$^c$(°C) |
|-------|-------------|------------|---------------|------------|
| 1     | C$_6$H$_5$  | 10         | 97            | 291–292    |
| 2     | 4-MeC$_6$H$_4$ | 25         | 95            | 269–270    |
| 3     | 2-MeOC$_6$H$_4$ | 60         | 90            | 181–183    |
| 4     | 4-MeOC$_6$H$_4$ | 75         | 93            | 224–225    |
| 5     | 2,4,5-(MeO)$_3$C$_6$H$_2$ | 30         | 95            | 261–262    |
| 6     | 2-HOC$_6$H$_4$ | 50         | 90            | 181–182    |
| 7     | 4-HOC$_6$H$_4$ | 35         | 90            | 286–287    |
| 8     | 4- Me$_2$NC$_6$H$_4$ | 60         | 90            | 286–287    |
| 9     | 4-ClC$_6$H$_4$ | 20         | 92            | 294–295    |
| 10    | 3-O$_2$NC$_6$H$_4$ | 18         | 97            | 302–304    |
| 11    | 2,6-Cl$_2$C$_6$H$_3$ | 8          | 95            | 219–221    |
| 12    | 4-O$_2$NC$_6$H$_4$ | 5          | 96            | 307–308    |
| 13    | 2-Furyl      | 40         | 92            | 284–285    |
| 14    | 2-Thienyl    | 25         | 95            | 341–344    |
| 15    | 2-Naphthyl   | 10         | 94            | 219–221    |

$^a$The products were characterised by comparison of their spectroscopic and physical data with authentic samples synthesised by reported procedures.

$^b$Yields refer to pure isolated products.

$^c$Found melting points.
Table 4. Comparison of methods for the synthesis of benzimidazoles and benzothiazoles.

| Entry | Product | Catalyst/reaction conditions | Time  | Yield (%) |
|-------|---------|-----------------------------|-------|-----------|
| 1     | ![](benzimidazole.png) | This work | 25 min | 95        |
| 2     | ![](benzimidazole.png) | nano-Ni(II)/Y zeolite/Solvent free/100 °C [35] | 6 min  | 89        |
| 3     | ![](benzimidazole.png) | Nano-MoO<sub>3</sub>/Ethanol/60 °C [36] | 40 min | 90        |
| 4     | ![](benzimidazole.png) | Nano-Fe<sub>3</sub>O<sub>4</sub>/CH<sub>3</sub>CN/r.t [37] | 45 min | 55        |
| 1     | ![](benzothiazole.png) | This work | 10 min | 97        |
| 2     | ![](benzothiazole.png) | H<sub>2</sub>O<sub>2</sub> (0.5 mL)/CuO/80 °C [38] | 30 min | 93        |
| 3     | ![](benzothiazole.png) | T3P (in AcOEt), DIPEA/MW, 160 °C [39] | 30 min | 77        |
| 4     | ![](benzothiazole.png) | Co dopped NiFe<sub>2</sub>O<sub>4</sub>/Solvent-free/70 °C [40] | 55 min | 97        |
| 1     | ![](benzothiazole.png) | This work | 20 min | 95        |
| 2     | ![](benzothiazole.png) | VOSO<sub>4</sub>/EtOH, rt [41] | 23 min | 95        |
| 3     | ![](benzothiazole.png) | SiO<sub>2</sub>/Solvent free/MW [42] | 5 min  | 70        |

*The products were characterised by comparison of their spectroscopic and physical data with authentic samples synthesised by reported procedures. Yields refer to pure isolated products. Found melting points.*

Figure 6. The reusability of the catalyst for the preparation of 2-phenylbenzimidazole.
within the limits of the experimental errors for 7 successive recycle runs. However, the little decrease in yield was associated with the blocked pores during the course of reaction.

As discussed, doping ZnO@SiO₂ with TTIP decreases the recombination of photogenerated electron/hole pairs and forms visible light photocatalytic activity; therefore, no UV-visible light is needed for irradiation. We propose that in the first step a complex is formed between H₂O₂ and Ti-doped ZnO (ZnO@SiO₂-TTIP) followed by homolytic cleavage of O-O bond of H₂O₂ to generate OH radicals. Generation of OH radical by coordination of H₂O₂ on the surface of other metal oxides is reported [43]. The possible mechanism for this synthesis is shown in Scheme 2. Before addition of H₂O₂, aldehyde was activated by forming a coordinate bond with the Lewis acid site of a ZnO@SiO₂-TTIP surface. Nucleophilic attack by 1,2-phenylenediamine on the aldehyde gives intermediate (I) which exist in equilibrium with the cyclic hydrobenzimidazoles (II). Then, the oxidation may be launched by a single electron transfer from hydroxyl to the intermediate (II) to produce hydroxide ion and a radical cation III that subsequently loses a proton to yield a radical IV which in turn is attacked by hydroxyl radical to afford product in the reaction mixture. The additional hydrogen peroxide then undergoes partial decomposition to O₂ and H₂O. To confirm that the reaction proceeds with formation of free radicals, a reaction between 1,2-phenylenediamine and benzaldehyde was performed in the presence of a radical scavenger, tert-butanol, affording trace amounts of product. This implies the involvement of free radicals in the reaction process.

3. Experimental

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Infra-red (IR) spectra were recorded on a Bruker FT-IR WQF-510 spectrophotometer in KBr with absorption in centimeters⁻¹. ¹H and ¹³C NMR spectra were recorded on a Bruker (200 MHz) spectrometer in CDCl₃ or DMSO as a
solvent. The morphology of ZnO@SiO₂ was investigated by scanning electron microscopy (SEM) using a TESCAN MIRA instrument. Transmission electron microscopy (TEM) measurements were carried out on a Philips CM120 1988. X-ray powder diffraction patterns were obtained on a SE1FERT-3003TT. BET analysis was carried out on a BELOSORP mini Czech.

3.1. General procedure for the preparation of ZnO@SiO₂-TTIP

Typical steps were given as follows: ZnO nanoparticles were dispersed into 50 mL of EtOH and then slowly transferred into the 500 mL round bottom flask. An appropriate amount of TEOS together with 50 mL of EtOH, 75 mL H₂O and 25 mL NH₃H₂O (35%) was then added into the reaction flask. The mixture containing the ZnO, TEOS, solvent and NH₃H₂O was stirred for 4 h. Products were collected by centrifugation, subsequently washed with EtOH for three times, and then dried in a vacuum oven at 160 °C for 2 h. Then titanium isopropoxide (TTIP) (0.6 mmol, 0.2 mL) was injected to ZnO/SiO₂ nanoparticles to produce ZnO@SiO₂-TTIP. Therefore, we performed the doping of ZnO@SiO₂ in the reaction mixture using an in situ method. Catalytic properties were reduced if ZnO@SiO₂ refluxed directly with TTIP since in this procedure we need Ti⁴⁺ to substitute with Zn²⁺. Therefore, in this study, TTIP was injected to reaction mixture.

3.2. General procedure for the synthesis of 2-substituted benzimidazoles and benzothiazoles

To a premixed solution of ZnO@SiO₂ (0.025 g) and TTIP (0.6 mmol, 0.2 mL) in EtOH (6 mL) was added 1,2-phenylenediamine (1 mmol, 0.1 g), aryl aldehyde (1 mmol) and 30% H₂O₂ (2 mmol, 0.2 mL); then, the mixture was stirred at room temperature. The progress of the reaction was monitored by TLC to determine the necessary reaction times (Table 3). After completion of the reaction, the catalyst was removed by filtration and was reused in the next run. The filtrate was poured into ethyl acetate and n-hexane. The pure solid product was filtered and dried to produce 2-substituted benzimidazole derivative in excellent yield. An identical procedure was employed using 2-aminothiophenol (1 mmol, 0.1 mL), aryl aldehyde (1 mmol) in the presence of 30% H₂O₂ (2 mmol, 0.2 mL), ZnO@SiO₂ (0.025 g) and TTIP (0.6 mmol, 0.2 mL) for the synthesis of 2-substituted benzothiazoles (Table 4).

4. Conclusion

In summary, we have synthesised ZnO@SiO₂-TTIP as a novel and nanostructured heterogeneous catalyst, and fully characterised by several techniques including FTIR, XRD, SEM, TEM and N₂ sorption-desorption. High BET surface area and decrease in the electron/hole pair recombination made the as-prepared catalyst highly reactive toward synthesis of 2-substituted benzimidazoles and benzothiazoles. Short reaction times, high yields, mild reaction condition and reusability of the catalyst are some advantages of this applied work.

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Disclosure statement

No potential conflict of interest was reported by the authors.
Notes on contributors

Dr. Kiumars Bahrami is working as a Professor of organic chemistry in faculty of chemistry, Razi university, Kermanshah, Iran. He has many papers in national and international journals. He has also participated and presented several papers at national and international conferences. To date, he has supervised 30 M.Sc. and 10 Ph.D. students. He is developing research programs in the areas of nanostructured materials in organic syntheses.

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