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Graphical Abstract

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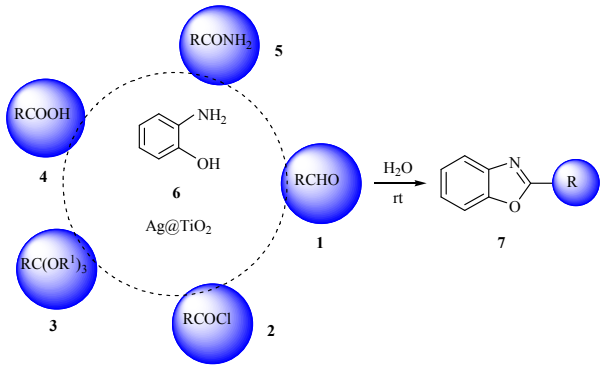
$Ag@TiO_2$ nanocomposite/water as novel catalytic system is used for the synthesis of benzoxazole derivatives. Less reaction time along with high product yield, catalyst stability and recyclability are merits of this novel protocol.



$Ag@TiO_2$ nanocomposite; synthesis, characterization and its application as a novel and recyclable catalyst for the one-pot synthesis of benzoxazole derivatives in aqueous media

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Abstract:

In the present study, we use of $Ag@TiO_2$ nanocomposite for the efficient synthesis of benzoxazole derivatives via the one-pot condensation of 2-aminophenol and several aromatic aldehydes or orthoesters or carboxylic acids or amides or acyl chlorides in water at room temperature. In all situations the favorite product were synthesized with excellent yield. The short reaction times, high yields, safety and mild conditions, simplicity, non-toxicity and easy workup are the main merits of this protocol.

Keywords: $Ag@TiO_2$ nanocomposite, Benzoxazole, 2-Aminophenol, Aldehydes, Orthoesters, Carboxylic acids, Amides, Acyl chlorides, Green chemistry

Introduction

The benzoxazole moiety is created in a variety of biologically active natural compounds[1] and pharmaceutical agents.[2-3] The benzoxazole derivatives are significant targets in drug discovery[4] and also find applications in materials chemistry as photochromic agents,[5] and as fluorescent blenching agent dyes such as 1,4-bis(benzo-xazolyl-2-yl) naphthalene and arenes.[6] Instead, the

benzoxazole scaffold is found in a varied spectrum of biologically active compounds such as antibiotic,[7] anticancer agent,[8] antimicrobial,[9] anti-fungal,[10] antiviral,[11] gram-positive anti-bacterials,[12] antipar-kinson,[13] anti-inflammatory,[14] antitumor,[15] anti-convulsant,[13-16] immunosuppressive agent,[17] anti-parasitic,[18] elastase inhibitor.[19] Further important significant physiological activities related with benzoxazoles are HIV reverse transcriptase inhibitor L-697,661,[20] H_2-antagonists,[21] $5HT_3$ receptor antagonist,[22] selective peroxisome proliferator-activated receptor γ antagonist JTP- 426467,[23] cytotoxicity towards P338 cells.[24]

Because of the importance of benzoxazoles in the pharmaceutical, dye, and photo industries, many synthetic methods for these compounds have been widely reported. The most traditional method for the synthesis of the benzoxazole has been included the condensation of 2-aminophenols with aldehydes,[25] orthoesters,[26] carboxylic acids,[27] amides,[28] acyl cholorides.[29]

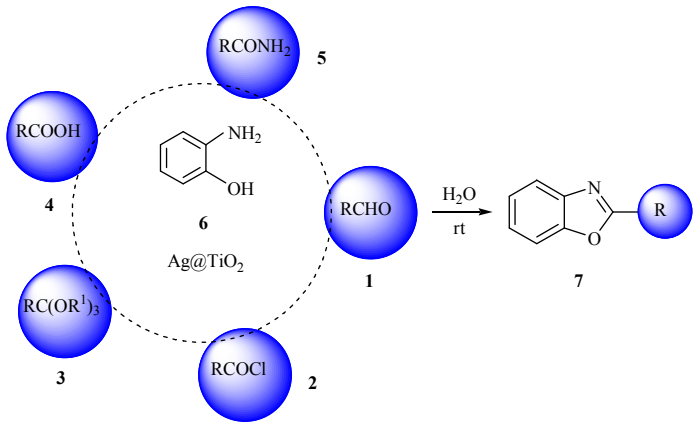
Nevertheless, most of these methods suffer from one or more of the subsequent drawbacks such as low yields of the products, the use of expensive, toxic or non-reusable catalysts, long reaction times, tedious work-up procedures, high temperatures, harsh reaction conditions such as requirement of strong acidic conditions, need to use extra amounts of reagent, the use of large amounts of toxic and hazardous solvents such as xylene and pyridine and co-occurrence of several side reactions. Hence, it is required to find a better catalyst for the synthesis of benzoxazoles in terms of working simplicity, non-toxicity, reusability, environmentally friendly and economical acceptability.

Results and discussions

As a part of continuing efforts in our laboratory towards the synthesis of various organic compounds and the use of nanoparticles in new synthetic methodology,[30] we reported on the synthesis benzoxazoles using $Ag@TiO_2$ nanocomposite as the catalyst. Preparing ultrathin nano-sized noble metal particles, particularly with diameters less than 5 nm and even less than 1 nm, is an efficient way to increase their catalytic activity while reducing the amount of noble metal used.[31] To improve photocatalytic activity, noble metals such as Ag, Au, Pt and Pd are deposited on a TiO_2 surface, because they act as an electron trap promoting interfacial charge transfer processes in the composites. However this type of catalyst structure is effective, metals on the surface of the semiconductor are easily oxidized and dissolved.[32] $Ag@TiO_2$ nanocomposite, in individual, are drawing much attention as catalysts in organic syntheses on account of their easy

preparation, physical and chemical stability, ease of recyclability, high oxidative influence, and low cost of production as compared to other catalysts.[33]

In this exploration, the synthesis of benzoxazole derivatives (**7**) from the condensation of 2-aminophenol (**6**) with various aromatic aldehydes, orthoesters, carboxylic acids, amides and acyl chlorides **(1-5)** in the presence of Ag (1.5%)@TiO_2 as heterogeneous and reusable nanocatalyst, in water at room temperature were studied (Scheme 1).



Scheme 1 Synthesis of benzoxazole derivatives using nano Ag@TiO_2

Recently, the development of environmentally benign and clean synthetic procedures has become the goal of organic synthesis. Water plays an essential role in life processes and also a medium for organic synthesis. The replacement of hazardous solvent with those that are environmentally benign is an active area of current research. Water is clean, non-toxic, and hazard-free in handling, non-inflammable, cheap and a readily available solvent. Therefore, it is important to carry out organic reactions in water instead of other solvents for environmental and economic reasons. Furthermore, because of its highly polarity, high surface tension, high specific heat capacity and network of hydrogen bonds, water plays a significant role in some reactions.[34]

Well-dispersed Ag@TiO_2 nanocomposite particles can be synthesized on a large scale by a clean photochemical route which does not require any additives.[35] 50 mg of nano TiO_2 powder and 1 mL (5 mol/L $AgNO_3$) of an aqueous metal salt solution were dispersed with 100 mL of deionized water in a Pyrex flask with capacity of about 250 mL under stirring. The flask was exposed to light from a high-

pressure Xe lamp (150 W). The reaction was carried for 25 min. Then, the powder was collected by centrifugation and washed twice by deionized water and ethanol. Finally, the resulting powder was dried at 60°C. Ag@TiO_2 nanocomposites dispersion in water was used as such for the reactions.

Ag@TiO_2 nanocomposite was characterized using atomic force microscopy (AFM), X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray micro analysis (EDX).

TiO_2 and Ag@TiO_2 were characterized by the SEM to determine the morphology of TiO_2 and Ag@TiO_2 nanoparticles (Fig. 1).

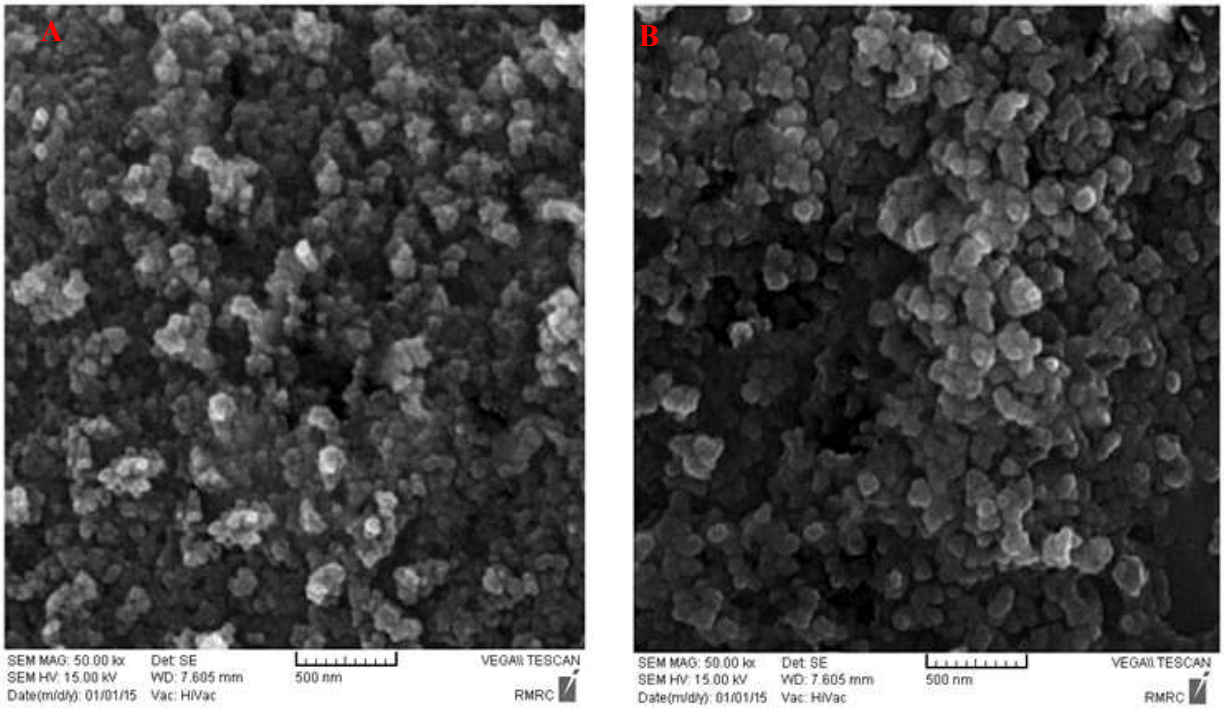


Fig. 1 SEM micrograph of: (A) pure TiO_2 and (B) Ag (1.5 %)@TiO_2 nanoparticles.

Fig. 2(a) shows two dimensional AFM image and Fig. 2(b) shows three dimensional AFM image of mentioned nano layer. The particle diameter was measured at different points of the surface by particle analysis tool (Fig. 2b) and revealed that the surface roughness was determined as equal to about 1.8 nm and the average size calculated was about 24 nm. In the line profile shown in (Fig. 2a) a similar surface roughness of 1.7 nm was observed for Ag@TiO_2.

The morphology of product was studied by tapping mode AFM. The atomic force microscopy (AFM) analysis indicated that the surface roughness was increased by the addition of benzoxazole to

the Ag@TiO_2. Fig. 3 shows the AFM images of benzoxazoles deposited on Ag@TiO_2 substrates and indicated that the surface roughness was determined as equal to about 13.5 nm and the average size calculated was about 65 nm (Fig. 3b). In the line profile shown in (Fig. 3a) a similar surface roughness of 28.3 nm was observed for Ag@TiO_2. The increased thickness is attributed to the benzoxazole compounds on the Ag@TiO_2.

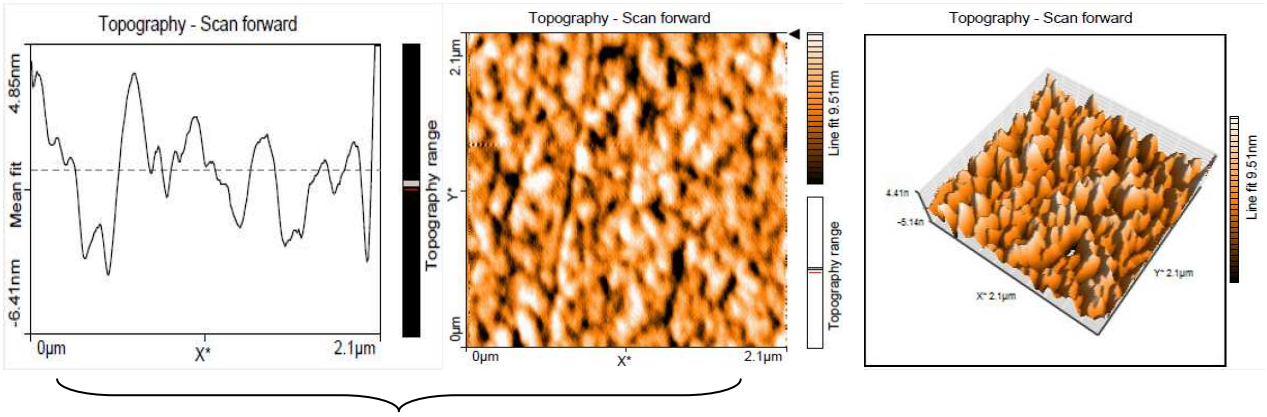


Fig. 2 Two-dimensional (a) and three-dimensional (b) AFM images of the Ag@TiO_2 composite particles synthesized.

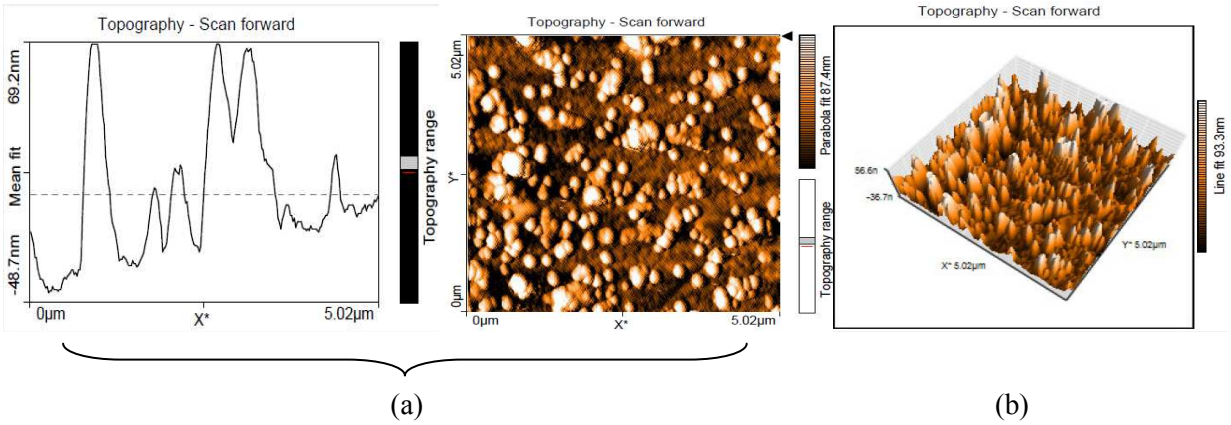


Fig. 3 Two-dimensional (a) and three-dimensional (b) AFM images of the 2-(2-hydroxyphenyl)benzoxazole deposited on Ag@TiO_2.

Fig. 4 shows the XRD pattern of pure and silver-modified TiO_2 powders by the optimum amounts of Ag prepared.

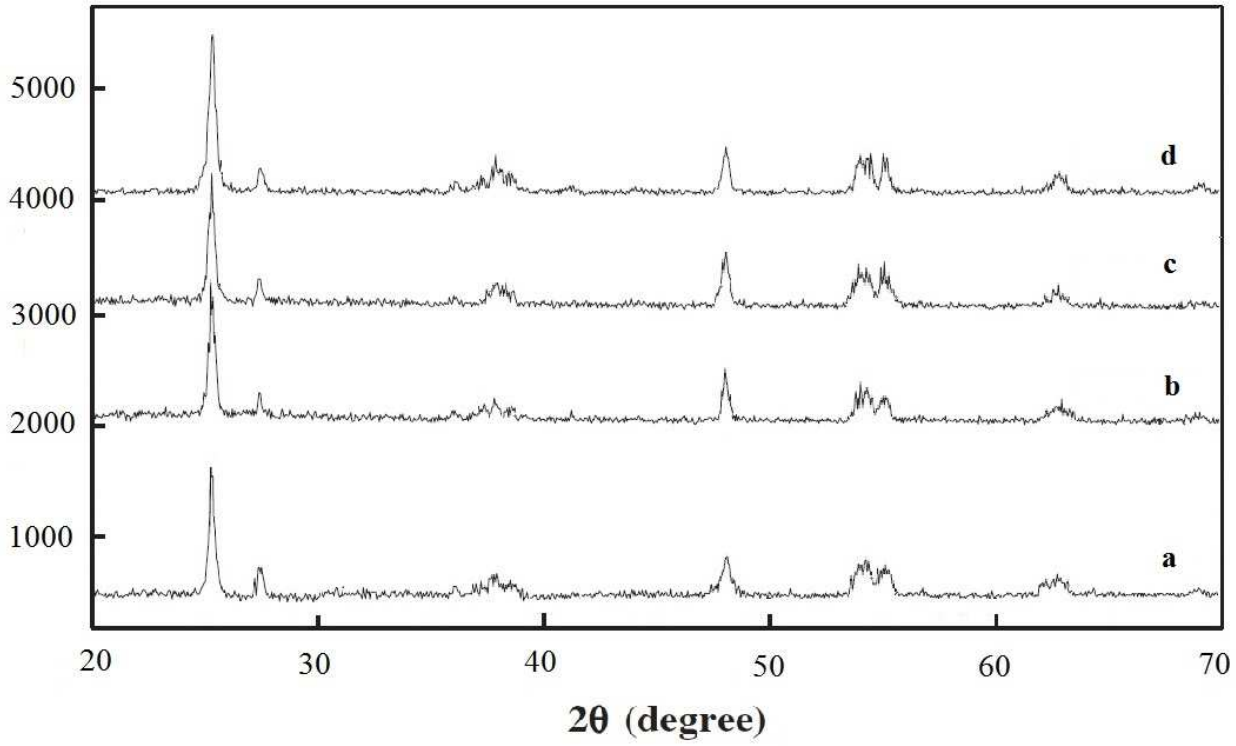


Fig. 4 XRD patterns of pure (a) TiO_2, (b) Ag (1%)@TiO_2, (c) Ag (1.5%)@TiO_2 and (d) Ag (2%)@TiO_2 nanoparticles.

Fig. 5 shows the EDX spectrum of synthesized nanoparticles. The spectrum shows the characteristic peaks for both Ti and Ag confirming the formation of nanoparticles.

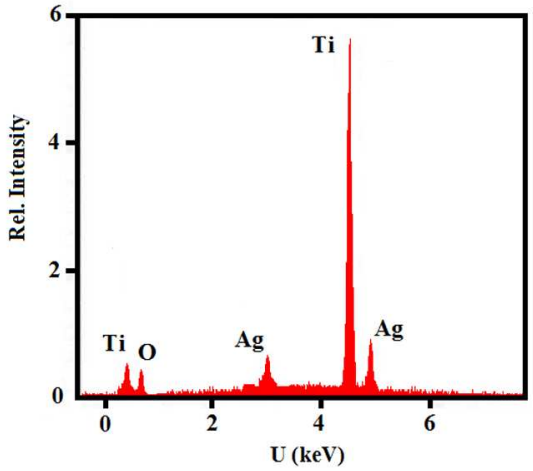


Fig. 5 EDX analysis of Ag (1.5%)@TiO_2 nanoparticles.

In order to optimize the reaction conditions, 2- aminophenol (1 mmol) and benzaldehyde (1 mmol) were selected as the model reaction in the presence of Ag@TiO_2. Different molar ratios of the catalyst, different solvents, and various temperatures were examined in the model reaction (Table 1, Entries 1-8). The best result was obtained in the presence of catalytic amount of Ag (1.5%)@TiO_2 nanocomposite (0.1 ml) in water at room temperature, and 2-phenylbenzoxazole was obtained in 92% yield after 5 min (Entry 2).

As shown in Table 1, when using catalytic amount of Ag (1.5%)@TiO_2, the reaction gave benzoxazoles with 92% yield in 5 min in water (entry 2), and further lowering the catalyst loading up to 1% led to lower yield of 82% in 10 min (entry 1). In the presence of Ag (2%)@TiO_2 catalyst the reaction affords the corresponding synthesis of 2-phenylbenzoxazole in 92% yield within 5 min (entry 3).

To investigate the effect of solvent in these reactions, the reactions were done in different solvents. The results are reported in (Table 1, entries 4-7). The best result is shown in water at room temperature. To indicate the need of Ag (1.5%)@TiO_2 for this condensation, we observed that the model reaction did not proceed in the absence of Ag (1.5%)@TiO_2 even after 12 h (entry 8).

Table 1 Optimization of reaction conditions for the synthesis of 2– (phenyl)-benzoxazole

Entry	Catalyst	Conditions	Time (min)	Yield[a] (%)
1	Ag (1%)@TiO_2 (0.1 ml)	H_2O/rt	10	82
2	Ag (1.5%)@TiO_2 (0.1 ml)	H_2O/rt	5	92
3	Ag (2%)@TiO_2 (0.1 ml)	H_2O/rt	5	92
4	Ag (1.5%)@TiO_2 (0.1 ml)	Toluene/rt	20	86
5	Ag (1.5%)@TiO_2 (0.1 ml)	Ethyl acetate/rt	15	82
6	Ag (1.5%)@TiO_2 (0.1 ml)	CH_2Cl_2/rt	10	74
7	Ag (1.5%)@TiO_2 (0.1 ml)	CH_3CN/rt	15	80

8	-[b]	H_2O/rt	12 (h)	--[c]

[a]Isolated yields. [b]In the absence of Ag (1.5%)@TiO_2, [c]No reaction

Having established the optimized reaction conditions, we turned over attention to explore the scope of this protocol. The results are listed in Table 2. As shown in Table 2, 2-amino phenol reacted with a wide variety of substituted benzaldehydes, orthoesters, carboxylic acids, amides and acyl chlorides completely and afforded the corresponding benzoxazoles in good to excellent yields under mild reaction conditions in water at room temperature. The reaction proceeds smoothly at room temperature in moderate to good yields. An analysis of the effect of the substituent in the reaction time and yields showed that as the electron-donating power of the substituent in the benzaldehydes, orthoesters, carboxylic acids, amides and acyl chlorides increased, the reaction time was longer and the yield diminished (Table 2, 2, 8, 17, 19, 24). Also, all the reactions were free from by-products usually found in classical reaction conditions. The total disappearance of the starting material was checked by thin-layer chromatography (TLC). The products were fully identified from their melting points and spectral data, which were in full agreement with the values described in the literature.

Table 2 Preparation of benzoxazole derivatives using Ag (1.5%)@TiO_2 (0.1 ml) as catalyst

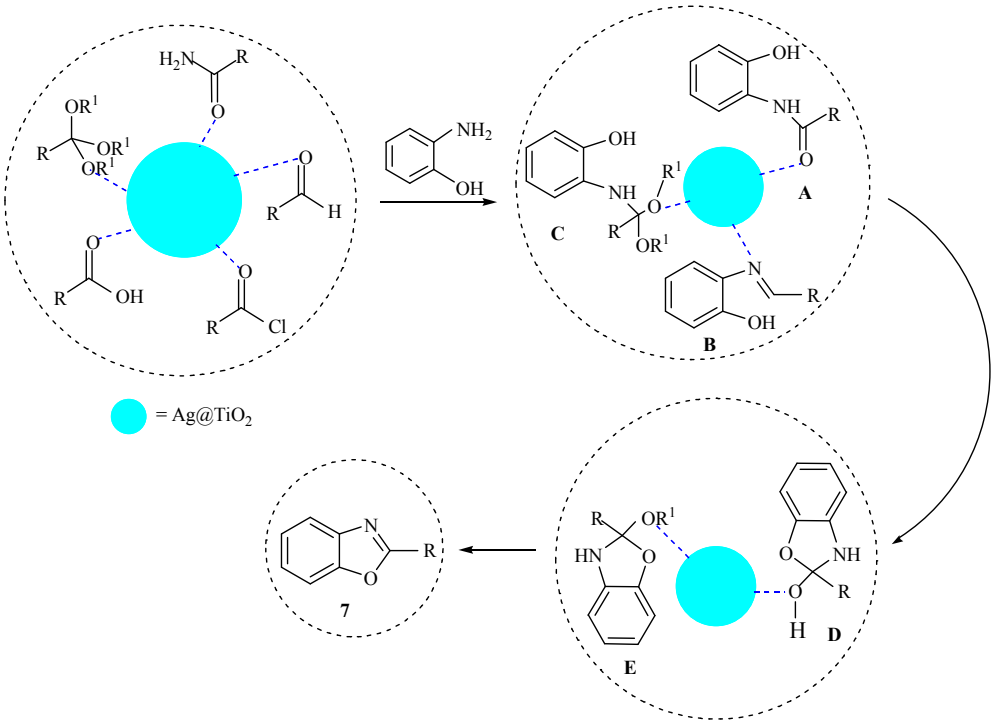
Entry	Compounds	Benzoxazoles (**7**)	Time	Yield[a]	Mp (^{0}C)	
	(1-5)	R	(min)	(%)	Found	Reported
1	C_6H_5CHO	C_6H_5	5	92	101-102	100-102 (ref. 25c)
2	4-$CH_3C_6H_4CHO$	4-$CH_3C_6H_4$	10	91	114-116	112-113 (ref. 25c)
3	4-$CH_3OC_6H_4CHO$	4-$CH_3OC_6H_4$	8	92	100-102	97-99 (ref. 29e)
4	4-$NO_2C_6H_4CHO$	4-$NO_2C_6H_4$	2	96	264-266	264-265 (ref. 25c)
5	4-CNC_6H_4CHO	4-CNC_6H_4	2	94	200-203	200-202 (ref. 25h)
6	4-ClC_6H_4CHO	4-ClC_6H_4	5	90	148-150	147-149 (ref. 25g)

7	4-BrC_6H_4CHO	4-BrC_6H_4	5	91	156-157	156-157(ref. 25g)
8	2-HOC_6H_4CHO	2-HOC_6H_4	10	88	122-124	122-124(ref. 25g)
9	2-ClC_6H_4CHO	2-ClC_6H_4	10	90	70-72	70-73 (ref. 29e)
10	3-$NO_2C_6H_4CHO$	3-$NO_2C_6H_4$	4	93	211-213	211-212 (ref. 25c)
11	2-$NO_2C_6H_4CHO$	2-$NO_2C_6H_4$	5	90	100-102	101-102 (ref. 25c)
12	C_6H_5COCl	C_6H_5	4	93	101-102	103-104 (ref. 29f)
13	4-ClC_6H_5COCl	4-ClC_6H_5	4	92	148-150	149-151 (ref. 29f)
14	3-$CH_3OC_6H_5COCl$	3-$CH_3OC_6H_5$	6	90	71-72	70-73 (ref. 25i)
15	$HC(OCH_3)_3$	H	4	93	Oil	Oil (ref. 26c)
16	$HC(OCH_2CH_3)_3$	H	5	90	Oil	Oil (ref. 26c)
17	$CH_3C(OCH_3)_3$	CH_3	7	87	Oil	Oil (ref. 26c)
18	$CH_3C(OCH_2CH_3)_3$	CH_3	8	84	Oil	Oil (ref. 26c)
19	$CH_3CH_2C(OCH_2CH_3)_3$	CH_3CH_2	10	82	Oil	Oil (ref. 26c)
20	C_6H_5COOH	C_6H_5	10	90	101-102	102 (ref. 27d)
21	4-ClC_6H_5COOH	4-ClC_6H_5	8	89	148-150	151-152 (ref. 29f)
22	3-$CH_3OC_6H_5COOH$	3-$CH_3OC_6H_5$	12	90	71-72	70-72 (ref. 27d)
23	$C_6H_5CONH_2$	C_6H_5	15	86	101-102	99-100 (ref. 28a)
24	CH_3CONH_2	CH_3	20	82	Oil	Oil (ref. 28a)
25	$HCONH_2$	H	15	84	Oil	Oil (ref. 28a)

[a]Isolated yields.

A possible mechanism of Ag@TiO_2-catalyzed reaction of 2-aminophenol with aldehydes or orthoesters or carboxylic acids or amides or acyl chlorides for the synthesis of benzoxazole is shown in Scheme 2.[25-29] The catalyst Ag@TiO_2 would presumably first coordinate with oxygen group in aldehydes or orthoesters or carboxylic acids or amides or acyl chlorides. Then,

intermediates **A-C** were formed through the reaction of amino group with activated aldehydes or orthoesters or carboxylic acids or amides or acyl chlorides under the present reaction conditions. Subsequently, hydroxyl groups in **A-C** attacked the carbonyl or imine groups to accomplish intermolecular addition/cyclization and generated intermediate product **D-E**, which followed by dehydration to form the desired benzoxazole product **7**.



Scheme 2 Plausible mechanism.

The reusability of the catalyst is an important factor from economic and environmental point of views and has attracted much attention in recent years. Therefore, the recovery and reusability of $Ag@TiO_2$ nanocomposite was investigated in the reaction of benzaldehyde with 2-aminophenol under optimized reaction conditions. The catalyst could be recovered simply by solvent extraction of the product from the reaction mixture using ethyl acetate. The recovered catalyst was dried at 60°C and reused. The results showed that the catalyst can be used 4 times without loss of its activity (Fig. 6).

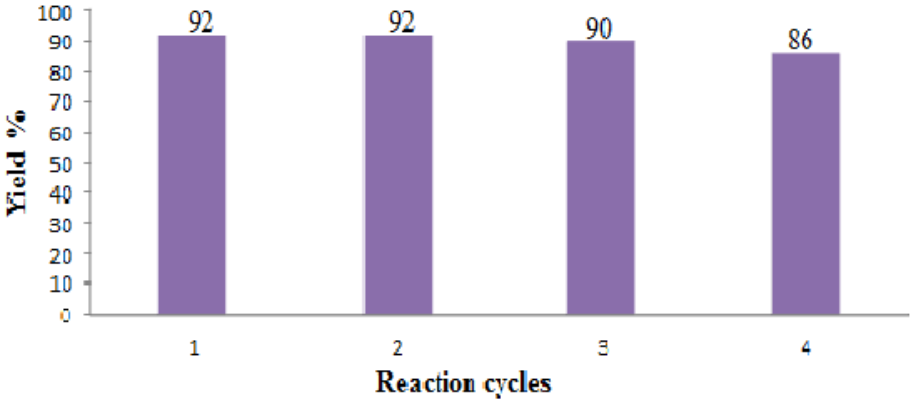


Fig. 6 Reusability of Ag (1.5%)@TiO_2 nanocomposite for model reaction.

Conclusions

In conclusion, we have reported an effective, simple, inexpensive and green method for the synthesis of benzoxazoles by condensation between 2-amino phenols with various aldehydes or orthoesters or carboxylic acids or amides or acyl chlorides in water at room temperature. The use of Ag@TiO_2 nanocomposite dispersed in water as a highly efficient, inexpensive and reusable catalyst makes the present procedure environmentally and economically acceptable. In addition, short reaction times, excellent yields of product, least catalyst loading, safety and mild reaction conditions and easy work-up procedure are other noteworthy advantages which make this method a valid contribution to the existing process in the field of these heterocyclic synthesis.

Experimental

All the chemicals and solvents used were of research grade reagents and were used as received from Merck and Sigma-Aldrich Co. without further purification. Titanium oxide (nano TiO_2, size ~21 nm), silver nitrate ($AgNO_3$, 99%), 2-aminophenol, aldehydes, orthoester, carboxylic acids, amides, and acyl chlorides from Sigma-Aldrich (United States); EtOH from Merck (China); in commercial grade. De-ionized water obtained from a PURE ROUP 30 water purification system was used in these experiments. The melting points of synthesized compounds were determined by open capillary method and were uncorrected. All ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO on a FT-NMR Bruker DRX (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz). All Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ = 0.00) as an internal standard and coupling constants (J) are given in Hz. The IR spectra were recorded on a Rayleigh

WQF-510 spectrometer using KBr discs. The particles size of Ag@TiO_2 and roughness of the films were evaluated by atomic force microscopy (AFM Easyscan 2 Flex). The crystalline phase of nanoparticles was analyzed by XRD measurements by using Rigaku D/Max-2200 model diffract meter equipped with horizontal goniometric in θ/2θ geometry. Morphological studies were conducted using a SEM (SEM, Viga II, 3×10^5, USA). The purity and homogeneity of compounds were checked using TLC technique. All products are known compounds and were characterized by comparison of their spectral and physical data with authentic samples prepared according to the literature methods.

General Procedure for the Synthesis of Benzoxazole Derivatives

A mixture of 2-aminophenol (1 mmol), aldehyde or orthoester or carboxylic acid or amide or acyl chloride (1 mmol), and Ag (1.5%)@TiO_2 nanocomposites dispersion in water (0.1 ml) in 5 ml of water [for insoluble aldehydes 0.2 ml of ethanol was added] was stirred at room temperature for an appropriate time (Table 2). The progress of the reaction was monitored by TLC using n-Hexane: EtOAc (5:2). After complete conversion, EtOAc was added to the mixture and the product was extracted into EtOAc, the organic phase was washed with H_2O and dried with $MgSO_4$. Evaporation of the solvent gave the crude product. The product recrystallized from ethanol (96%, 2 ml) to get pure benzoxazole derivatives. All products were identified by comparison of their physical and spectroscopic data with those reported for authentic samples.

Acknowledgments

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