

Silica nanosphere–graphene oxide (SiO₂–GO) hybrid catalyzed facile synthesis of functionalized quinoxaline derivatives

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Received: 5 May 2016/Accepted: 15 July 2016 © Springer Science+Business Media Dordrecht 2016

Abstract Herein, fabrication of spherical SiO₂ nanoparticles (5 \pm 0.2 nm) with uniform size is followed by their homogeneous distribution on graphene oxide (SiO₂–GO) by using a simple in situ one-step method. These as synthesized catalytic materials are further characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and others. This spectroscopic characterization demonstrated that GO acted as a good supportive substrate for controlling the size and activity of SiO₂ nanospheres with their cooperation towards catalytic reactions. The optimized hybrid exhibited high catalytic activity for the synthesis of functionalized quinoxalines. Significantly, the as-synthesised SiO₂–GO nanohybrid catalysed reaction, for the first time, was shown to be highly efficient in mild conditions (i.e., room temperature, air) with excellent product yield (92 %) and good recyclability (up to four cycles) at room temperature.

Graphical Abstract



Electronic supplementary material The online version of this article (doi:10.1007/s11164-016-2667-8) contains supplementary material, which is available to authorized users.

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¹ Department of Chemistry, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, India Keywords SiO_2 nanospheres \cdot Graphene oxide (GO) \cdot SiO_2 -GO nanohybrid \cdot Functionalized quinoxaline \cdot Cyclocondensation reaction

Introduction

Heterocyclic compounds have attracted considerable attention because of their ample biological activities and other pharmaceutical contributions. Interestingly, a variety of six-membered heterocycles with two nitrogen-containing heteroatoms have received meticulous attention recently. Likewise, quinoxaline derivatives have acquired tremendous scope due to their tunable and varied biological and pharmaceutical applications, especially for anti-bacterial [1], anti-cancer [2], anti-viral [3], anti-HIV [4], and kinase inhibition [5]. Moreover, they are also active ingredients of several anti-tumor agents such as chloroquinoxaline sulfonamide (CQS), NCGS5879-01 [6], and XK469 that are known to be effective by targeting different pathways leading to cancer. Furthermore, varenicline is used for treating nicotine addiction, and brimonidine is used for treating glaucoma [7, 8]. Apart from its medicinal significance, this scaffold finds wider technical applications in dye industries [9], efficient electron luminescent materials [10], organic semiconductors [11], cavitands [12, 13], as well as in the agricultural field as fungicides, herbicides, and insecticides [4].



Considering the significance of functionalized quinoxalines, various synthetic approaches have been reported in the literature, for example, by reaction of 1, 2-phenylenediamine with α -diketones [14], diazenylbutenes [15], oxidative coupling of epoxides [16], and α -hydroxycarbonyls [17]. Moreover, for the condensation of diamine with phenacyl bromide, different catalysts were used such as PEG-400 [18], KF-alumina [19], sodium hexaflurophosphate-Amberlite [20], CeCl₃.7H₂O [21],

CTAB [22], sodium tetrachloroaurate (III) dehydrate [23], TMSCI-water [24], β -cyclodextrin [25], pyridine [26], and HClO₄-SiO₂ [27]. Significantly, Brahmachari et al., reported Mn-Fe₃O₄ based nanohybrids for synthesis of substituted benzimidazole and quinnoxalines by using 1, 2-diamine and 1, 2-diketone [28]. Kadam et al. and Roy et al., developed efficient methods for synthesizing quinoxaline derivatives using graphite [29] and reduced graphene oxide [30], respectively.

In fact, unfortunately, smaller nanoparticles of metal/metal oxide aggregates easily and usually form larger particles, which decreases their surface sensitivity and furthermore, its catalytic performance [31, 32]. In order to further improve their performance and to avoid the above said issues of a decrement in their reactivity, metal alloy, metals/metal oxide-based nanostructures have been further hybridized with a variety of solid supports to take advantage over both the surfaces due to their synergetic effect [33, 34]. Along with existing diverse kind of supports, graphene oxide (GO) has recently opened a new avenue for utilizing 2-D platforms and it is taken as a promising and ideal candidate for further enhancement in the activity of hybrids, because of its unique features such as high surface area (surface/volume ratio, accessible surface, and active sites) with controllable chemical composition [35–38]. In view of this, such a GO-based hybrid system has recently been used as an active catalytic domain because of having special features, which are responsible for an effective conversion and improved selectivity [39–46].

On the other hand, in recent literature, it also been noted that the two or more different potential systems combined together benefit from their special/enhanced properties because of their cooperative interactions. More interestingly, in view of the unique and superior platform and having special reactive sites on GO, it gains special attention towards the fabrication of potential candidates like SiO₂, TiO₂, ZnO and Al₂O₃ for various and tunable applications. Among the all GObased hybrids, SiO₂-GO hybrids have been recently gaining more attention due to their lower cost, easier preparation methods, wider availability of active sites on both, and biocompatibility and hence, excellent catalytic activity. Interestingly, from the view point of catalysis, the SiO₂ nanospheres can facilitate the effective diffusion of substrates and products because of their large surface area and thus, it accelerates their reaction rate (high turnover number). Moreover, there are several advantages of SiO2-GO hybrids including, generation of distinct and additional reactive sites, which are beneficial for the efficient interactions with substrate and further conversion resulting in higher selectivity with excellent product yield.

Herein, we report such an enhanced catalytic activity towards one-pot condensation of benzene-1, 2-diamine with p-bromo phenacyl bromide, and 1, 2-dicarbonyl respectively using a SiO_2 -GO hybrid. The higher catalytic activity (lower reaction time and higher product yield) indicates the origin of the extraordinary performance is from their co-operative interactions between SiO_2 nanospheres and GO after hybrid formation. More significantly, further tuning of the

size of the GO and its distribution could offer several promising characteristics specially required for the development of high performance catalytic centers.

Experimental

Synthesis of graphene oxide (GO)

Graphene oxide (GO) was prepared via exfoliation of graphite powder using the modified Hummer's method [47]. In a typical synthesis, 1gm of graphite powder was mixed with an acidic solution containing 45 mL of concentrated nitric acid and 90 mL of sulfuric acid in a round-bottom flask, and the mixture was stirred in an ice bath for 30 min. The dispersion in the round-bottom flask was sonicated over an ultrasonicator at room temperature for 2 h. The dispersion was subsequently refluxed for the next 24 h, during which the reaction progressed with time and gradually formed a brown-grey paste with diminished effervescence. The browngrey paste was further separated via centrifugation, and then re-dispersed in deionized (DI) water by sonication for 3 h. The dispersion was filtered and the solid material was washed with 1 M HCl, followed by a copious amount of DI water until the hydrated gel turned into a black powdered material. The black powdered material (graphite oxide) was dispersed in anhydrous THF and sonicated for 1 h to exfoliate the graphite oxide into GO sheets. The solution containing GO was then separated from the residual unreacted graphite, which quickly precipitated out in the THF solution. The solid product was recovered from the solution via centrifugation of the dispersion and then dried under high vacuum at 40 °C, yielding GO in powdered form. The GO was dispersed in DI water, giving a brownish suspension that remained stable for over 2 weeks. This as-synthesized GO was then used for formation of a hybrid with SiO₂ NPs in subsequent steps.

Synthesis and surface functionalization of monodispersed SiO₂ nanospheres

The spherical silica (SiO_2) nanoparticles were synthesized by the reported Stober method [48]. Typical steps involve, hydrolysis of TEOS (tetraethyl orthosilicate) using NH₄OH (base) in a mixture of ethanol–water as a reaction medium. In more detail, NH₄OH (6.5 mL) was stirred with a mixture of water (7 mL) and ethanol (100 mL) at room temperature, then was added TEOS (6.2 mL), and the stirring was continued for a further 3 h at room temperature to get a white turbid suspension. The resulting turbid suspension was centrifuged for 20 min as the white precipitate was washed with ethanol and was used for spectroscopic and microscopic characterization along with further functionalization. After washing with 500 mg of the SiO₂, the nanospheres were transferred into dry toluene (250 mL), sonicated for the next 4 h, and then was added APTS (3-Aminopropyltriethoxysilane) with stirring it at 70 °C for 6 h to functionalize the SiO₂ surface with amino groups. After washing with ethanol to remove the unbound (unfunctionalized) excess amine, $-NH_2$ terminated SiO₂ nanospheres were obtained.

Synthesis of SiO₂–GO hybrids

 SiO_2 nanoparticles were deposited on GO nanosheets by in situ hydrolysis of TEOS (Tetraethylortosilicate). In brief, 50 mg of GO was dispersed in 120 mL of THF by sonication for 1 h, and then TEOS (0.5 mL) was added to the solution. After being vigorously sonicated for 1 h, the mixture was stirred further for the next 20 h at RT. Then the SiO₂–GO suspension was centrifuged and washed several times with alcohol to remove excess/unbound TEOS and resulting product was characterized by various microscopic and spectroscopic techniques.

General procedure for quinoxaline derivatives

A mixture of substituted 1, 2-diamines (1 mmol) and substituted phenacyl bromides (1 mmol) were stirred in the presence of a well-dispersed catalytic system of a SiO₂–GO hybrid (20 mg) at room temperature in acetonitrile for the as mentioned specified time in Table 6. After completion of the reaction, the catalytic material from the reaction mixture was separated by centrifugation and ultra-filtration simultaneously. The residual catalyst was further washed with water, then ethanol followed by acetone, and was further dried and reused for the next reaction cycle. The organic extract i.e. reaction mixture (crude product) was poured on crushed ice and was then separated by simple filtration followed with recrystallization using ethanol.

2-(*4*-bromophenyl) quinoxaline (*3a*) Solid m.p.132–134 °C (reported 138 °C) ¹H NMR (CDCl₃, 400 MHz) δ 7.72–7.84 (m, 4H, Ar–H), 8.11–8.18 (m, 4H, Ar–H), 9.33 (s, 1H, CH=N); ¹³C NMR (CDCl₃, 100 MHz) 125.01, 129.03, 129.19, 129.62, 129.85, 130.53, 132.39, 135.65, 141.71, 142.24, 142.84, 150.68.

2-(**4**-chlorophenyl)quinoxaline (**3**c) Solid m.p.134–136 °C (reported 136–138 °C) ¹H NMR (CDCl₃, 400 MHz) δ 7.55–7.83 (m, 4H, Ar–H), 8.14-8.18 (m, 4H, Ar–H), 9.32 (s, 1H, CH=N); ¹³C NMR (CDCl₃, 100 MHz) 128.79, 129.18, 129.42, 129.61, 129.81, 130.50, 135.19, 136.59, 141.67, 142.22, 142.89, 150.59.

2,3-diphenylquinoxaline (5a) Solid m.p.125–127 °C ¹H NMR (CDCl₃, 400 MHz) δ 7.33–7.35 (m, 6H), 7.50–7.53 (m, 4H), 7.76–7.91 (m, 2H), 8.16–8.20 (m,2H); ¹³C NMR (CDCl₃, 100 MHz) 153.50, 141.17, 139.10, 129.16, 128.75, 128.11.

Results and discussion

Characterization of SiO₂–GO hybrid catalysts

Furthermore, anchoring of SiO_2 on GO and formation of a hybrid has been further confirmed by TEM analysis. The typical TEM images show that the exfoliated GO has a planer structure with an average thickness of ca. 2 nm (Fig. 1a) indicating GO is a few layered nanostructure. Moreover, it also been revealed that from the TEM image that flattened GO nanosheets are randomly stacked together, displaying a



Fig. 1 a Transmission electron microscopy (TEM) image of a GO size ~ 2 nm; b TEM image SiO₂-GO hybrid of SiO₂ embedded in GO having a size of 5 ± 0.2 nm

flake-like structure similar to a reported few layered graphene. Moreover, similar to the morphology reported in our earlier reports and also from literature, wrinkles on the surface are observed, meaning that the GO sheets have a very flexible nature [49]. Significantly, the adjacent interlayer distance in the GO sample is 0.373 nm, which is closer to the d-spacing of the (002) crystal plane of graphite (0.335 nm). Moreover, TEM images for SiO_2 -GO shown in Fig. 1b, reveal that the graphene sheets are brighter than SiO₂ nanospheres. The structural details are reflected by TEM images of high magnification (inset of Fig. 1b). An individual SiO₂ nanosphere is composed of a rigid ball-like structure having a size of about 5 nm. The average diameter of nanospheres is about 5 ± 0.2 nm shown by TEM images of high magnification (in inset of Fig. 1b), and it indicates that shells of SiO₂ nanospheres seem to be rough, highly porous, and partially non-solid. This feature endows SiO₂ nanospheres with high surface area. It is also observed from these TEM images of nanosheets that they can be seen rippled like a silk weave due to the extremely small thickness of graphene. This suggests and supports the flexible structures of GO sheets. It clearly shows that SiO₂ nanospheres with monodispersed sizes are decorated homogeneously on GO nanosheets.

The crystal structure of the as-synthesized SiO₂–GO hybrid along with SiO₂ nanospheres and GO were determined by powder the X-ray diffraction (PXRD) method (Fig. 2a). The prominent and common peak appeared at around 25.82° in the SiO₂–GO hybrid and GO is attributed to the (002) direction of graphene having an interlayer space of 0.35 nm, which is in good agreement with results from TEM. Moreover, three weak signals that can be assigned to (101), (110), and (201) planes of a few layers graphene. Significantly, SiO₂ nanospheres and the SiO₂–GO hybrid mainly showed the broad shoulder at ~22° is due to the amorphous/disordered surface structure and the porous nature of SiO₂. A comparison of the PXRD pattern for GO versus SiO₂–GO reveals that the GO possesses a greater degree of graphitization, but after hybrid formation the degree of graphitization comes down



Fig. 2 a Superimposed powder X-ray diffraction pattern of GO, SiO₂ nanospheres, and a SiO₂–GO hybrid. **b** FTIR spectrum of a SiO₂–GO hybrid indicates significant bands corresponding Si–O–Si/Si–O-C that indicates hybrid formation through Si–O–C. **c** EDS analysis of SiO₂–GO hybrid

and could be due to the amorphous/disordered nature of encapsulated SiO_2 nanospheres.

FTIR analysis was employed to investigate the extent of surface oxidation of GO and its bonding interactions with SiO₂ nanospheres during the hybrid formation process. As shown in Fig. 2b, the signal at 1081 cm⁻¹ which is attributed to the C-O bond from GO, confirmed the presence of oxide and/or other oxygen containing functional groups. Moreover, the signals in the range of 1630 cm⁻¹ to 1650 cm⁻¹ show that the C=C bond still remained before and after the oxidation process. The absorbed water in GO is shown by a broad peak at 2885 cm⁻¹ to 3715 cm⁻¹ contributed by the O–H stretch of H₂O molecules. In addition to this, the FTIR spectrums corresponding to GO and SiO₂ NPs presented in supplementary data confirm the involvement of functional groups during nanocomposite formation.

Significantly, an additional signal appeared after hybrid formation at 801 and 1100 cm^{-1} , for the Si–O-Si (symmetric vibrations) and Si–O-Si/Si–O-C (asymmetric vibrations), respectively, and signal the disappearance of peak at 1720 cm⁻¹ related to the –C=O of the carboxylic group of GO, and confirms interaction of SiO₂ nanospheres with GO. In addition, we have also used functionalized SiO₂ for APTS (3-Aminopropyltriethoxysilane) via. –NH₂ for the anchoring with a GO surface, and is confirmed by a signal at 1260 cm⁻¹ that proves the effective attachment with SiO₂ and results in hybrid formation. In addition to this, the SiO₂–GO hybrid was

further characterized by the spot EDS mapping to prove the local elemental composition (Fig. 2c) composed of C, O, and Si confirming formation of a composite of SiO_2 NPs and GO have homogenous distribution, and these results were in good agreement with morphological studies shown in Fig. 1(b). These above as-synthesized and well-characterized catalytic nanomaterials were tested for synthesis of quinoxaline derivatives.

Optimization of the reaction condition

Initially, the model reaction was carried out by the condensation of benzene-1, 2-diamine, and p-bromo phenacyl bromide, which gave the corresponding quinoxaline derivative (Scheme 1).

As-synthesized SiO_2 nanospheres and GO were used as catalysts for the model reaction at the initial stage in an ethanol medium at rt, which gave the desired product but in poor yields even after the longer reaction time (Table 1 entries 1 and 2). Significantly, our aim was to increase the product yield along with its reduction in reaction time. Hence, by considering two different views in mind that were to keep intact the chemical stability of GO and further enhancement in catalytic performance, surface modification was done, which was successfully performed by the suitable deposition of SiO_2 nanospheres on the GO as a result of this SiO_2 -GO hybrid formation. Surprisingly, it was observed that excellent product yield was obtained within the shorter reaction time (Table 1, entry 3), and it could be due to their cooperative interactions after hybrid formation.

Encouraged by the above results of selection of the catalytic system, we further examined the effect of different solvents including water, ethanol, methanol, acetonitrile, dichloromethane, etc. that were investigated by using a SiO₂–GO hybrid system for selecting the best medium. Significantly, it was observed that in water, ethanol, methanol, and DCM the desired product was obtained with very poor yield i.e., 40, 55, 50 and 30 %, respectively, (Table 2 Entries 1, 2, 3, and 5). But acetonitrile afforded the desired product in a shorter reaction time with excellent product yield (92 %) (Table 2, Entry 4).

We further checked the effect of catalyst loading on the model reaction. Accordingly, the reaction was carried out by all other parameters the same with different catalyst loadings such as 15, 20, 25, and 30 mg, and it was observed that the catalyst loading to 20 mg was sufficient to afford the desired product with





Table 1 Screening of catalyst	Entry	Catalyst		Solvent	Time (min)	Yield (%)
	1	GO		Ethanol	45	40
	2	SiO ₂ nanosp	heres	Ethanol	45	45
	3	SiO ₂ –GO		Ethanol	15	75
Table 2 Effect of solvent on	Entry	Solvent	Temp	erature (°C)	Time (min)	Yield ^b (%)
S1O ₂ –GO hybrid catalyzed synthesis of quinoxaline			- 1			
derivatives	1	Water	RT		15	40
	2	Ethanol	RT		15	55
^a Departion conditions 10	3	Methanol	RT		15	50
(1 mmol) $2a(1 \text{ mmol})$ SiO ₂ -	4	Acetonitrile	RT		15	92
GO hybrid (20 mg), solvent (10 mL)	5	DCM	RT		15	30
Table 3 Optimization of catalyst amount for the synthesis	Entry	Catalys	st (mg)	Tim	e (min)	Yield ^a (%)
of quinoxaline	1	15		15		70
Reaction conditions 1a	2	20		15		92
(1 mmol), 2a (1 mmol),	3	25		15		91
Acetonitrile (10 mL), catalyst, stirred at RT, ^a Isolated yields	4	30		15		91

excellent yield. There was no significant increment in the product yield and decrease in reaction time with the amount of catalyst (Table 3).

To highlight the advantage of the present work over the others reported in the literature, we accordingly did a comparison of catalytic performance of a SiO₂–GO hybrid with different catalysts such as reduced graphene oxide (rGO), graphite, Amberlite IR-120H, glycerine, and $MnFe_2O_4$ nanomaterials that are shown in Table 4.

Another beauty of this methodology is reusability of the SiO_2 -GO hybrids as a catalytic material for multiple times (Table 5). In brief, after completion of the reaction, the catalyst was centrifuged for 5 min at 4000 rpm and separated by a simple filtration method, washed several times with ethyl acetate, and dried in air and then directly reused for next four consecutive reactions without significant loss in yield. It is worthy to mention that there was no loss of catalytic activity, and it was confirmed by taking TEM images after four consecutive runs (not shown due to brevity). It was shown there was no change in the morphology of the hybrid catalyst. Moreover, up to the fourth run, it gave better yield; there was some loss in the yield, and this could be due to the loss of catalyst during each separation.

Under the optimized reaction condition, the present protocol was extended by using different substituted phenacyl bromides and substituted o-phenylenediamine as shown in Table 6. The phenacyl bromide containing electron withdrawing and electron donating groups did not affect significantly on the product yield.

Entry	Catalyst	Amount of catalyst	Time	Temperature (°C)	Yield (%)	References
1	Reduced- GO	20 mg	3 h	100	95	[27]
2	Graphite	2 eq	1 h	RT	92	[26]
3	Amberlite IR-120H	200 mg	5 h	110	95	[28]
4	Glycerine CeCl ₃ .7H ₂ O	2 mg	4–6 h	RT	95	[29]
5	MnFe ₂ O ₄ nano- material	10 mol %	2.5 h	RT	91	[25]
6	SiO ₂ –GO Hybrid	20 mg	15–25 min	RT	92	Present work

Table 4 Comparison of the catalytic performance of SiO_2 -GO catalyst with some recently reported catalysts

Table 5 Recycling and reuse of catalyst

Entry	Run	Yield
1	I	92
2	Π	91
3	III	89
4	IV	88

Reaction conditions **1a** (1 mmol), **2a** (1 mmol), Acetonitrile (10 mL), catalyst(20 mg), stirred at RT, ^a Isolated yields

Encouraged by the high reactivity and effectiveness of the catalyst, the present methodology is further extended for the synthesis of the same core moiety with different functional groups, i.e., for the reaction of benzene-1, 2-diamine with 1, 2-diketone (benzil). The results are summarized in (Table 5 Entries 5a-5d). It was observed that the reaction was carried out very smoothly, and the desired product was obtained with excellent yield. At this stage different derivatives with methyl substituted benzene-1, 2-diamine and substituted benzil were used.

Conclusion

In summary, we have demonstrated the efficient a SiO_2 –GO hybrid nanostructured catalytic system for synthesis of quinoxaline derivatives by the condensation of 1, 2-diamine with substituted phenacyl bromide at rt in the presence of acetonitrile as solvents. This hybrid offers a wider scope, providing excellent results for various 1, 2-diamine and substituted phenacyl bromide and provides very high selectivity (i.e., formation of quinoxaline) within a very short reaction time. Moreover, this nanostructured SiO₂–GO hybrid can be easily recovered by a simple filtration method and reused further for a minimum of four cycles without losing considerable

0 Pr				0 Ar		
		SiO ₂ -GO CH ₃ CN, RT	- R	SiO ₂ -GO CH ₃ CN, RT	$ = \bigvee_{R}^{N} \bigvee_{N}^{Ar} Ar $	
3(a-p)					5(a-d)	
Entry ^a	Product	R	R′	Time (min)	Yield ^c (%)	Melting Point (°C)
1	3a	-H	4-Br	15	92	132–134
2	3b	-H	-H	15	90	77–78
3	3c	-H	4-Cl	20	91	134–136
4	3d	-H	4-F	20	90	113–115
5	3g	-H	4-CH ₃	15	89	87–88
6	3h	-H	4-OMe	20	88	96–97
7	3i	4-Me	4-Br	15	89	126-126
8	3j	4-Me	-H	25	90	116-119
9	3k	4-Me	4-Cl	20	91	126-128
10	31	4-Me	4-F	15	90	117-118
11	3m	4-Me	3-NO ₂	15	91	182–183
12	3p	4-Me	4-OMe	15	88	93–94
R	Br	O R' SiO ₂ -GO CH ₃ CN, RT	R R NH2	O Ar O Ar SiO ₂ -GO CH ₃ CN, RT	R N Ar	
3(a-p)					5(a-d)	
Entry ^b	Product	R	Ar	Time (min)	Yield ^c (%)	Melting Point (°C)
13	5a	-H	C ₆ H ₅	35	89	125–127
14	5b	-H	-4CH ₃ C ₆ H ₅	40	90	147–148
15	5c	CH_3	C ₆ H ₅	40	90	115–116
16	5d	CH ₃	-4CH ₃ C ₆ H ₅	40	89	130–131

Table 6	Synthesis of	quinoxaline	derivative in the	presence of SiO	-GONPs
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Reaction conditions ^a diamine (1 mmol), phenacyl bromide (1 mmol), SiO₂–GO catalyst (20 mg), solvent (10 mL), stirred at RT, ^b diamine (1 mmol), diketone (1 mmol), SiO₂–GO catalyst (20 mg), solvent (10 mL), stirred at RT, ^c isolated yield

catalytic activity. The easy recoverability of the catalyst and milder reaction conditions for the efficient synthesis of quinoxaline leads to its applicability toward various other scientific prospects.

Acknowledgments An Emeritus Scientist Fellowship awarded to MSS by the Council of Scientific and Industrial Research, New Delhi (Project vide NO. 21(0919)/12/EMR-II Dated 25-04-2013) is gratefully acknowledged. The authors are grateful to the UGC for the award of a Teacher fellowship. The authors are also grateful to the Department of Chemistry, Dr. B. A. Marathwada University, Aurangabad, for

providing the laboratory facilities. We also thank SAIF Division, CDRI, Lucknow, for providing analytical data.

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