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Sulfonated carbon/nano-metal oxide composites: a novel and recyclable solid acid catalyst for organic synthesis in benign reaction media

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Novel sulfonated carbon/nano-metal oxide composites were successfully synthesized by the partial 10 carbonization of starch in the presence of different nano-metal oxides (nano-titania, nano-ceria and nano-zirconia) followed by sulfonation. The catalytic activity of the prepared catalysts was evaluated for the one-pot synthesis of gem-bisamides, bis(heterocyclyl)methanes and for the one-pot three component synthesis of *β*-aminocarbonyl compounds *via* Mannich reaction. Different nano-metal oxides have been investigated as support materials, with a view to select the most 15 active solid acid catalyst. Among the various catalysts, sulfonated carbon/nano-titania composite (C/TiO$_2$-SO$_3$H) was found to be the most active and selective, and could be recycled several times without significant loss of activity. All the catalysts were characterized by FTIR and CHNS analysis, and the most active catalyst was further characterized by XRD, SEM, TEM, HRTEM, EDX and TGA.

20 Introduction

Homogeneous acid catalysts such as Lewis and Bronsted acids represent an important class of catalysts that are commonly employed in the large-scale synthesis of industrial bulk chemicals as well as in the production of fine chemicals[1]. The 25 electrophilic activation of a substrate by means of a Bronsted acid is, undoubtedly, the most straightforward and a common approach used to promote a chemical reaction, so Bronsted acids have been widely utilized as efficient catalysts for numerous organic transformations[2]. However, a restriction on 30 the use of these homogeneous catalysts in industry is their difficulty in separation, high volatility, toxicity, waste generation and limited solubility/phase contact with the starting materials. Using the eco-friendly reusable heterogeneous solid acids instead of conventional, toxic and 35 polluting homogeneous acid catalysts, is thus strongly recommended from the view point of "Green chemistry"[3]. To successfully obtain a highly active heterogeneous catalyst, a rational choice is immobilization of homogeneous catalyst on a suitable insoluble support material. Recently, carbon based 40 materials have been attracting attention as potential supports in heterogeneous catalysis[4]. Their high surface area ensures a high density of catalytic active sites when used as catalysts and catalyst supports. Because of their unique properties, such as resistance to acidic and basic conditions, good electric 45 conductivity, tunability of surface chemistry, stability against various chemical environments and low cost, carbon based catalysts find wide applications in organic syntheses and in industrial manufacturing of materials[5-12]. Recently, it was found that carbon materials when dispersed over inorganic 50 supports leads to organic/inorganic hybrid composites with more stability, activity and selectivity[13,14]. Among the various sulfonated carbon/inorganic support composites prepared so far, silica derived composites have been extensively studied, whereas composites derived from other inorganic support 55 materials especially metal oxides like titania, ceria, zirconia etc. have been poorly explored[15]. Metal oxides are of high importance as catalyst supports in heterogeneous catalysis because of their interesting acid–base and redox properties, high chemical stability and being commercially available and 60 non-toxic[16]. In this context, metal oxides can be efficiently utilized for the development of novel sulfonated organic/inorganic hybrid materials, thereby showing the synergistic effect of the composite on catalytic performance of the novel solid acid catalyst.

65 Amide and bisamide functionalized moieties represent important biological and medicinal scaffolds. Further, symmetrical and unsymmetrical *N,N'*-alkylidene bisamides and their derivatives are found as key structural subunits for the construction of peptidomimetic frameworks[17].The 70 preparation of symmetrical *N,N'*-alkylidene bisamides is an important organic transformation and several methods have been reported in literature for their synthesis[18-21].

Bis(heterocyclyl)methanes represent an important class of compounds that constitute the building blocks of natural and 75 unnatural porphyrins[22]. These occur widely in various natural products and show versatile biological and pharmacological activities[23-25]. Synthetic strategies mediated through protic acids[26] and Lewis acids[27], ionic liquids[28], ion exchange resins[29] and rare earth metals[30] have been reported in the 80 literature for the preparation of bis(heterocyclyl)methanes.

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Mannich reaction, one of the most important carbon–carbon bond forming reactions has been enormously used for the preparation of secondary and tertiary amine derivatives[31]. These reactions provide synthetically and biologically

85 important β-amino carbonyl compounds, which are important intermediates for the construction of various nitrogen-containing natural products and pharmaceuticals[32]. Mannich reaction of aromatic ketones, aromatic aldehydes and aromatic amines has been reported to be catalyzed by various Lewis

90 and Bronsted acid catalysts[33-44].

Most of the methods reported for the synthesis of gem-bisamides, bis(heterocyclyl)methanes and β-aminocarbonyl compounds suffer from drawbacks such as the use of corrosive reagent, expensive and large amount of catalyst,

95 long reaction time, harmful reaction media, and low yields. Therefore, there is still a demand for the development of greener synthetic protocol for the synthesis of gem-bisamides, bis(heterocyclyl)methanes and β-amino carbonyl compounds under mild conditions using inexpensive catalysts.

100 In the present work, we report the synthesis of novel sulfonated carbon/nano-metal oxide composites derived from inexpensive and renewable biomaterial, starch as carbon source and commercially available, non-toxic nano-metal oxides as inorganic support. The carbon material used

105 provides high surface area for sulfonation and the inorganic support used provides thermal and mechanical stability to the composites formed. The catalytic activity of sulfonated carbon/nano-metal oxide composites was evaluated for the one-pot synthesis of gem-bisamides,

110 bis(heterocyclyl)methanes and for one-pot three component Mannich reaction.

Results and discussion
Characterization of sulfonated carbon/nano-metal oxide composites

120 Sulfonated carbon/nano-metal oxide composites have been prepared by the incomplete carbonization of starch in the presence of different inorganic supports like nano-titania, nano-ceria and nano-zirconia to form carbon/nano-titania (C/TiO$_2$), carbon/nano-ceria (C/CeO$_2$) and carbon/nano-

125 zirconia (C/ZrO$_2$) composites respectively, which on sulfonation with conc. sulfuric acid gave corresponding sulfonated carbon/nano-metal oxide composites. We have used starch as a cheaper and green carbon precursor alternative to the commonly used high cost resins[45], ionic

130 surfactants[46] and triblock co-polymers[47]. Starch molecule has more hydroxyl groups and the amount of amylopectin ratio present in starch is important for the formation of small polycyclic aromatic rings that provide anchoring sites for −SO$_3$H groups. It has been reported that the carbonization

135 temperature has great effect on the catalytic activity of final sulfonic acid catalyst due to the pore structure and surface acid groups[48]. The carbon catalysts prepared under lower temperature carbonization process show better catalytic performance due to the smaller size of carbon sheets and

140 hence availability of more surface active sites for the grafting of sulfonic groups. Whereas with increasing carbonization temperature, carbon materials become harder and the flexibility of the polycyclic aromatic carbon decreases through plane growth and carbon sheet stacking[49]. In

145 consideration with these facts, the partial carbonization has been done at 673 K to get higher sulfonic acid densities in the final catalyst.
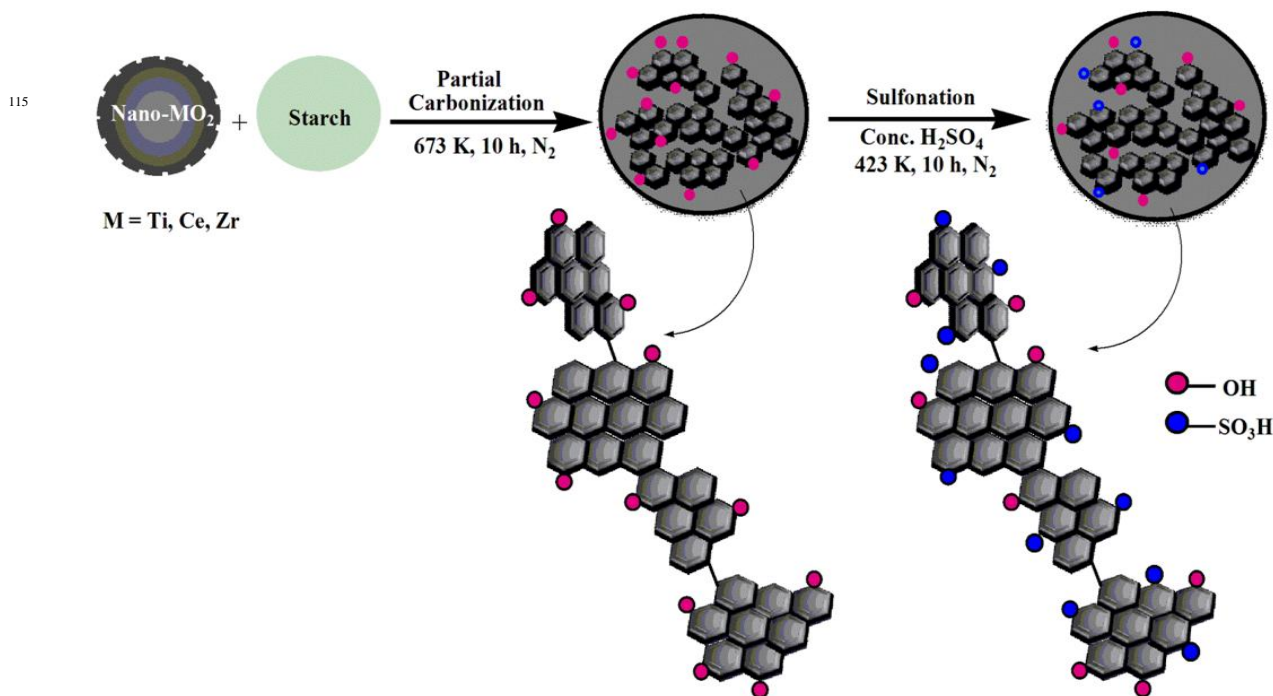
Scheme 1 General procedure for the synthesis of sulfonated carbon/nano-metal oxide composites.

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The partial carbonization of starch leads to pyrolysis followed by dehydration and dissociation of C-O-C linkages thereby leading to the formation of polycyclic aromatic carbon rings with surface hydroxyl groups. The presence of these groups provide anchoring sites to sulfonic acid groups during the sulfonation step. The general procedure for the synthesis of sulfonated carbon/nano-metal oxide composites is represented in **Scheme 1**. The characterization of the sulfonated carbon/nano-metal oxide composites thus prepared (C/TiO$_2$-SO$_3$H, C/CeO$_2$-SO$_3$H and C/ZrO$_2$-SO$_3$H) was carried out with FTIR and CHNS analysis. The most active catalyst C/TiO$_2$-SO$_3$H was further characterized by XRD, SEM, TEM, HRTEM, EDX and TGA.

The FTIR spectra of the sulfonated carbon/nano-metal oxide composites exhibited a strong and broad band in the range 3100-3400 cm^{-1} attributed to phenolic –OH groups present in the polycyclic aromatic rings. Further, bands in the range 1700-1720 cm^{-1} and 1580-1620 cm^{-1} were assigned to C=O groups and aromatic C=C stretching modes respectively. The C=O groups were produced by the oxidation of carbon by small amounts of sulfuric acid used for sulfonation. The absorption bands in the range 1210-1230 cm^{-1} and 1030-1040 cm^{-1} were due to asymmetric and symmetric stretching modes of SO$_2$ group indicating the successful incorporation of SO$_3$H groups into the carbon framework. The presence of a well defined band at 654 cm^{-1} in the spectra of C/TiO$_2$-SO$_3$H is attributed to Ti-O stretching frequency characteristic of TiO$_2$ (ESI **Fig. S1**). The characteristic absorption bands of different composites prepared are presented in **Table 1**.

Table 1. Major absorption frequencies in FTIR (ν_{max} in cm^{-1}) of sulfonated carbon/nano-metal oxide composites

| Entry | Catalyst | Phenolic -OH | C=C | SO$_2$ stretch | | M-O |
				Asym.	Sym.	
1.	C/TiO$_2$-SO$_3$H	3394	1614	1224	1035	654
2.	C/CeO$_2$-SO$_3$H	3161	1587	1211	1037	693
3.	C/ZrO$_2$-SO$_3$H	3240	1620	1230	1030	750

^{a}FTIR was recorded on Perkin-Elmer FTIR spectrophotometer using KBr discs.

The sulfur content of different composites was determined by CHNS analysis and it was found that C/TiO$_2$-SO$_3$H contained 1.2 wt%, C/CeO$_2$-SO$_3$H contained 0.58 wt% and C/ZrO$_2$-SO$_3$H contained 0.89 wt% of sulfur, equivalent to SO$_3$H loading of 0.32, 0.18, 0.28 mmol per g of the catalyst. The acid densities and the amount of C, H and S present in all the three catalysts is presented in **Table 2** as determined by elemental analysis. Among the three solid acids, C/TiO$_2$-SO$_3$H exhibited the highest SO$_3$H density. The most active sulfonated carbon/nano-titania composite (C/TiO$_2$-SO$_3$H) was further characterized by XRD, SEM, TEM, HRTEM, EDX

and TGA. The presence of titania nanoparticles in the sulfonated carbon/nano-titania composites was confirmed by XRD data (ESI **Fig. S2**). The XRD pattern exhibited well defined sharp peaks that can be indexed to the presence of crystalline titania nanoparticles in anatase phase[50]. The diffraction peaks at 25.5^o, 36.3^o, 48.2^o and 54.4^o could be ascribed to characteristic reflections from (101), (004), (200) and (211) planes of tetragonal TiO$_2$ respectively. An additional broad peak between 2θ=20-30° attributed to the presence of amorphous carbon was also observed[51]. The average crystallite size of nano-titania as determined by the Debye Scherrer equation, was found to be 17 nm. The surface morphology of the catalyst was studied using the SEM analysis. The SEM micrographs showed the presence of aggregates of particles with somewhat spherical morphology.

Table 2. Acid densities and amount of C, H and S present in sulfonated carbon/nano-metal oxide composites

Entry	Catalyst	-SO$_3$H (mmol g^{-1})^a	S (wt%)^a	C (wt%)^a	H (wt%)^a
1.	C/TiO$_2$-SO$_3$H	0.32	1.2	19.6	1.5
2.	C/CeO$_2$-SO$_3$H	0.18	0.58	20.1	1.7
3.	C/ZrO$_2$-SO$_3$H	0.28	0.89	18.2	1.2

^{a}Determined by elemental analysis

A marked tendency to form large clusters was observed along with a slight roughening of the catalyst surface depicting the amorphous nature of composite material formed. A typical SEM image of the prepared catalyst is shown in **Fig. 1a and 1b**. The morphology and fine structure of sulfonated carbon/nano-titania composites was examined by TEM **(Fig. 1c and 1d)** and HRTEM analysis **(Fig. 1e and 1f)**. The TEM image of the catalyst exhibited the presence of spherical particles as were observed in SEM micrographs also. The amorphous carbon appears as semitransparent background and the dark spots overlapping it represent the titania nano-paticles, thereby the spherical particles as a whole depict the presence of composites. The TEM image provided the average size of composites as the titania nano-particles are not well resolved in the micrographs. A high resolution TEM image however, provided a clear idea about average particle size of titania nanoparticles. The average size of the composites as determined from TEM was found to be 60-65 nm (ESI, **Fig. S3** for particle size distribution histogram) and those of titania nanoparticles from HRTEM was found to be 25-27 nm (ESI, **Fig. S4** for particle size distribution histogram) which is somehow greater than that obtained from XRD data. It might be due to the agglomeration of one or more crystallites leading to an increase in particle size as determined from HRTEM. The HRTEM image showed clear lattice fringes with interplanar spacing of 3.3 A^o corresponding to the (101) plane of anatase TiO$_2$[50]. The reused catalyst was further

examined after 5th run by TEM analysis and as is clear from the TEM images, there is insignificant change in the structure of the catalyst, thereby showing the stability of the catalyst even after subsequent reaction cycles (ESI, **Fig. S5**). The components of C/TiO$_2$-SO$_3$H were also analysed by using energy dispersive spectroscopy (EDX) which confirmed the presence of Ti in addition to C, O and S in the catalyst (ESI **Fig. S6**). To examine the thermal stability of C/TiO$_2$-SO$_3$H, thermal gravimetric analysis was carried out in the temperature range of 40-700 ^{o}C in a static atmosphere of nitrogen (ESI **Fig. S7**). The TGA analysis of C/TiO$_2$-SO$_3$H showed a weight loss below 100 ^{o}C that was attributable to the loss of adsorbed solvent or trapped water from the catalyst.

of benzamide and 4-methylbenzaldehyde was taken as a model reaction under solvent-free conditions at 100 ^{o}C. It was found that among various composites, sulfonated carbon/nano-titania composites (C/TiO$_2$-SO$_3$H) efficiently catalyzed the synthesis of symmetrical gem-bisamides both in terms of reaction time and yield. The resuls are summarized in **Table 3**. Further, in order to optimize the amount of catalyst, we analyzed the reaction by varying the amount to 0.05 (1.6 mol% SO$_3$H), 0.1 (3.2 mol% SO$_3$H), 0.15 (4.8 mol% SO$_3$H), 0.2 (6.4 mol% SO$_3$H) and 0.3 g (9.6 mol% SO$_3$H) of C/TiO$_2$-SO$_3$H, and the optimum amount of catalyst turns out to be 0.2 g (6.4 mol% SO$_3$H) in order to obtain the best results. To study the solvent effect on the reaction of benzamide and 4-methylbenzaldehyde in presence of C/TiO$_2$-SO$_3$H, we carried
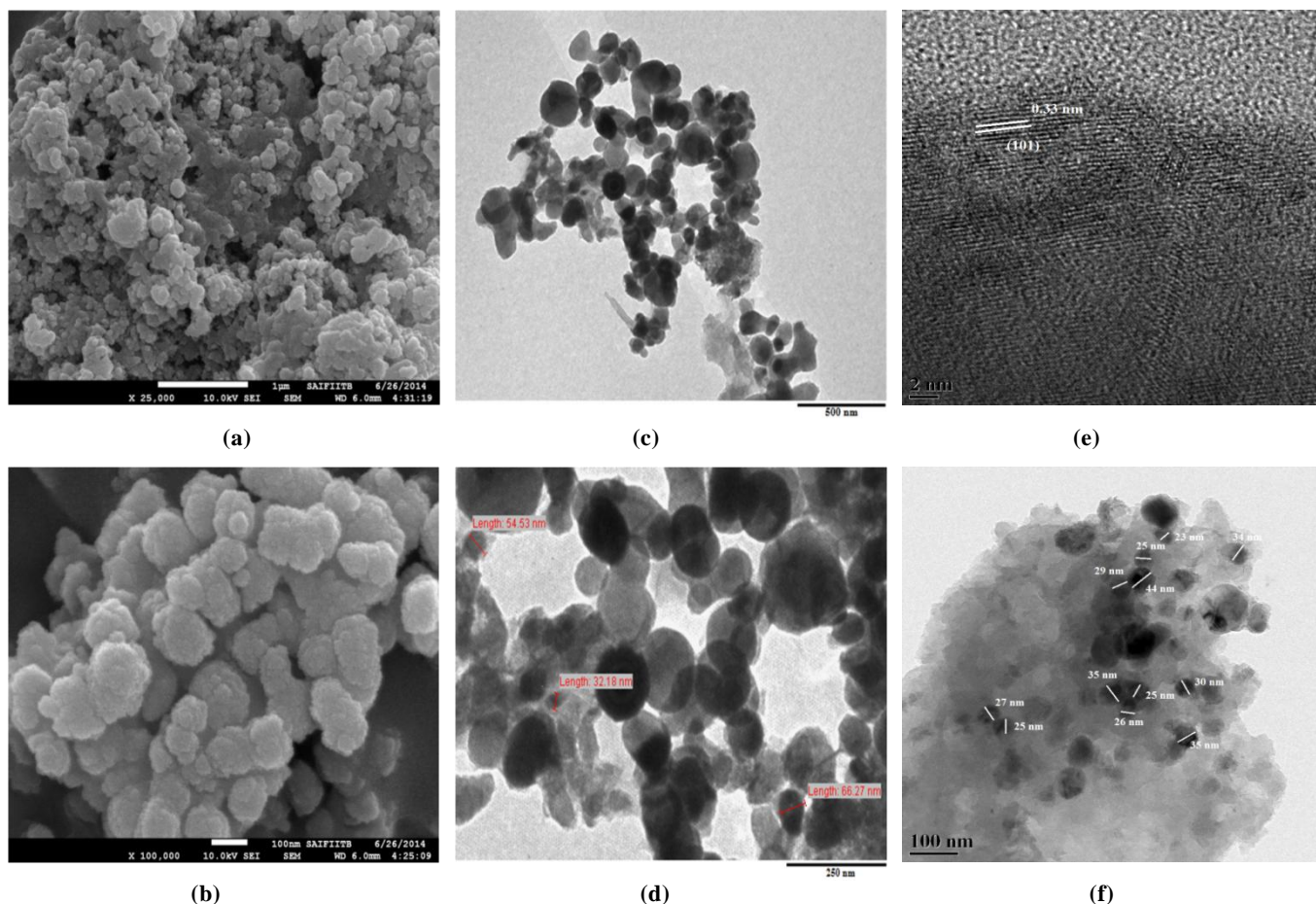
Fig. 1 SEM (**a** and **b**), TEM (**c** and **d**) and HRTEM (e and f) images of sulfonated carbon/nano-titania composite (C/TiO$_2$-SO$_3$H).

Further weight loss from 240-700 ^{o}C was due to the loss of organic functionality. Thus, from the TGA analysis, it can be concluded that the catalyst is stable upto 240 ^{o}C, confirming that it could be safely used in organic reactions below 240 ^{o}C.

Catalytic testing for the one-pot synthesis of symmetrical gem-bisamides

Our initial efforts were focused on finding the most effective catalyst among the various sulfonated carbon/nano-metal oxide composites. In order to screen the catalysts, the reaction

out the reaction in different solvents such as ethanol, acetonitrile, water and toluene. When the reaction was performed in ethanol, acetonitrile and water only trace amount of product formation was observed (**Table 4, entry 1, 2 and 6**), whereas in toluene appreciable amount of product formation take place (**Table 4, entry 7**), but reaction didnot proceed to completion even when run for longer reaction times or with an increased amount of catalyst. Surprisingly, when the reaction was carried out under solvent-free conditions at 100 ^{o}C, both the yield and reaction time were significantly improved.

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Table 3. Comparison of catalytic activities of different sulfonated carbon/nano-metal oxide composites for the one-pot synthesis of symmetrical gem-bisamides, bis(heterocyclyl)methanes and β-aminocarbonyl compounds

Entry	Sulfonated carbon/nano-metal oxide composites[a]	Bisamides[b]		Bis(heterocyclyl)methanes[c]		Mannich[d]	
		Time (h)	Yield[e] (%)	Time (h)	Yield[e] (%)	Time (h)	Yield[e] (%)
1.	C/TiO$_2$-SO$_3$H	2	90	0.5	92	3	94
2.	C/CeO$_2$-SO$_3$H	6	85	0.75	80	7	86
3.	C/ZrO$_2$-SO$_3$H	2	70	0.75	82	5	85

[a]C/TiO$_2$-SO$_3$H: sulfonated carbon/nano-titania composite; C/CeO$_2$-SO$_3$H: sulfonated carbon/nano-ceria composite; C/ZrO$_2$-SO$_3$H: sulfonated carbon/nano-zirconia composite. [b]Reaction conditions: 4-methylbenzaldehyde (1 mmol), benzamide (2 mmol), sulfonated carbon/nano-metal oxide composite (0.2 g) at 100 ^{o}C under solvent-free conditions. [c]Reaction conditions: 4-methylbenzaldehyde (1mmol), dimedone (2 mmol), sulfonated carbon/nano-metal oxide composite (0.2 g) at 100 ^{o}C in water (5 mL). [d]Reaction conditions: 4-bromobenzaldehyde (1 mmol), acetophenone (1 mmol), aniline (1 mmol), sulfonated carbon/nano-metal oxide composite (0.1 g) at 60 ^{o}C in water (5 mL). [e]Isolated yield.

Further increase in reaction temperature had no significant effect on the amount of product formation. Thus, the optimum conditions selected are: benzamide (2 mmol), aldehyde (1 mmol), C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H) under solvent-free conditions at 100 ^{o}C. In order to explore the scope and limitations of this novel catalytic method, we investigated various aromatic aldehydes containing either electron-withdrawing or electron-donating groups under the optimized reaction conditions and excellent results were obtained (**Table 5, products 3a-o**). The reaction is also compatible with various aliphatic aldehydes (**Table 5, products 3n, 3o**).

Catalytic testing for the synthesis of bis(heterocyclyl)methanes

Initial attempts to optimize the reaction conditions for the synthesis of bis(heterocyclyl)methanes was done using dimedone as the C-H activated compound. To select the appropriate carbon/nano-metal oxide composite, 4-methylbenzaldehyde was selected as the test substrate and the reaction was carried out with different sulfonated composites at 100 ^{o}C. It was found that C/TiO$_2$-SO$_3$H again turned out to be the most active catalyst for the synthesis of 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cycloxene-1-one) (**Table 3, entry 1**). Further, 0.2 g (6.4 mol% SO$_3$H) of C/TiO$_2$-SO$_3$H gave the best results in terms of reaction time and yield. The effect of different solvents on the reaction rate was also examined by carrying out the reaction in a variety of protic and aprotic solvents (**Table 4**), and the best results were obtained using water as solvent (**Table 4, entry 6**). Since the reaction in water at 100 ^{o}C was completed in 30 min. in the case of test substrate, so we thought that the reaction may be successful at room temperature. Then the test reaction was also carried out at room temperature, and found that 2,2'-(4-Methylphenylmethylene)bis(3-hydroxy-5,5-dimethyl-2-

cycloxene-1-one) was formed in 70% yield in 6 h (**Table 4, entry 3**). These observations clearly indicate the significant effect of temperature on the reaction time and yield, so the reaction with rest of the substrates was carried out in water at 100 ^{o}C (**Table 6, products 5a-j**).

Ilangovan *et al.* have reported that the reaction of dimedone and aromatic aldehydes leads to the formation of two different products under different set of conditions[52]. The open chain products, 2,2'-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cycloxene-1-ones) were formed when the reaction was carried out in aqueous media, whereas the formation of cyclized products, 1, 8-dioxooctahydroxanthenes took place under solvent-free conditions. To examine the possibility of the cyclized product with our catalytic system, the reaction with test substrate was carried out under solvent-free conditions at 80, 100 and 120 ^{o}C. The formation of open chain product, 2,2'-(4-Methylphenylmethylene)bis(3-hydroxy-5,5-dimethyl-2-cycloxene-1-one) was observed at 80 and 100 ^{o}C (**Table 4, entries 8, 9**), whereas, an increase in the reaction temperature to 120 ^{o}C, led to the formation of cyclized product, 3,3,6,6-tetramethyl-9-(4-tolyl)-1,8-dioxo-octahydroxanthene in excellent yields (**Table 4, entry 10**). Based on these results, it was concluded that C/TiO$_2$-SO$_3$H in water at 100 ^{o}C gave the open chain products, 2,2'-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cycloxene-1-ones), whereas, C/TiO$_2$-SO$_3$H under solvent-free conditions at 120 ^{o}C gave 1,8-dioxooctahydroxanthenes. In order to examine the substrate scope, various aromatic and heteroaromatic aldehydes with different substituents were choosen and excellent results were obtained (**Table 6, products 5a-j, 6a-j**). With these encouraging results, we turn to explore the scope of the reaction using other C–H activated compounds, pyrazolone and indole and the reaction was carried out using aromatic aldehydes in aqueous media at 100 ^{o}C as well as under solvent-free conditions at 120 ^{o}C.

Table 4. Effect of different solvents on C/TiO$_2$-SO$_3$H catalyzed one-pot synthesis of symmetrical gem-bisamides, bis(heterocyclyl) methanes and β-aminocarbonyl compounds

Entry	Solvent	Temperature	Bisamides[a]		Bis(heterocyclyl)methanes[b]		Mannich[c]	
			Time (h)	Yield[e] (%)	Time (h)	Yield[e] (%)	Time (h)	Yield[e](%)
1.	Ethanol	Reflux	6	30[f]	1	80	5.5	90
2.	Acetonitrile	Reflux	6	26[f]	2	72	6	89
3.	Water	Rt	-	-	6	70	-	-
4.	**Water**	**60 °C**	-	-	1.5	82	**3**	**94**
5.	Water	80 °C	-	-	1	85	2.5	92
6.	**Water**	**Reflux**	6	Trace	**0.5**	**92**	2.25	94
7.	Toluene	Reflux	12	60[f]	-	-	-	-
8.	Solvent-free	80 °C	6	76	1.5	87	4.5	85
9.	**Solvent-free**	**100 °C**	**2**	**90**	1	90	4	88
10.	Solvent-free	120 °C	2	91	0.25	94[d]	-	-

[a]Reaction conditions: 4-methylbenzaldehyde (1 mmol), benzamide (2 mmol) and C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H).

[b]Reaction conditions: 4- methylbenzaldehyde (1mmol), dimedone (2 mmol) and C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H).

[c]Reaction conditions: 4-bromobenzaldehyde (1 mmol), acetophenone (1 mmol), aniline (1 mmol) and C/TiO$_2$-SO$_3$H (0.1 g, 3.2 mol% SO$_3$H).

[d]Refers to the yield of 1.8-dioxooctahydroxanthenes.

[e]Isolated yield.

[f]Column chromatographic yield.

In case of both indole and pyrazolone, no cyclized product was formed, and 4,4′-arylmethylene bis(3-methyl-1-phenyl-1H-pyrazol-5-ol) in case of pyrazolone and bis(indolyl)methanes in case of indole were obtained as the sole products. The milder conditions employing water at 100 °C were selected as the optimum reaction conditions. Further, a series of 4,4'-arylmethylene bis(3-methyl-1-phenyl-1H-pyrazol-5-ols) and bis(indolyl)methanes were synthesized in excellent yields using different aromatic aldehydes with electron-donating and electron-withdrawing groups (**Table 6, products 7a-j, 8a-j**).

Catalyst testing for the one-pot three component Mannich reaction

Mannich reaction was carried out by stirring a mixture of aromatic aldehyde, ketone and amine in the presence of sulfonated carbon/nano-metal oxide composites in water.

To select the appropriate sulfonated composite, the reaction of 4-bromobenzaldehyde, acetophenone and aniline was selected as the model reaction. Again C/TiO$_2$-SO$_3$H was found to be the best catalyst for the one-pot three component synthesis of β-amino carbonyl compounds both in terms of reaction time and yield (**Table 3, entry 1**). In order to optimize the amount of C/TiO$_2$-SO$_3$H, we carried out the model reaction with varying amounts 0.05 (1.6 mol% SO$_3$H), 0.1 (3.2 mol% SO$_3$H), 0.15 (4.8 mol% SO$_3$H), 0.2 (6.4 mol% SO$_3$H) and 0.3 g (9.6 mol% SO$_3$H) of C/TiO$_2$-SO$_3$H. The optimum amount of

C/TiO$_2$-SO$_3$H was found to be 0.1 g (3.2 mol% SO$_3$H) in order to obtain the best results. Further, the efficiencies of several organic solvents as reaction media and solvent-free system were investigated for the synthesis of β-aminocarbonyl compounds. Polar solvents such as ethanol and acetonitrile were found to be the better solvents, however, a significant improvement was observed in aqueous media. To optimize the reaction temperature, the Mannich reaction was carried at 60, 80 and 100 °C using water as the reaction medium and found that 60 °C was the optimum reaction temperature (**Table 4, entry 4**). Thus the optimum conditions selected are: aromatic aldehyde (1 mmol), aromatic ketone (1 mmol), aromatic amine (1 mmol), C/TiO$_2$-SO$_3$H (0.1 g, 3.2 mol% SO$_3$H), water (5 mL) and 60 °C as the reaction temperature. To determine the scope of the designed protocol, a number of commercially available aromatic aldehydes, aromatic ketones and aromatic amines were choosen for the one-pot synthesis of β-aminocarbonyl compounds and the results are summarized in **Table 7**. The reaction proceeded smoothly with substrates having either electron-donating or with-drawing groups affording products in good to excellent yields.
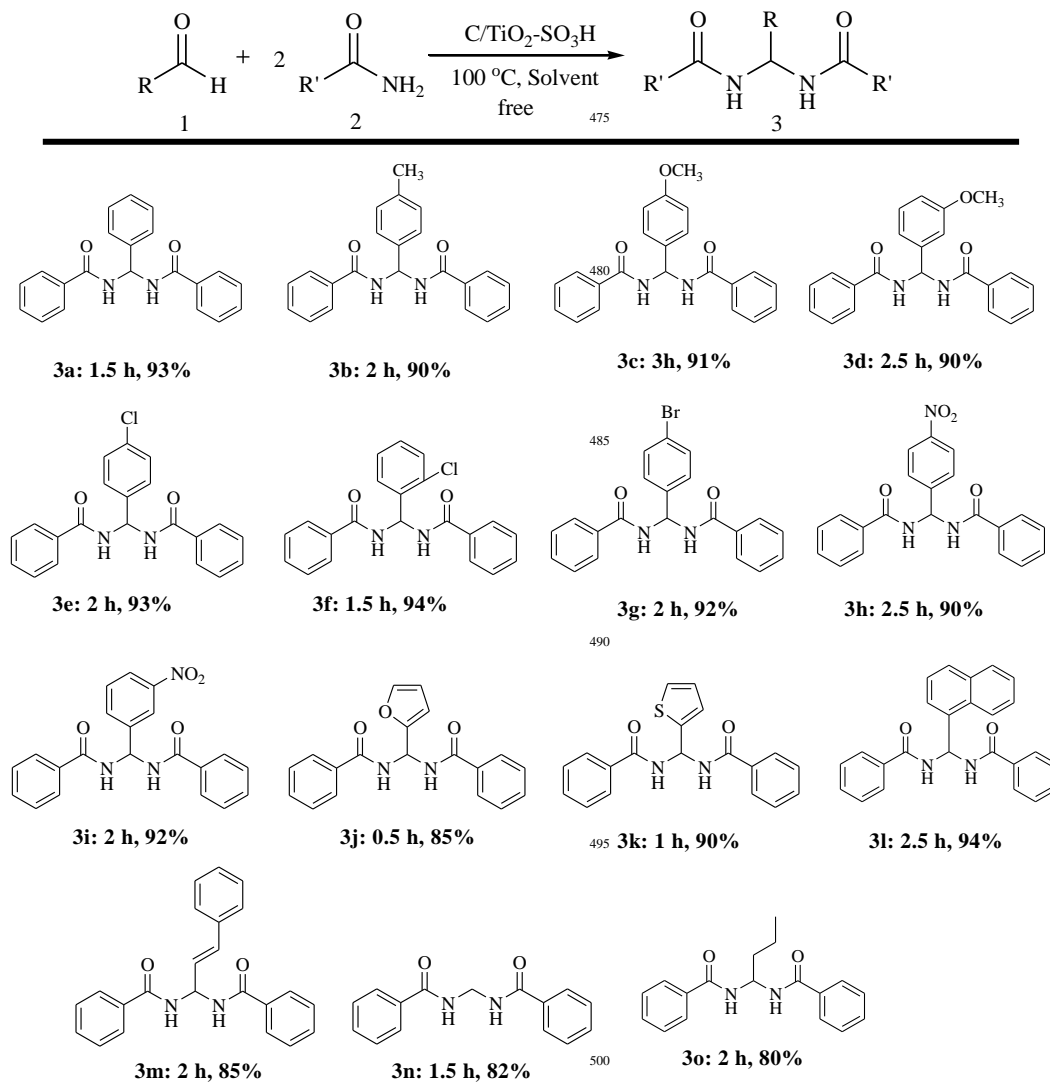
In order to find out the role of C/TiO$_2$-SO$_3$H as heterogeneous catalyst for the one-pot synthesis of gem-bisamides, bis(heterocyclyl)methanes and β-aminocarbonyl compounds *via* Mannich reaction, the test reaction in each case was carried out in the presence of nano-titania, amorphous carbon, non-sulfonated carbon/nano-titania, sulfonated amorphous

carbon, sulfonated carbon/silica composite and without using any catalyst. The results summarized in **Table 8** clearly demonstrate the higher catalytic activity of sulfonated
415 carbon/nano-titania composite in comparison to other solid acid catalysts both in terms of reaction time and product yield. Thus, C/TiO$_2$-SO$_3$H was selected as the heterogeneous catalyst to carry out the desired organic transformation. Further, to study the merits of the current protocol for the
420 synthesis of gem-bisamides, bis(heterocyclyl)methanes and β-aminocarbonyl compounds, a comparison of the efficacy of C/TiO$_2$-SO$_3$H with some of the reported catalytic systems in the literature was done. The results presented in **Table 9** clearly depict the superiority of the present catalytic system in
425 terms of higher value of TOF compared to others reported in literature. In addition, the present method comparatively affords a truly green process using benign reaction media along with higher product yields in shorter reaction time (**Table 9**, bold entries).

Recyclability and Heterogeneity

455 For practical applicability of a heterogeneous catalyst, recyclability is a very important factor. Therefore, we investigated the efficiency of C/TiO$_2$-SO$_3$H in repeated cycles of reaction (**Table 5, 3b, Table 6, 5b, Table 7, 12c).** After completion of the reaction, the catalyst could be easily
460 separated by simple filteration, washed with distilled water, dried and could be reused for subsequent runs. The results shown in **Fig. 2** clearly demonstrate that the catalyst is recyclable upto 5th run without significant loss of activity. Furthermore, the amount of SO$_3$H in the used catalyst after 5th
465 run was determined by elemental analysis, and found that 0.28 mmol g^{-1} of SO$_3$H was still grafted onto the surface of the catalyst compared to 0.32 mmol g^{-1} in fresh catalyst. These results indicate the high stability and activity of the catalyst after subsequent reaction cycles.

Table 5. C/TiO$_2$-SO$_3$H catalyzed one-pot synthesis of symmetrical gem-bisamides^{a,b}

3a: 1.5 h, 93%   3b: 2 h, 90%   3c: 3h, 91%   3d: 2.5 h, 90%

3e: 2 h, 93%   3f: 1.5 h, 94%   3g: 2 h, 92%   3h: 2.5 h, 90%

3i: 2 h, 92%   3j: 0.5 h, 85%   3k: 1 h, 90%   3l: 2.5 h, 94%

3m: 2 h, 85%   3n: 1.5 h, 82%   3o: 2 h, 80%

^{a}Reaction conditions: aldehyde (1 mmol), benzamide (2 mmol), C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H) at 100 ^{o}C under solvent-free conditions.

^{b}Isolated yield.

Table 6. C/TiO$_2$-SO$_3$H catalyzed one-pot synthesis of bis(heterocyclyl)methanes[a,b,c]

5a: 0.25h , 92%   5b: 0.5h, 92%   5c: 3h, 94%   5d: 0.25h, 93%   5e: 0.25 h, 94%

5f: 0.5h, 90%   5g: 3h: 90%   5h: 3h, 91%   5i: 1.5h, 92%   5j: 0.5h, 88%

6a: 0.25h, 94%   6b: 0.5h, 92%   6c: 1.5h, 90%   6d: 1h, 90%   6e: 0.5h, 94%

6f: 1h, 94%   **6g: 2h, 90%**   **6h: 1.5h, 92%**   **6i: 2.5h, 90%**   **6j: 1h, 85%**

7a: 0.5h, 92%   **7b: 0.5h, 94%**   **7c: 0.5h, 92%**   **7d: 1h, 94%**   **7e: 0.5h, 90%**

7f: 0.5h, 94%   **7g: 0.5h, 90%**   **7h: 0.5h, 91%**   **7i: 0.5h, 92%**   **7j: 2h, 90%**

8a: 4h, 90%   **8b: 3.5h, 93%**   **8c: 5h, 94%**   **8d: 4.5h, 92%**   **8e: 4.5h, 94%**

8f: 3h, 92%   **8g: 3h, 94%**   **8h: 3.5h, 92%**   **8i: 5h, 92%**   **8j: 6h, 90%**
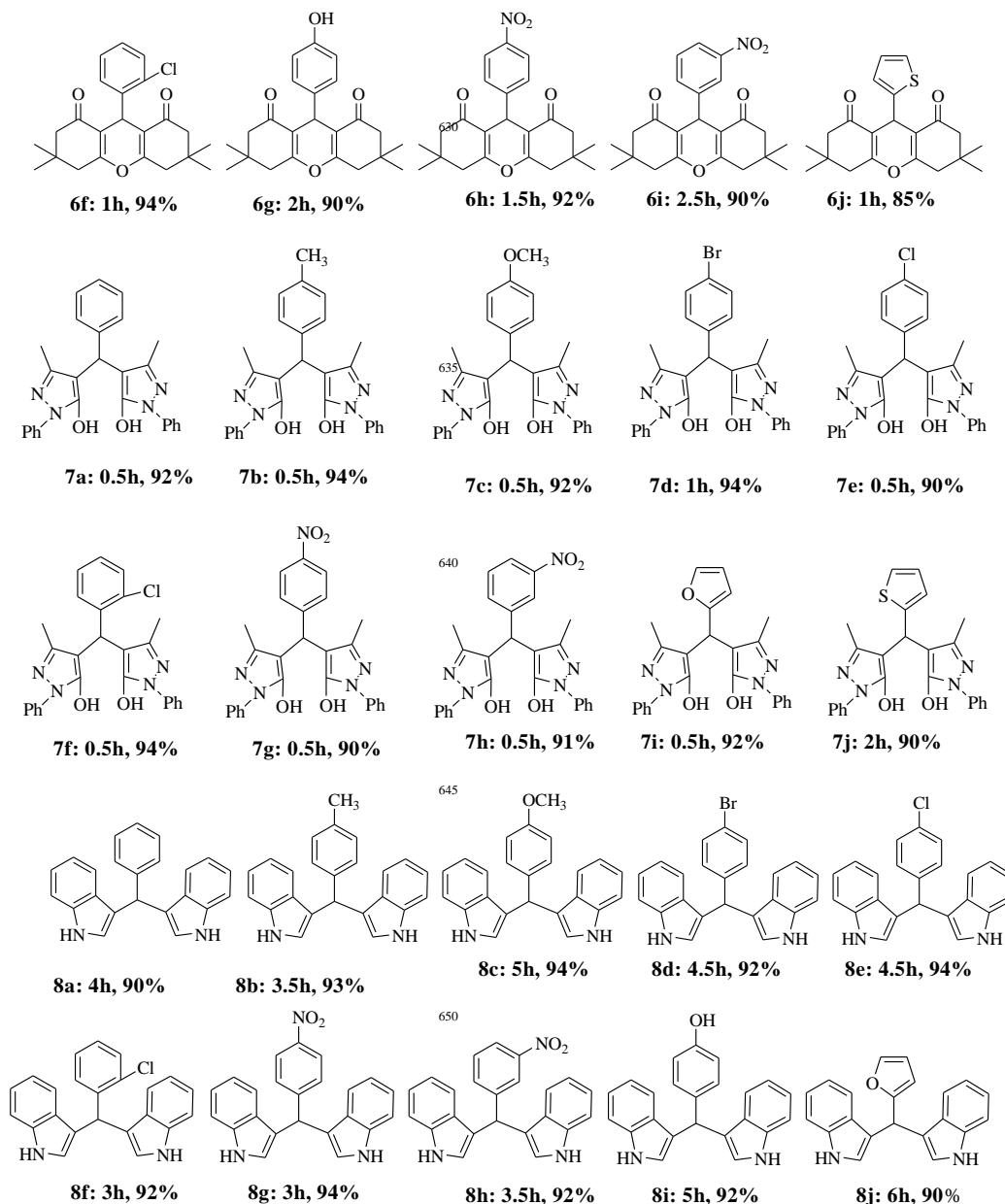
[a]Reaction conditions: aldehyde (1mmol), dimedone or pyrazolone or indole (2 mmol), C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H) at 100 °C in water (5 mL) for products 5a-j, 7a-j, 8a-j. [b]Reaction conditions: aldehyde (1mmol), dimedone (2 mmol), C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H) at 120 °C under solvent-free conditions for products 6a-j. [c]Isolated yield.

The heterogeneity of C/TiO$_2$-SO$_3$H was tested by the hot filtration test to check any possibility of leaching of sulfonic acid groups from the catalyst surface. The reaction in case of **product 12c**, **Table 7** has been carried out in the presence of C/TiO$_2$-SO$_3$H, until the conversion was 40% (1 h) after which the catalyst was filtered off at the reaction temperature. The reaction was then continued further under same set of conditions without the catalyst and found that no significant conversion was observed. Thus, it can be concluded that the catalyst is heterogeneous in nature and no significant leaching of sulfonic acid groups takes place from the catalyst surface.

Conclusion

In conclusion, we have developed a green, sustainable and economic protocol for the one-pot synthesis of symmetrical gem-bisamides, bis(heterocyclyl)methanes and β-amino carbonyl compounds using novel sulfonated carbon/nano-metal oxide composites as solid acid catalyst. The highly active, stable solid acid catalyst was prepared from inexpensive, natural biomaterial starch and commercially available nano-metal oxides. The highlights of the developed protocol are novelity, operational simplicity, environmental friendliness, excellent yields and recyclability.
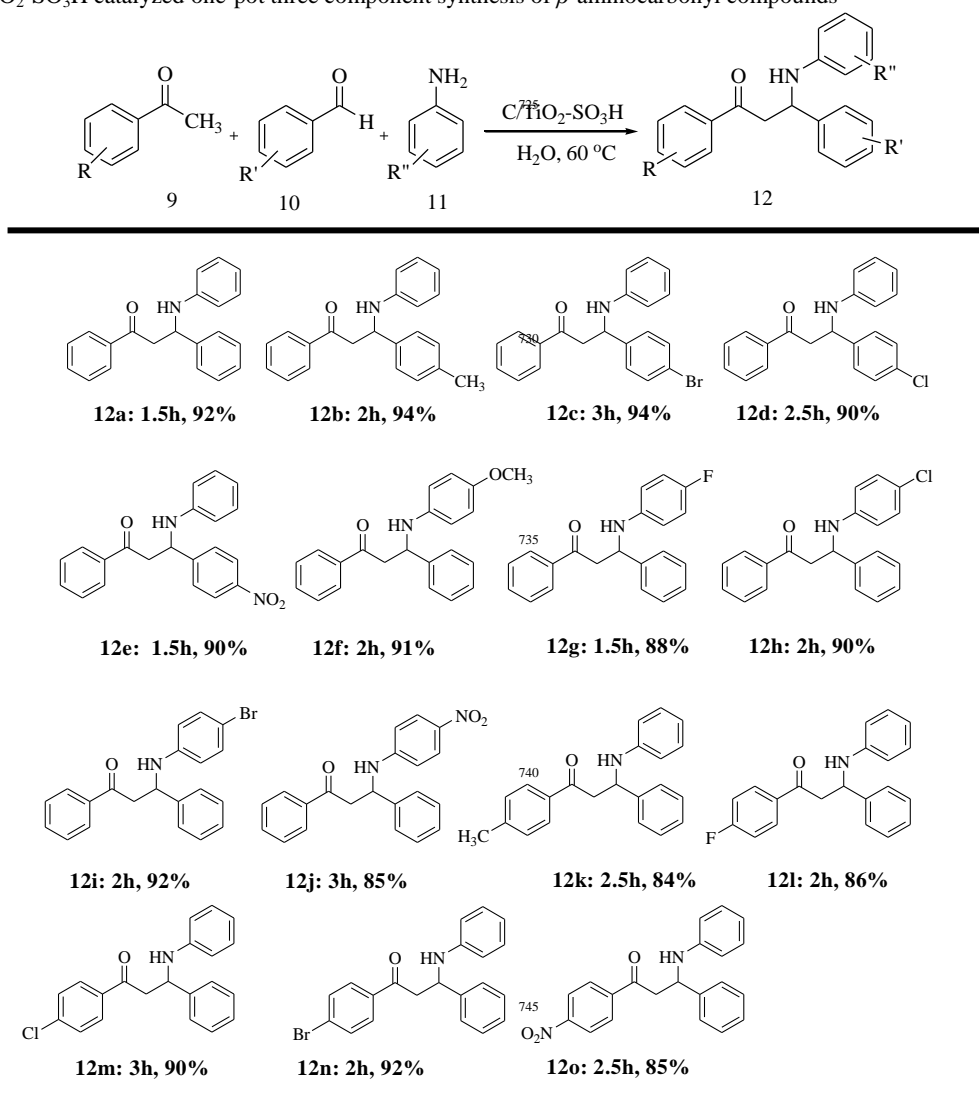
Experimental
General

All starting materials were purchased from commercial sources and used without further purification. The ^{1}H and ^{13}C NMR data were recorded in CDCl$_3$ or DMSO-d_6 or CDCl$_3$+DMSO-d_6 on Bruker Avance III (400 MHz) spectrometer. The FTIR spectra were recorded on Perkin-Elmer FTIR spectrophotometer and mass spectral data on Bruker Esquires 3000 (ESI). CHNS analysis was recorded on ThermoFinnigan FLASH EA 1112 series. SEM images were recorded using FEG SEM JSM-7600F Scanning Electron Microscope, Transmission Electron Micrographs (TEM) were recorded on Philips CM-200. EDX analysis was carried out using OXFORD X-MAX JSM-7600 and TGA was recorded on Perkin Elmer, Diamond TG/DTA. X-ray diffractograms (XRD) was recorded in 2 theta range of 10-80 °C on a Bruker AXSDB X-ray diffractometer using Cu Kα radiations.

General procedure for the synthesis of sulfonated carbon/nano-metal oxide composites

The mixture of starch and nano-metal oxides (10 g) in the ratio of 1: 1.2 taken in a round-bottom flask, was heated at 353 K for 10 h. The mixture was then subjected to incomplete carbonization by heating at 673 K under nitrogen atmosphere for 10 h. The carbonization step leads to the dehydration and dissocation of C-O-C linkages present in the starch, thereby forming amorphous carbon/nano-metal oxide composites. The resulting mixture was then sulfonated by heating in concentrated sulfuric acid (15 mL, >96 wt%) at 423 K for 10 h under N$_2$ atmosphere. The composite material obtained was then washed repeatedly with hot distilled water (>353 K) until sulfate anions were no longer detected in the filtered water. Sulfonated carbon/nano-metal oxide composites were finally dried in an oven at 373 K for 2 h (7 g).

Table 7. C/TiO$_2$-SO$_3$H catalyzed one-pot three component synthesis of β-aminocarbonyl compounds[a,b]

12a: 1.5h, 92%   12b: 2h, 94%   12c: 3h, 94%   12d: 2.5h, 90%

12e: 1.5h, 90%   12f: 2h, 91%   12g: 1.5h, 88%   12h: 2h, 90%

12i: 2h, 92%   12j: 3h, 85%   12k: 2.5h, 84%   12l: 2h, 86%

12m: 3h, 90%   12n: 2h, 92%   12o: 2.5h, 85%

[a]Reaction conditions: Ketone (1mmol), aromatic aldehyde (1 mmol), aromatic amine (1 mmol), C/TiO$_2$-SO$_3$H (0.1 g, 3.2 mol% SO$_3$H) at 60 °C in water. [b]Isolated yield

Table 8. Comparison of activity of C/TiO$_2$-SO$_3$H with nano-titania, amorphous carbon, non-sulfonated carbon/nano-titania, sulfonated amorphous carbon, sulfonated carbon/silica composite for the synthesis of gem-bisamides, bis(heterocyclyl) methanes and β-aminocarbonyl compounds.

Entry	Catalyst	Bisamides[a]		Bis(heterocyclyl) methanes[b]		Mannich[c]	
		Time (h)	Yield (%)	Time (h)	Yield (%)	Time (h)	Yield(%)
1.	No Catalyst	10	NR[f]	5	20[d]	10	10[d]
2.	Nano-Titania	10	18[d]	5	25[d]	10	12[d]
3.	Amorphous Carbon	10	20[d]	5	28[d]	10	15[d]
4.	Non-sulfonated carbon/nano-titania	10	25[d]	5	30[d]	10	20[d]
5.	Sulfonated amorphous carbon	2	45[d]	0.25	65[d]	3	50[d]
6.	Sulfonated carbon/silica composite	2	70[e]	0.25	80[e]	3	78[d]
7.	Sulfonated carbon/nano-titania composite	2	90[e]	0.25	94[e]	3	94[e]

[a]Reaction conditions: 4-methylbenzaldehyde (1 mmol), benzamide (2 mmol), catalyst (0.2 g) at 100 °C under solvent-free conditions. [b]Reaction conditions: 4-methylbenzaldehyde (1mmol), dimedone (2 mmol), catalyst (0.2 g) at 120 °C under solvent-free conditions for the synthesis of 1,8-dioxooctahydroxanthenes. [c]Reaction conditions: 4-bromobenzaldehyde (1 mmol), acetophenone (1 mmol), aniline (1 mmol), catalyst (0.1 g) at 60 °C in water. [d]Column chromatographic yields. [e]Isolated yields. [f]NR: No reaction.

General procedure for the synthesis of symmetrical gem-bisamides (3a-o)

To a mixture of aldehyde (1mmol) and amide (2 mmol) in a round bottom flask (25 mL), C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H) was added and the reaction mixture was heated at 100 °C under solvent-free conditions for an appropriate time. On completion of the reaction (monitored by TLC), hot ethanol (5×10 mL) was added and the catalyst was separated by simple filteration. Removal of the solvent under reduced pressure afforded the product, which was further purified by crystallization from ethanol.

General procedure for the synthesis of bis(heterocylyl)methanes (5a-j, 6a-j, 7a-j, 8a-j)
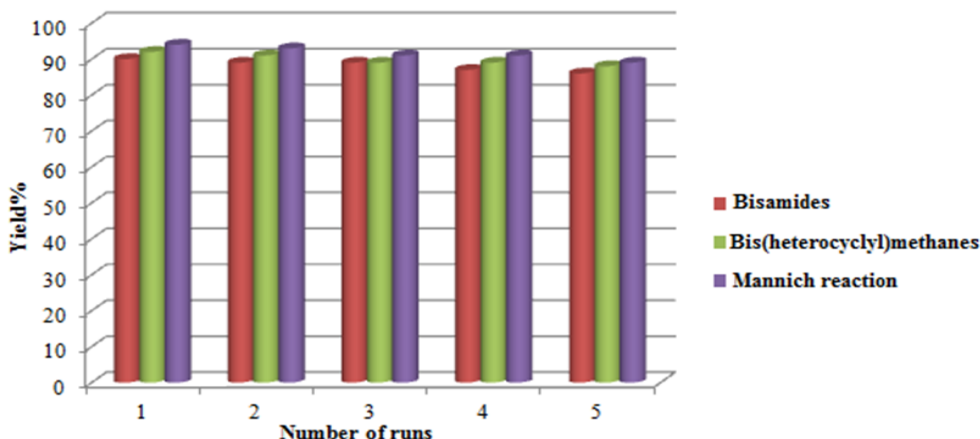
Fig. 2 Recyclability of C/TiO$_2$-SO$_3$H.

Reaction conditions: 4-methylbenzaldehyde (1 mmol), benzamide (2 mmol), C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H) at 100 °C under solvent-free conditions for 2 h [bisamides]; 4-methylbenzaldehyde (1 mmol), dimedone (2 mmol), C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H) at 100 °C in water (5 mL) for 0.5 h [bis(heterocyclyl)methanes]; 4-bromobenzaldehyde (1 mmol), acetophenone (1 mmol), aniline (1 mmol), C/TiO$_2$-SO$_3$H (0.1 g, 3.2 mol% SO$_3$H) at 60 °C in water (5 mL) for 3 h [Mannich reaction].

Table 9. Comparison of the catalytic activity of C/TiO$_2$-SO$_3$H with reported catalytic systems for the one-pot synthesis of symmetrical gem-bisamides, bis(heterocyclyl) methanes and β-aminocarbonyl compounds via Mannich reaction.

Reaction	Catalyst	Reaction Conditions	Yield[d] (%)	Time (h)	TOF[e] (min.$^{-1}$)
Bisamides[a]	Phosphotungstic acid[53]	Toluene, 110 °C, Catalyst (0.3 mmole), 18h	85	18	0.0026
	Boric acid[54]	Toluene, 120 °C, Catalyst (0.3 mmole)	80	60	0.0006
	SBSSANPs[55]	Toluene,120 °C, Catalyst (0.08g)	91	6	0.0263
	Silica sulfuric acid[56]	EtOAc, 90 °C, Silica sulfuric acid (25 mol%)	85	0.58	0.097
	C/TiO$_2$-SO$_3$H[f]	**Solvent-free, 100 °C, C/TiO$_2$-SO$_3$H (0.2g)**	**90**	**2**	**0.117**
Bis(heterocyclyl) methanes[b]	TBAHS[26b]	1,4-dioxane/water, reflux, TBAHS (10 mol%)	91	3.5	0.043
	VSA NRs[57]	Solvent-free, 80 °C, VSA NRs (10 mol%)	90	0.5	0.3
	Silica-bonded N-propyl sulfamic acid[58]	Ethanol, 80 °C, Catalyst (0.03g)	92	4	0.37
	PPA-SiO$_2$[59]	Solvent-free, 140 °C, PPA-SiO$_2$ (10 mol%)	83	0.5	0.27
	C/TiO$_2$-SO$_3$H[f]	**Solvent-free, 120 °C, C/TiO$_2$-SO$_3$H (0.2g)**	**94**	**0.25**	**0.979**
Mannich[c]	SiO$_2$-OAlCl$_2$[37]	Ethanol, rt, SiO$_2$-OAlCl$_2$ (.05g, 20 mol% Al)	91	6	0.012
	CSA[60]	Solvent-free, rt, CSA (5 mol%)	83	8	0.034
	CBSA[5c]	Ethanol, rt, CBSA (0.1 g)	88	7	0.007
	HClO$_4$-SiO$_2$[61]	Ethanol, rt, HClO$_4$-SiO$_2$ (4 mol%)	75	17	0.0183
	C/TiO$_2$-SO$_3$H[f]	**Water, 60 °C, C/TiO$_2$-SO$_3$H (0.1g)**	**94**	**3**	**0.163**

[a]Reaction conditions: 4-methylbenzaldehyde and benzamide; [b]Reaction conditions: 4-methylbenzaldehyde and dimedone for the synthesis of 1,8-dioxooctahydroxanthenes; [c]Reaction conditions: 4-bromobenzaldehyde, acetophenone and aniline; [d]Isolated yield; [e]Turn over frequency; [f]Our work.

To a mixture of aldehyde (1 mmol) and C-H activated compound (dimedone or indole or pyrazolone, 2 mmol) and C/TiO$_2$-SO$_3$H (0.2 g, 6.4 mol% SO$_3$H) in a round bottom flask (25 mL), water (5 mL) was added and the reaction mixture was stirred at 100 °C in case of synthesis of 2,2'-arylmethylenebis(3-hydroxy-5,5-dimethyl-2-cycloxene-1-ones), 4,4'-arylmethylenebis(3-methyl-1-phenyl-1H-pyrazol-5-ols) and bis(indolyl)methanes or 120 °C under solvent-free conditions in case of synthesis of 1,8-dioxo-octahydroxanthenes for an appropriate time. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with hot EtOAc (5×10 mL) and filtered. The organic layer was washed with water and dried over anhyd. Na$_2$SO$_4$. Finally, the product was obtained after removal of the solvent under reduced pressure followed by crystallization with EtOAc: pet ether.

General procedure for the one-pot three component synthesis of β-amino carbonyl compounds via Mannich reaction (12a-o)

To a mixture of aromatic ketone (1 mmol), aromatic aldehyde (1 mmol), aromatic amine (1 mmol) and C/TiO$_2$-SO$_3$H (0.1 g, 3.2 mol% SO$_3$H) in a round-bottom flask (25 mL), water (5 mL) was added and the reaction mixture was stirred at 60 °C for an appropriate time. After completion of the reaction (as monitored by TLC), the reaction mixture was diluted with ethyl acetate (5×10 mL) and filtered. The organic layer was washed with water (100 mL) and dried over anhyd. Na$_2$SO$_4$. Finally, the product was obtained after removal of the solvent under reduced pressure and purified by crystallization with EtOAc: pet ether.

The catalyst was washed with double distilled water followed by CH$_2$Cl$_2$ (3×10 mL). It was dried at 90 °C for 2 h and reused for subsequent reactions. The structures of the products were confirmed by ^{1}H and ^{13}C NMR, mass spectral data and comparison with authentic samples obtained commercially or prepared according to the literature methods.

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