Site-specific role of bifunctional graphitic carbon nitride catalyst for the sustainable synthesis of 3,3-spirocyclic oxindoles in aqueous media†

Anshu Dandia, a,∗ Dinesh Kumar Mahawar, b Pratibha Saini, a Surendra Saini, a Shyam L. Gupta, a,b Kuldeep S. Rathore, c and Vijay Parewa, a,∗a

Functionalized graphitic carbon nitride (Sg-C3N4) has been manufactured and used as a reusable catalyst for the one-pot production of various spiro-pyranochromenes and spiro indole-3,1′-naphthalene tetracyclic systems in aqueous media. An ultrasound-assisted method has been used for the functionalization of g-C3N4. The catalytic functionalities and the structural integrity of the catalyst were characterized via different analytical tools. The catalytic site-specific role of Sg-C3N4 was confirmed via various control experiments in one-pot reaction sequences. We recognized that Sg-C3N4 acts as a bifunctional acid–base catalyst for the first reaction sequence whereas it is an acidic catalyst for the second reaction sequence during the one-pot production of various spiro-pyranochromenes. In addition, the bifunctional acid–base catalytic role of Sg-C3N4 has been confirmed for the first reaction sequence whereas it has a basic catalytic role for the second reaction sequence during the one-pot production of spiro indole-3,1′-naphthalene tetracyclic systems. Diverse C–C, C–O, and C–N bonds, six-membered cycles, stereogenic centers, and spiro frameworks were formed in a single reaction, enhancing the biocidal profile and possibly resulting in the discovery of new medicinal properties. The mild reaction environment, simple workup, easy separation, low cost, heterogeneity, and recyclability of Sg-C3N4 are some rewards of this approach.

1 Introduction

Carbon is one of the most multifaceted elements in the periodic table. Carbon-based substances have achieved insightful consequences in many areas of science and technology because of their noteworthy properties. In previous decades, many scientists worked on developing inventive carbon-based compounds for wide-ranging applications. Carbon materials have a splendid ability to provide at the nano-scale because they have fabulous thermal and electrical conductivity as well as lightness and elevated mechanical strength that traditional bulk substances cannot possess. With the multiplicity of their nanostructures, these distinctive values can be attained over an enormously broad range of environments. Therefore, they are exhaustively investigated for innumerable applications in optoelectronics and photonics, nanomedicine and biotechnology, advanced electrodes and polymer composites. It is the chemical genius of carbon that it can create different nanostructures with entirely different properties. Amongst carbon-based substances, graphitic carbon nitride (g-C3N4), has elicited a huge focus in organic transformation because of its robust nature. g-C3N4 as an abundant and nontoxic substance are potential candidates for a variety of applications in numerous fields. The significance of g-C3N4 as a catalyst or catalytic support has also been extensively recognized for numerous chemical reactions. However, the preparation of bifunctional g-C3N4 with acid and base sites is still a difficult task for the chemist. Enormous efforts have been made to introduce acidic groups into basic g-C3N4. But in these methods the inherent reasonable basic groups of g-C3N4 have been destroyed and the resulting material has very low or even no basicity. Therefore, there is a still a need for a mild and efficient protocol for the concurrent introduction of acid and base sites in g-C3N4 to make it a bifunctional catalyst.

Organic compounds with a spiro heterocyclic moiety are receiving wide scientific interest because of their distinctive conformational and chemical characteristics as well as the biological properties that are often coupled with the asymmetric spiro carbon atom. More specifically, the spiro-oxindole...
A nucleoside is found in a variety of biologically active heterocyclic compounds and natural products and can be of interest in the development of innovative clinically significant heterocyclic motifs. For example, a novel class of marine toxins isolated from dinoflagellates and shellfish, like pteriatoxin and pinna-toxins, shows that a spiro aza system is responsible for the activity. 

**Fig. 1** Examples of spirocyclic oxindoles in natural products and pharmaceutical applications.

**Scheme 1** The synthesis of various spiro-oxindole derivatives.
biological activity. Synthetic derivatives of spiro-oxindole ring systems, for example spirotryprostatin B, elacomine, alstonisine and horsfline, have become imperative synthetic targets as these structural frameworks form the central units of numerous naturally occurring compounds with important biological activities.\textsuperscript{13}

Several spiro-oxindole derivatives show interesting biological activities (Fig. 1): for example, as progesterone receptor modulators,\textsuperscript{14} potent nonpeptide inhibitors of the p53–MDM2 interaction, and antitubercular,\textsuperscript{15} anticancer,\textsuperscript{16} anti-HIV,\textsuperscript{17} and antimalarial\textsuperscript{18} agents. Notably, the spiro-oxindole subunit is also found in spirotryprostatin A and B, which have been recognized as innovative inhibitors of microtubule assembly.\textsuperscript{19}

In addition such spiro-oxindole heterocycles have been reported to be potent therapeutic agents against malaria. Isopteropodine and pteropodine have been found to modulate the utility of muscarinic serotonin receptors.\textsuperscript{20}

As a result of the extensive variety of the biological relevance of a 3,3-spirocyclic oxindole ring system with a quaternary center, enormous endeavors have been made to construct these bioactive spiro-oxindole derivatives by synthetic chemists. Numerous solvents and catalysts have been used to achieve this transformation.\textsuperscript{21} Recently, Shirini \textit{et al.} described the synthesis
of spiro-oxindoles using an Fe$_3$O$_4$/$\text{g-C}_3\text{N}_4$ nanocomposite. Albeit with a subtle boost in reaction conditions, somewhere down the line they still fall short of the required flexibility. During our investigations on the synthesis of spiro derivatives and a detailed literature survey, it was observed that traditional methods suffer from many disadvantages: a multi-step process with a tedious workup procedure, prolonged refluxing in elevated harsh conditions using volatile or corrosive solvents and reagents with strong acidic/basic catalysts which may lead to the formation of the target product in lower yields. Furthermore, indigenous overheating can result in substrate, product or reagent decomposition, with a decrease in the yield of the required product, the formation of a mixture of products and a complicated isolation process with further purification using chromatographic techniques. Furthermore, the major shortcoming of nearly all current methods is that the catalysts are damaged in the workup process and cannot be recovered or recycled, reducing the turn over number (TON) or turn over frequency (TOF). In these environmentally conscious days, for reasons of economy and pollution, environ-economic green chemical procedures have to be developed to eliminate pollution problems, and replacing or reducing corrosive acids or volatile organic solvents in the reaction medium are among the most promising ways to reach these goals. Therefore, in an extension of our attempts towards the enlargement of novel synthetic methodologies for heterocyclic frameworks and nanoparticle synthesis, we have developed a bifunctional g-$\text{C}_3\text{N}_4$ (by the simultaneous incorporation of –SO$_3$H and –NH$_2$ groups) by the reaction of melamine-derived g-$\text{C}_3\text{N}_4$ and aqueous H$_2$SO$_4$ under ultrasound irradiation. The bifunctional g-$\text{C}_3\text{N}_4$ ($\text{Sg-C}_3\text{N}_4$) has been characterized by diverse analytical techniques and used as a metal-free catalyst for the synthesis of various spiro-oxindole derivatives. Due to the admirable assistance between acid and base sites, the catalyst demonstrates a very high reactivity and selectivity for the synthesis of spiro-

2 Results and discussion

To achieve the goal of the convenient synthesis of bifunctional g-$\text{C}_3\text{N}_4$, we have firstly prepared pristine g-$\text{C}_3\text{N}_4$ from the easily available starting material melamine. Bifunctionalization of g-$\text{C}_3\text{N}_4$ has been accomplished by a simple ultrasound-assisted method through the reaction of pristine g-$\text{C}_3\text{N}_4$ and aqueous H$_2$SO$_4$ (30%). The as-prepared nanomaterials were characterized by XRD, SEM, EDAX, XPS and FT-IR analyses.

The crystal or amorphous structures and phase purity levels of the prepared g-$\text{C}_3\text{N}_4$ and Sg-$\text{C}_3\text{N}_4$ catalysts were investigated with X-ray diffraction (XRD) patterns (Fig. 2). There are two sharp diffraction peaks at 12.4° and 27.4°, corresponding to the (100) and (002) reflection of graphitic carbon of synthesized g-$\text{C}_3\text{N}_4$. The diffraction peaks of the XRD pattern of the synthesized Sg-$\text{C}_3\text{N}_4$ catalyst (H$_2$SO$_4$-treated sample) are similar to those of the prepared catalyst g-$\text{C}_3\text{N}_4$. Despite the intensity of the (002) peak of Sg-$\text{C}_3\text{N}_4$ being higher with a minor change in its 2θ value compared to g-$\text{C}_3\text{N}_4$, this result indicates that the graphitic-like structures of the prepared catalyst still remained after the acid treatment. The extra exposed graphitic-like structural units of Sg-$\text{C}_3\text{N}_4$ are responsible for the increase in the intensity.

The micro-structures of g-$\text{C}_3\text{N}_4$, as revealed in the SEM images (Fig. 3) indicate the large aggregation of g-$\text{C}_3\text{N}_4$ units. The SEM image of the acid-treated sample (Sg-$\text{C}_3\text{N}_4$) reveals that there are no aggregations present in this sample because they are shattered into tiny particles with a more exposed and discrete surface, which is favorable for the strong interaction between the substance and the active acidic sites. The ordered
stacking of the CN layers was enhanced after H₂SO₄ treatment because H₂SO₄ treatment could exfoliate the g-C₃N₄ layers and generate more exposed g-C₃N₄ units.²⁴

Elemental analysis of simple graphitic carbon nitride achieved by EDAX analysis verifies the existence of C and N in g-C₃N₄ (Fig. 4 & 5). After acid treatment, the value of the carbon-nitrogen ratio reduces. Additionally, elemental analysis of the acid-treated sample (Sg-C₃N₄) verifies the existence of S, N, and C in the acid-treated sample. This proves that S was incorporated after the acid treatment. Similar results were also found in the elemental analysis (CNOS) of the samples (Table S1†).

![Fig. 6 FT-IR spectra of g-C₃N₄ and Sg-C₃N₄.](image)

![Fig. 7 XPS spectra: (a) the N 1s spectrum of Sg-C₃N₄, (b) the C 1s spectrum of Sg-C₃N₄, (c) the O 1s spectrum of Sg-C₃N₄, and the (d) S 2p spectrum of Sg-C₃N₄.](image)

![Fig. 8 XPS survey scans of g-C₃N₄ and Sg-C₃N₄.](image)
### Table 1  Optimization of the reaction conditions for the production of spiro-pyrano chromen (4a)

| S. No. | Catalyst          | Solvent | Time (min) | Yield\(^b\) (%) | TOF\(^c\) |
|--------|-------------------|---------|------------|------------------|-----------|
| 1      | —                 | H\(_2\)O | 5 h        | 42 n.c.          |           |
| 2      | I\(_2\) (20 wt\%) | H\(_2\)O | 60         | 52               | 0.092     |
| 3      | PTSA (20 wt\%)    | H\(_2\)O | 60         | 59               | 0.105     |
| 4      | MWCNTs (20 wt\%)  | H\(_2\)O | 60         | 28               | 0.050     |
| 5      | Graphite (20 wt\%)| H\(_2\)O | 60         | —                | —         |
| 6      | Activated carbon (20 wt\%) | H\(_2\)O | 60     | 14               | 0.025     |
| 7      | GO (20 wt\%)      | H\(_2\)O | 60         | 43               | 0.076     |
| 8      | rGO (20 wt\%)     | H\(_2\)O | 60         | 20               | 0.035     |
| 9      | g-C\(_3\)N\(_4\) (20 wt\%) | H\(_2\)O | 10     | 34               | 0.363     |
| 10     | Sg-C\(_3\)N\(_4\) (20 wt\%) | H\(_2\)O | 10     | 96               | 1.024     |
| 11     | Sg-C\(_3\)N\(_4\) (10 wt\%) | H\(_2\)O | 20     | 57               | 0.686     |
| 12     | Sg-C\(_3\)N\(_4\) (30 wt\%) | H\(_2\)O | 10     | 96               | 0.598     |
| 13     | Sg-C\(_3\)N\(_4\) (20 wt\%) | CH\(_3\)CN | 30   | 28               | 0.099     |
| 14     | Sg-C\(_3\)N\(_4\) (20 wt\%) | EtOH | 30     | 17               | 0.060     |
| 15     | Sg-C\(_3\)N\(_4\) (20 wt\%) | THF | 30     | 39               | 0.139     |
| 16     | Sg-C\(_3\)N\(_4\) (20 wt\%) | CH\(_2\)Cl\(_2\) | 30 | 36               | 0.128     |

\(^a\) All reactions were performed with isatin (2.0 mmol), malononitrile (2.0 mmol), and 4-hydroxycoumarin (2.0 mmol) under reflux. \(^b\) Isolated yield. \(^c\) TOF (\(\times 10^{-5}\) mol g\(^{-1}\) min\(^{-1}\)). \(^d\) Multi-walled carbon nanotubes.

### Scheme 2  Various control experiments for the synthesis of spiro-pyrano chromen.
FT-IR spectra of the prepared carbon nitride materials g-C₃N₄ and Sg-C₃N₄ are presented in Fig. 6. The sharp band at 808 cm⁻¹ is assigned to the tris-s-triazine layers of the synthesized samples. Broad peaks at around 3040–3380 cm⁻¹ are instigated by the N–H vibration modes for –NH₂ groups. An absorption band at 1635 cm⁻¹ corresponds to the typical stretching modes of CN heterocycles. A range of bands in the region of 1462–1570 cm⁻¹ can be related to the tris-s-triazine of the melamine constituent. A signal at 1407 cm⁻¹ is equivalent to the stretching vibrations of C–N bonds in tertiary N-atoms in the units of the prepared catalyst. Various bands in the range of 1209–1314 cm⁻¹ correspond to sp² hybridized C–(NH) entities. After the acid treatment, a sharp band at 649 cm⁻¹ is attributed to the presence of –SO₃H functionality in the Sg-C₃N₄ catalyst. The appearance of two strong peaks at 1352 and 1148 cm⁻¹ (because of asymmetric and symmetric stretching vibrations) also confirms the occurrence of an –SO₃H group. The broad peaks at around 3000–3400 cm⁻¹ are instigated by free amino and hydroxyl functionalities. These results confirm that acid-treated samples initiate several new functional groups (NH₂ & SO₃H) in the carbon nitride nanosheet.

The occurrence of different surface atoms (chemical environment) and oxidation states in the prepared g-C₃N₄ and Sg-C₃N₄ catalysts were examined using the X-ray photoelectron spectroscopic (XPS) method (Fig. 7, and S3†). The XPS deconvoluted C 1s spectra of the samples show two characteristic peaks with binding energies of 288.2 and 284.4 eV owing to the occurrence of sp²-hybridized C elements in the prepared samples. The three peaks at 397.7, 399.2 and 400.3 eV in the N 1s spectrum of the samples belong to N element (sp²-bonded), tertiary N element and primary N element, respectively. The two peaks in the O 1s spectra of the samples with binding energies of 530.6 eV and 528.7 eV correspond to –OH functional groups. On the other hand, a study of the XPS survey spectrum of g-C₃N₄ with Sg-C₃N₄ reveals that intensity of the C 1s spectrum is reduced while the intensity of the N 1s and O 1s spectra is enhanced. A peak at around 232 eV in both survey spectra may arise due to the Auger spectra of C KLL. The XPS survey spectrum in Fig. 8 demonstrates the occurrence of C, N, O atoms in a simple carbon nitride sample, whereas the XPS spectrum of the Sg-C₃N₄ sample has C, N, S and O species without other impurities. XPS analysis of the elemental S 2p spectrum of Sg-C₃N₄ allocates three peaks with

![Scheme 3](image-url)  
Scheme 3  The probable mechanistic pathway for the production of spiro-pyrano chromens.
binding energies of 164.0 eV (C–S bond), 165.8 eV (N–S bond) and 169.1 eV (N–S bond). Furthermore, the characteristic peak at 169.1 eV is ascribed to the –SO3H group in Sg-C3N4, which further verifies the existence of –SO3H functionalities in the prepared Sg-C3N4 sample. FT-IR and X-ray photoelectron spectroscopy examinations verify the healthy incorporation of SO3H and NH2 functionalities into g-C3N4 after acid treatment.

After the identification of the fundamental nature of the samples, we assessed the catalytic activity of these samples towards the synthesis of spiro-oxindoles. Our preliminary attempts concentrated on optimization of the production of spiro-pyranochromen derivatives. The reaction of isatin 1 (2.0 mmol), malononitrile 2 (2.0 mmol) and 4-hydroxycoumarin 3 (2.0 mmol) was selected as a model reaction. Without any catalyst a lower yield of the product was formed. To enhance the efficacy of the protocol, different metal-free materials were screened as catalysts. As mentioned in Table 1, the most appealing outcome was obtained with Sg-C3N4 as the catalyst in terms of turnover frequency (TOF) compared to other catalysts. It was found that 20 wt% Sg-C3N4 in H2O is enough to drive the reaction forward. Any excess of Sg-C3N4 beyond this amount did not show any further increase in yield. g-C3N did not show any significant impact on the reaction, which demonstrates that acid treatment generated functionality plays a vital role in the reaction.

To confirm which functionality in Sg-C3N4 plays a vital role in the reaction, Sg-C3N4 was employed in basic conditions (refluxed with NaOH and NaCl) to acquire base-treated Sg-C3N4 (BStg-C3N4). The FT-IR intensity of the –SO3H group in BStg-C3N4 was relatively weak because of the deprotonation of the –SO3H group (Fig. S1; see ESI†). The intensity of the FT-IR band due to the sp2-C mode was improved because of the additional room in the π–π* network caused by the dehydration reaction forced by the base. The FT-IR band of –NH2 groups is stable in basic conditions so this intensity remains unchanged. This BStg-C3N4 was further converted into BaSg-C3N4 by acidic treatment with 0.1 M HCl. The FT-IR intensity of the –SO3H group can be restored because of reprotonation of the –SO3H group (Fig. S2; see ESI†). But the intensity of the FT-IR band due to –NH2 groups could not be restored due to the neutralization of basic groups by the acid treatment.

To investigate the mechanism for the catalytic action of the catalyst, some control trials were executed using BStg-C3N4 and BaSg-C3N4 catalysts (Scheme 2). When the model reaction was tried with BStg-C3N4, isatylidene malononitrile (X) was isolated as a major product instead of spiro-pyranochromen. While

Table 2  Synthesis of spiro-pyranochromens

| Entry | Reaction Conditions | Product | Yield (%) |
|-------|---------------------|---------|-----------|
| 1     | Sg-C3N4, H2O, 30 min| 4a       | 96%       |
| 2     | Sg-C3N4, H2O, 30 min| 4b       | 94%       |
| 3     | Sg-C3N4, H2O, 30 min| 4c       | 90%       |
| 4     | Sg-C3N4, H2O, 30 min| 4d       | 95%       |
| 5     | Sg-C3N4, H2O, 30 min| 4e       | 93%       |
| 6     | Sg-C3N4, H2O, 30 min| 4f       | 88%       |
| 7     | Sg-C3N4, H2O, 30 min| 4g       | 92%       |
| 8     | Sg-C3N4, H2O, 30 min| 4h       | 89%       |
| 9     | Sg-C3N4, H2O, 30 min| 4i       | 93%       |
| 10    | Sg-C3N4, H2O, 30 min| 4j       | 95%       |
| 11    | Sg-C3N4, H2O, 30 min| 4k       | 92%       |
| 12    | Sg-C3N4, H2O, 30 min| 4l       | 91%       |

All reactions were performed with substituted isatins (2.0 mmol), malononitrile/ethyl cyanoacetate (2.0 mmol), and 4-hydroxycoumarin (2.0 mmol) using 20 wt% Sg-C3N4 in water and were completed in 30 to 45 min.
BaSg-C$_3$N$_4$ confirmed substantial recovery in catalytic activity for the selective synthesis of spiro-pyrano chromen. However, an excellent yield of spiro-pyrano chromen was observed with Sg-C$_3$N$_4$. No side product was formed under these conditions (Scheme 2a).

To further confirm the site-specific role of this bifunctional catalyst, we carried out the stepwise synthesis of the desired product under control conditions. When the reaction of isatins with malononitrile was run with Sg-C$_3$N$_4$, corresponding Knoevenagel adducts were produced in excellent yield. While moderate yields were observed with BSg-C$_3$N$_4$ and BaSg-C$_3$N$_4$ catalysts (Scheme 2b). This outcome confirms the vital role of the –SO$_3$H group and –NH$_2$ groups for the formation of an Knoevenagel adduct. Moreover, we prepared the Knoevenagel adduct and subjected this adduct with 4-hydroxycoumarin to the control conditions. Sg-C$_3$N$_4$ was found to be the best catalyst for the synthesis of the desired product. BSg-C$_3$N$_4$ gave an inferior yield of the product. Significant improvement in catalytic activity was detected with BaSg-C$_3$N$_4$ (Scheme 2c). These experiments illustrate that –SO$_3$H groups are the sites in Sg-C$_3$N$_4$ responsible for the above transformation.

Thus, these reaction profile indicates that the sites responsible for the Knoevenagel reaction are the –SO$_3$H group and –NH$_2$ groups and a further attack on 4-hydroxycoumarin was facilitated by the –SO$_3$H groups of the Sg-C$_3$N$_4$ catalyst in a one-pot process.

Various solvents (like ethanol, CH$_3$CN, THF, DCM and H$_2$O) were also tested on the model reaction. The outcomes suggested that the solvents had a remarkable impact on the product yield. The best transformation was noticed when the conversion was carried out in water. g-C$_3$N$_4$ treated with 30% aqueous H$_2$SO$_4$ demonstrates the highest yield of the product among the different examined concentrations (10%, 20%, 30% and 40%).

Based on these outcomes, a probable mechanistic pathway for the synthesis of spiro-pyrano chromen is presented in Scheme 3. Firstly, Sg-C$_3$N$_4$ acts as a bifunctional catalyst and activates isatins and malononitrile for the Knoevenagel reaction and produces isatylidene malononitrile (X). Afterwards, the –SO$_3$H group of Sg-C$_3$N$_4$ facilitates Michael addition and forms intermediate Y. Subsequent cyclization of intermediate Y followed by tautomerization produces desired product 3a.

Table 3  Synthesis of spiro indole-3,1′-naphthalene tetracyclic systems

| Reaction | Time (min) | Yield (%) |
|----------|-----------|-----------|
| 6a; 12 min | 95% |
| 6b; 12 min | 94% |
| 6c; 15 min | 92% |
| 6d; 12 min | 93% |
| 6e; 12 min | 92% |
| 6f; 15 min | 91% |
| 6g; 15 min | 89% |
| 6h; 10 min | 92% |
| 6i; 12 min | 93% |
| 6j; 15 min | 92% |
| 6k; 10 min | 91% |

* All reactions were performed with substituted isatins (2.0 mmol), malononitrile (4.0 mmol), and cyclic ketones (2.0 mmol) using 20 wt% Sg-C$_3$N$_4$ in water and were completed in 30 to 45 min.
To demonstrate the scope and versatility of this methodology under identical reaction conditions, a library of substituted medicinally relevant spiro-pyrano chromens was produced (Table 2). Isatins with different electron donating and withdrawing groups on the aromatic ring do not influence the reaction profile that much and give the desired product in excellent yield. N-substituted isatins also tolerate the reaction conditions and produce the desired product in good to excellent yield. The same one-pot method also proceeded efficiently with ethyl cyanoacetate in place of malononitrile. No noteworthy deviation in yields of the products was detected in the case of ethyl cyanoacetate. The conversion completes well and the desired compounds are isolated in good yields.

Encouraged by these results, we broadened the scope of the above approach for the production of other types of pharmaceutically imperative spiro indole-3,1'-naphthalene tetracyclic systems. According to the literature, synthesis of these compounds requires the previous production of Knoevenagel adducts, which involves two extra steps in the synthesis of target compounds. We have also done some control experiments to confirm which catalytic site in Sg-C3N4 was responsible for the above conversion (Scheme 4). To accomplish the appropriate conditions to afford the spiro indole-3,1'-naphthalene tetracyclic system, a modal reaction was performed between isatin, malononitrile and cyclohexanone under control conditions using, Sg-C3N4, Bsg-C3N4 and BaSg-C3N4 catalysts (Scheme 4a). An admirable yield of the product was viewed with Sg-C3N4. No side product was produced under these conditions. Selective synthesis of a spiro indole-3,1'-naphthalene tetracyclic system was also observed with Bsg-C3N4, but the yield of the product was lower compared to Sg-C3N4. While with BaSg-C3N4, Knoevenagel adducts were formed instead of a spiro indole-3,1'-naphthalene tetracyclic system. We have already established the bifunctional role of Sg-C3N4 for the synthesis of isatylidene malononitrile (Scheme 2b). Analogous results were found for the formation of cyclohexanone malononitrile (Scheme 4b). Moreover, we also carried out the reaction of isatylidene malononitrile and cyclohexanone malononitrile with Sg-C3N4, Bsg-
C$_3$N$_4$ and BaSg-C$_3$N$_4$ catalysts (Scheme 4c). Sg-C$_3$N$_4$ produced the desired product in excellent yield. BSg-C$_3$N$_4$ also acts as an active catalyst for the above transformation, but the yield of the product was lower compared to Sg-C$_3$N$_4$. A substantial loss in catalytic activity was observed when the reaction was tried with BaSg-C$_3$N$_4$. The desired product was not formed and the reactants remained unchanged under these conditions.

Hence, these results illustrate that the sites responsible for the Knoevenagel reaction are the $\text{–SO}_3\text{H}$ group and $\text{–NH}_2$ groups, and furthermore the reaction of isatylidene malononitrile and cyclohexanone malononitrile was encouraged by the $\text{–NH}_2$ groups of the Sg-C$_3$N$_4$ catalyst in a one-pot process.

Based on these outcomes, a probable mechanistic pathway for the production of a spiro indole-3,1'-naphthalene tetracyclic system is presented in Scheme 5. The $\text{–SO}_3\text{H}$ group and $\text{–NH}_2$ groups of Sg-C$_3$N$_4$ facilitate the Knoevenagel reaction and produce isatylidene malononitrile (X) and cyclohexanone malononitrile (A). The $\text{–NH}_2$ group of Sg-C$_3$N$_4$ activates the cyclohexanone malononitrile and forms anion B, which attacks the activated double bond of X with further cyclization into anion C. Subsequent intramolecular nucleophilic addition on the CN group forms an imine D. Isomerization of imine D yields the corresponding product 6.

**Scheme 5** A probable mechanistic pathway for the synthesis of a spiro indole-3,1'-naphthalene tetracyclic system.

**Table 4** Recyclability experiments with Sg-C$_3$N$_4$ for various spiro-oxindole derivatives

| Cycle | Yield | Cycle | Yield |
|-------|-------|-------|-------|
| 1     | 96%   | 1     | 95%   |
| 2     | 96%   | 2     | 95%   |
| 3     | 96%   | 3     | 95%   |
| 4     | 96%   | 4     | 95%   |
| 5     | 95%   | 5     | 93%   |
| 6     | 95%   | 6     | 93%   |
The high recyclability and the heterogeneous nature of the used Sg-C₃N₄ catalyst were also established (see ESI†). The results show that the Sg-C₃N₄ sheets are heterogenous in nature and can be successfully reused for six cycles (Table 4).

XRD, SEM and FT-IR of the reused catalyst confirmed the analogous characteristic nature of the catalyst compared to fresh catalyst. These outcomes suggest that the morphology and structure of Sg-C₃N₄ sheets remain unchanged during the reaction.

3 Experimental section

A general part including instruments used is provided in the ESI.†

3.1. Synthesis of g-C₃N₄

Melamine (5 g) was heated at 550 °C (at a rate of 4 °C min⁻¹) using a closed crucible with a lid in a muffle furnace for 3 h. After that, the obtained material was ground into a fine powder using a mortar and pestle and referred to as g-C₃N₄.

3.2. Synthesis of Sg-C₃N₄

The as prepared g-C₃N₄ and 30% aqueous H₂SO₄ were placed in flask. And then it was fixed to a 12 mm tip diameter probe and the solution was sonicated at 50% power of the processor and 230 W output in a 4 s pulse mode for 4 h. The resulting mixture was poured into ice-cold water and centrifuged (12 000 rpm for 10 min twice). The obtained solid material was dried under vacuum for 24 h and referred to as Sg-C₃N₄.

3.3. Synthesis of spiro-pyrano chromene derivatives

A mixture of isatins (2.0 mmol), ethyl cyanoacetate/ malononitrile (2.0 mmol), and 4-hydroxycoumarin (2.0 mmol) with 20 wt% Sg-C₃N₄ in 20 ml of water were mixed. The solution was heated under reflux conditions for an appropriate time. The progress of the conversion was monitored with TLC. After completion of the conversion the Sg-C₃N₄ and solid product were filtered from the solution. The precipitate was dissolved in ethyl acetate and the catalyst was recovered by centrifugation (12 000 rpm). The above residual solution was removed under reduced pressure. The final (crude) product was subjected to purification by recrystallization using ethanol.

4 Conclusions

In summary, a functionalized graphitic carbon nitride (Sg-C₃N₄) catalyst was prepared using an ultrasound-assisted technique and it was employed for the one-pot production of various spiro-pyranochromene and a spiro indole-3,1'-naphthalene tetracyclic system in aqueous media. Characterizations using different analytical tools showed that bifunctional acidic (-SO₃H) and basic (-NH₂) sites were created after functionalization. Additionally, the bifunctional nature ( acidity/basicity) of the used catalyst Sg-C₃N₄ was confirmed via numerous control tests in one-pot reaction sequences. The uniqueness of this study is the simultaneous activation of the first reaction sequence by the synergistic participation of the bifunctional acidic and basic sites present in Sg-C₃N₄. The acidic sites present in Sg-C₃N₄ activated the second reaction sequence for the one-pot production of various spiro-pyranochromenes, whereas the basic sites present in Sg-C₃N₄ activated the second reaction sequence for the one-pot production of a spiro indole-3,1'-naphthalene tetracyclic system. Sg-C₃N₄ showed no loss in activity or catalytic functionality over several runs. Diverse C-C, C-O, and C-N bonds, six-membered cycles, stereogenic centers, and spiro frameworks were designed in a single reaction.

Conflicts of interest

There are no conflicts to declare.

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