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Sulfonic acid-functionalized magnetic carbon nitride as highly efficient ionic composite for sustainable assembly of 1,2,3-triazoles

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Abstract

An efficient and straightforward method for constructing of biologically active 4-aryl-NH-1,2,3-triazoles by the 1,3-dipolar cycloaddition reaction of β -nitrostyrene and sodium azide in the presence of acidic graphitic carbon nitride (Fe₃O₄@g-C₃N₄–SO₃H) ionic nanocomposite has developed. Using a magnetically recoverable acidic ionic catalyst allows eco-friendly and facile conversion and simplifies experimental setup and work-up procedure that enables the direct synthesis of triazole derivatives under mild conditions. The designed catalytic system provides a broader scope under short reaction times in good to excellent yields. Fe₃O₄@g-C₃N₄–SO₃H could be simply recovered by magnetic separation using an external magnet, maintaining stable activity up to five cycles without appreciable loss of activity.

Graphic abstract



Keywords $Fe_3O_4@g-C_3N_4-SO_3H \cdot Cycloaddition reaction \cdot Green chemistry \cdot Magnetically recoverable catalyst \cdot \beta-nitrostyrene \cdot 1,2,3-triazoles$

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Introduction

Privileged nitrogen-containing rings, 1,2,3-triazoles, and their derivatives are a remarkable group of active heterocyclic compounds and have a massive significance in biology, medicine, nanotechnology, catalysis, and corrosion inhibitors [1, 2]. The 1,2,3-triazole core has engaged a unique place in material science as versatile ligands in the optical materials as well as light stabilizers and optical brightening agents [3]. Many of the approved nitrogen-rich five-membered drugs such as celecoxib, pyrazofurin, HIV protease inhibitors have a triazole moiety [4]. Furthermore, conjugation of fluorophores such as coumarin and its derivatives with sugar scaffold provided as a fluorescent triazole extensively used in analytical chemistry as chemosensors, biosensing, bio labeling, and bioimaging (Fig. 1) [5]. The widespread applications of triazole derivatives have led to the extension of numerous procedures for their synthesis, involving the cyclization of triazenes, Wolff's cyclo condensation of α -diazo ketones, and α -diazoamides. [6–8] Thermal 1,3-dipolar cycloaddition (Huisgen cycloaddition) between an organic azide and alkyne was the classical procedure for 1,2,3-triazole synthesis [9]. Click chemistry is a newer and greener approach to the synthesis 1,2,3-triazole by the Cu catalyzed cycloaddition of azide and alkyne or organocatalytic cycloaddition reactions of azides with enolizable groups due to its simple work-up, purification steps, and good to excellent yields [10–23].

Graphene-based nanocomposite, one of the thinnest materials in the universe, has inspired huge interest in biosensors, energy storage devices, materials science, condensed matter physics, and biology [24, 25]. Due to its exceptional properties, such as excellent mechanical, electrical, and thermal properties, graphene research has reached an unexpectedly great height and has emerged as a champion in composite materials [26–28]. Various synthesis routes have recently been devised for producing different polymer and metalbased nanocomposite and fabricating hybrid nanocomposite to address the needs of the composite industry [29].

Graphitic carbon nitride $(g-C_3N_4)$ is the new type of sheet-like polymeric carbon-based material with broad interdisciplinary attention. [30–32] It can be fabricated from direct thermal condensation of economic nitrogen-rich compounds such as urea, cyanamide, and melamine. [33–35] As an analog of graphene, it has to contain two-dimensional frameworks of tri-s-triazine connected via a nitrogen atom. Along with high physicochemical stability, this unique structure has been the hotspot in the various research fields in recent years. [36–38] However, g-C₃N₄ suffers from several drawbacks, such as a small specific surface area and low catalytic activity, limiting its practical application. As a result, modification of its texture and surface functionalization is required to improve its properties.

Experimental section

General

All substances and solvents are commercially accessible and were obtained from commercial sources and used as received. Melting points were recorded on a Buchi R-535 apparatus.

Fabrication of Fe₃O₄@g-C₃N₄-SO₃H nanocomposite

The $Fe_3O_4@g-C_3N_4$ -SO₃H catalyst was prepared according to our previous paper (Scheme 1) and used directly after characterizations. [39].

The g-C₃N₄ nanosheet was constructed by a simple hydrothermal method. Melamine (10.0 g) loaded in an alumina crucible with a cover and heated to 550 °C for 4 h with a ramp rate of 5 °C/min and then cooled to room temperature. The obtained light yellow product was collected and ground well into a powder. g-C₃N₄ nanosheets obtained by thermal oxidation of bulk $g-C_3N_4$ in the semiclosed system. 2.0 g bulk g- C_3N_4 powders were transferred into a 70 mL crucible with a cover and were sustained for 2 h at 500 °C to obtain a g-C₃N₄ nanosheet. The Fe₃O₄@g-C₃N₄ prepared by a onestep solvent, thermal method, and the schematic exhibited in Scheme 1. g- C_3N_4 nanosheets (1.0 g) dispersed in water (100 mL) using ultrasonic for 2 h to form a uniform suspension. Then, FeCl₃.6H₂O (2.0 g in 15 mL water), FeCl₂.4H₂O (0.8 g in 10 mL water), and 8 mL of ammonia (32% aqueous solution) were added, and the mixture was stirred at 80 °C for 30 min. After that, the resulting suspension heated for another 30 min at 90 °C to provide the Fe₃O₄@g-C₃N₄ nanocomposite after washing with deionized water and absolute alcohol and drying in a vacuum oven at 60 °C. Sulfonation of Fe₃O₄@g-C₃N₄ also performed using our reported procedure. [33] Briefly, $Fe_3O_4@g-C_3N_4$ (1.0 g) was taken in a round-bottomed flask equipped with a constant pressure



Scheme 1 Preparation of Fe₃O₄@g-C₃N₄-SO₃H nanocomposite

dropping funnel and a gas inlet tube for passing HCl gas and dried dichloromethane (100 mL) added to it. Next, chlorosulfonic acid (1.2 mL) was added dropwise to the above suspension for 40 min and further stirred for 12 h at room temperature. Subsequently, $Fe_3O_4@g-C_3N_4-SO_3H$ nanocomposite was collected using an external magnet, washed with dichloromethane, water and ethanol, and dried at 60 °C in a vacuum oven for 8 h.

General procedure for synthesizing 4-aryl-NH-1,2,3-triazoles

In a 5 mL round-bottomed flask equipped with a magnetic stirrer, a solution of the respective β -nitrostyrene derivatives (0.5 mmol), NaN₃ (0.8 mmol), DMF (4 mL), and $Fe_3O_4@g-C_3N_4-SO_3H$ (20 mg) was added. The resulting mixture was stirred vigorously at 70°C for 60-240 min. After completion of the reaction as monitored by TLC, the mixture was allowed to cool down to room temperature. Next, water (10 mL) was added under vigorous stirring. The nanocomposite was removed by an external magnetic and washed with 5 M HCl and ethyl acetate, and reused for the next reactions. The resulting crude products were washed with 5 M sodium hydroxide solution and recrystallized from ethanol or ethyl acetate to give the corresponding pure 1,2,3-triazoles as identified by melting points. In the cases of the crude oil products, ethyl acetate (2×10 mL) was added, and the contents were transferred to a separating funnel. The combined organic layers were washed with water, dried over Na₂SO₄, and filtered. The solvent's evaporation gave the crude product, which was purified by silica gel column chromatography (ethyl acetate: petroleum ether) to obtain the desired products.

Selected data

Table 1, entry 1: ¹H NMR (DMSO-*d6*, 500 MHz): δ = 7.34 (s, 1H, triazole ring), 7.47-8.01 (m, 5H, ArH), 9.87 (s, 1H, NH, triazole ring). ¹³C NMR (125.7 MHz, DMSO-*d6*): δ = 125.1, 128.2, 128. 9, 129.8, 131.1, 161.9.

Table 1, entry 2: ¹H NMR (DMSO-*d6*, 500 MHz): $\delta = 3.94$ (s, 3H, OMe), 3.97 (s, 3H, OMe), 7.01 (d, J=7.8 Hz, 1H, ArH), 7.41–7.44 (m, 2H, ArH), 8.61 (br. s, 1H, triazole ring). ¹³C NMR (125.7 MHz, DMSO-*d6*): $\delta = 56.8$, 57.9, 108.9, 111.9, 119.1, 129.2, 136.4, 149.3, 149.7, 150.7

Table 1, entry 3: ¹H NMR (DMSO-*d6*, 500 MHz): $\delta = 7.34-7.36$ (m, 1H, ArH), 7.49 (s, 1H, ArH), 7.58-7.92 (m, 3H, ArH), 8.69 (br s, 1H, triazole ring), 9.25 (br s, 1H, triazole ring). ¹³C NMR (125.7 MHz, DMSO-*d*6): $\delta = 119.1$, 126.2, 127.9, 129.2, 129.8, 131.0, 142.8.

Table 1, entry 4: ¹H NMR (DMSO-*d6*, 500 MHz): δ =7.55 (d, *J*=7.2 Hz, 2H, ArH), 7.88 (d, *J*=7.3 Hz, 2H,

ArH), 8.24 (br s, 1H, triazole ring), 13.12 (br s, 1H, NH). ¹³C NMR (125.7 MHz, DMSO-*d*6): δ = 128.4, 128.9, 129.3, 129.8, 130.1, 135.2.

Table 1, entry 6: ¹H NMR (DMSO-*d6*, 500 MHz): δ =7.35-7.37 (m, 1H, ArH), 7.49 (t, *J*=7.2 Hz, 1H, ArH), 7.76-7.59 (m, 2H, ArH), 8.40 (br s, 1H, triazole ring), 12.18 (br s, 1H, NH). ¹³C NMR (125.7 MHz, DMSO-*d6*): δ =119.7, 126.1, 128.3, 129.5, 129.9, 131.6, 144.1.

Table 1, entry 7: ¹H NMR (DMSO-*d6*, 500 MHz): δ =7.36 (s, 1H, ArH), 7.68 (d, *J*=7.1 Hz, 1H, ArH), 7.79 (d, *J*=7.1 Hz, 1H, ArH), 8.12 (br s, 1H, triazole ring), 14.12 (br s, 1H, NH). ¹³C NMR (125.7 MHz, DMSO-*d6*): δ =121.7, 126.8, 128.9, 129.9, 130.3, 134.6, 140.2.

Table 1, entry 11: ¹H NMR (DMSO-*d6*, 500 MHz): $\delta = 2.27$ (s, 3H, Me), 7.25 (d, J = 5.8 Hz, 2H, ArH), 7.78 (d, J = 5.7 Hz, 2H, ArH), 8.12 (s, 1H, triazole ring) 14.26 (br s, 1H, NH).. ¹³C NMR (125.7 MHz, DMSO-*d6*): $\delta = 24.2$, 126.7, 130.4, 130.9, 138.6.

Table 1, entry 13: ¹H NMR (DMSO-*d6*, 500 MHz): δ = 7.49 (d, *J* = 7.2 Hz, 2H, ArH), 7.90 (d, *J* = 7.4 Hz, 2H, ArH), 8.24 (br s, 1H, triazole ring), 12.15 (br s, 1H, NH). ¹³C NMR (125.7 MHz, DMSO-*d6*): δ = 125.3, 127.2, 128.6, 129.8, 130.2, 134.6.

Table 1, entry 15: ¹H NMR (DMSO-*d6*, 500 MHz): $\delta = 6.47$ -7.42 (m, 3H), 7.92 (s, 1H, triazole ring). ¹³C NMR (125.7 MHz, DMSO-*d6*): $\delta = 108.6$, 112.3, 129.5, 140.3, 143.7, 147.1.

Results and discussion

In a continuation of our interest toward the synthetic applications of graphitic carbon nitride as a highly active catalyst in organic synthesis, [40-42] we wish to report herein an acidic graphitic carbon nitride (Fe₃O₄@g-C₃N₄-SO₃H) as a magnetic catalyst for the assembly of 1,2,3-triazoles from the reaction between β -nitrostyrene derivatives and sodium azide under mild conditions. We investigated our study by optimizing the reaction conditions using β -nitrostyrene (1a) and sodium azide as model substrates. Initial testing of β -nitrostyrene (1a) (0.5 mmol) with sodium azide (0.8 mmol) with Fe₃O₄@g-C₃N₄-SO₃H (20 mg) as a catalyst in the water at room temperature was not good and provided low yields of the desired triazoles (2a). Various solvents were examined in the model reaction (Table 1, entries 2-14), and the solvent plays a significant role in this cycloaddition reaction. The result of 1a with NaN₃ in different solvents (water, methanol, ethanol, THF, toluene, CHCl₃, and CH₂CN) failed to produce the desired products in longer reaction times. The reaction proceeds quickly in DMF with a catalytic amount of Fe₃O₄@g-C₃N₄-SO₃H (20 mg) to afford 1,2,3-triazole 2a in both good isolated yields and purity. We then investigated the effect of reaction temperature and the



Anti cancer agent

Fig. 1 Triazole-based drugs



Fig. 2 Reusability experiments of magnetic nanocatalyst

amount of catalyst and DMF under various conditions. The best result was obtained at 70 °C with 20 mg of catalyst in 4 mL of DMF (Table 1, entry 6). The reaction underwent completion in 60 min to obtain 1,2,3-triazoles in 97% yields with simple work-up. Furthermore, a comparative findings of catalysts efficiency of different elements of the composite such as Fe₃O₄, g-C₃N₄, Fe₃O₄@g-C₃N₄, g-C₃N₄–SO₃H, Fe₃O₄@SO₃H (Table 1, entries 15-19) are outlined in Table 1 which indicated that Fe₃O₄@g-C₃N₄–SO₃H nanocomposite superior to all elements of the composite due to self ionic properties and high surface area of the catalyst.

Following these optimized procedures, the scope and limitations of the reaction were examined with β -nitrostyrene derivatives (Table 2). As will be readily seen from Table 2, this reaction is tolerant of a wide range of functional groups and demonstrated to be a straightforward system for the preparation of

Tak	ol	e	1	Solvent	screening	for	the	mode	l reaction
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	1a Solvent (mL)	+ NaN ₃ $\xrightarrow{Fe_3O_4@g-C_3N_4-SO_3H}$ Temp. Time, Solvents		N=N N⊨N NH	
				2a	
Entry		Catalyst (mg)	Temp.	Time (min)	Yields (%) ^a
1	DMF (1 mL)	20	rt	600	40
2	DMF (2 mL)	20	rt	600	58
3	DMF (3 mL)	20	rt	600	64
4	DMF (4 mL)	20	rt	600	68
5	DMF (4 mL)	20	50	600	74
6	DMF (4 mL)	20	70	60	97
7	DMF (4 mL)	20	100	60	97
8	CHCl ₃ (4 mL)	20	70	60	45
9	Toluene (4 mL)	20	70	60	60
10	THF (4 mL)	20	70	60	42
11	Water (4 mL)	20	70	60	25
12	EtOH (4 mL)	20	70	60	30
13	MeOH (4 mL)	20	70	60	32
14	CH ₃ CN (4 mL)	20	70	60	56
15 ^b	DMF (4 mL)	20	70	60	42
16 ^c	DMF (4 mL)	20	70	60	35
17 ^d	DMF (4 mL)	20	70	60	48
18 ^e	DMF (4 mL)	20	70	60	90
19 ^f	DMF (4 mL)	20	70	60	81
20	DMF (4 mL)	5	70	60	45
21	DMF (4 mL)	10	70	60	60
22	DMF (4 mL)	15	70	60	76
23	DMF (4 mL)	25	70	60	97
24	DMF (4 mL)	50	70	60	97

 a Isolated yields. b Fe₃O₄ as catalyst. c g-C₃N₄ as catalyst. d Fe₃O₄@g-C₃N₄ as catalyst. e g.-C₃N₄–SO₃H as catalyst. f Fe₃O₄@SO₃H as catalyst.

Table 2Magneticnanocomposite-catalyzedcycloaddition reaction ofnitroolefins with NaN3 underoptimized conditions

Entry	Ar-	Yield (%) ^[a]	Time (min)	M.P. (founded)	M.P. (reported)
1		97	60	145–148	149–151 [63]
2		79	240	100–103	102–104 [47]
3	CI	82	190	173–175	172–173 [46]
4	-CI	84	200	152–153	150–152 [47]
5	NO ₂	77	120	184–187	185–186 [64]
6		85	150	95–97	94–96 [47]
7		79	240	166–168	168–170 [64]
8		78	80	191–193	191–192 [44]
9		88	220	146–149	148–152 [63]
10	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	92	240	168–170	167–172 [63]
11		95	180	156–159	158–160 [63]
12	H ₃ C	89	220	54–57	53–54 [64]
13	——————————————————————————————————————	83	90	184–187	185–189 [63]
14		87	120	88–89	87–88 [64]
15		77	160	64–66	63–64 [64]
16	∽ ∫ S →	75	160	84–86	85–87 [64]

Table 3	Comparison of t	the activity of magnetic aci	carbon nitride nanocomposite	with the reported methods
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Entry	catalyst	Reaction conditions	Starting materials	Azide source	Yield (%)	Ref.
1	Pd-MCM-41	DMF, 80 °C, .083 h;	β-nitrostyrenes	TMSN ₃	99	45
2	Sulfated tungstate	DMF, 60 °C, 1 h	β-nitrostyrenes	NaN ₃	95	49
3	CXH–SO3H	DMSO, 60 °C, 4 h	β-nitrostyrenes	NaN ₃	92	47
4	-	DMSO, 90, 12 h	Nitroalkenes or vicinal acetoxy	NaN3	78	48
5	Al-MCM-41	Ethanol/water, 80 °C, 0.5 h, MW	Benzaldehydes and nitromethane	NaN3	24	49
6	Amino sulfonic acid	DMF, 60 °C, 12 h	β-nitrostyrenes	NaN3	94	50
7	Amberlyst-15	DMF, 50 °C, 4 h	β-nitrostyrenes	NaN3	95	51
8	Cu/ascorbate	H ₂ O, 100, 1 h	Nitroolefins/alkynes	NaN3	99	52
9	Fe3O4@nSiO2-SO3H@ MS-NHCOCH3	Methanol/DMF 140 °C, 8 h, sealed tube;	Benzaldehydes and nitromethane	NaN3	98	53
10	NH4OAc	DMF, 80 °C, 12 h,	Enolizable ketones and NH4OAc	4-nitrophenyl azide	93	54
11	p-TsOH	DMF, 60 °C, 6 h,	β-nitrostyrenes	NaN3	89	55
12	CuFe2O4	DMSO, 120 °C, 0.08333 h, MW	Benzaldehydes and nitromethane	NaN3	90	56
13	GO-Fe ₃ O ₄ @CuO	H2O, 45 °C, 80 min. US	Coumarin alkyne	Sugar-N3	97	57
14	Fe ₃ O ₄ @CD-CIT/CuSO4	H2O, 45 min. rt, US	Sugar alkyne	Coumarinazide c	96	58
15	L-phenylalanine/CuSO4	H2O, 80 min. 40 °C, US	Phenylacetylene	3-azidocoumain	97	59
16	Cu/ascorbate	H2O, 55 min. 40 °C, US	Glucose alkyne	Coumarin azide	97	60
17	CuO/rGO	H2O, 100 °C, 1 h	Flavanones	Aryal azide	89	61
18	Cs/PVA-CuNp	EtOH/water, 100 min., rt	Phenyl acetylene	Phenyl azide	92	62
19	Cu(PPh3)NO3	Neat, rt, 2 h	Phenyl acetylene	1-azido-4-nitro benzene	98	63
20	Cu@Fe NPs	H2O, rt, 12 h	Phenyl acetylene	Benzyl azide	88	64
21	$Fe_3O_4@g-C_3N_4-SO_3H$	DMF, 70 °C, 1 h	β-nitrostyrenes	NaN3	97	This work

4-aryl-NH-1,2,3-triazoles in a simpler manner. A variety of β -nitrostyrene bearing substitutions with various steric and electronic properties at the *ortho-*, *meta-*, and *para*-positions with the electron-donating groups and the electron-withdrawing group was converted to triazole products in good to excellent yields. Furthermore, heterocyclic substituted β -nitrostyrene derivatives also screened, and the pure triazoles could directly obtain in good yields (Table 2, entries 15,16).

The stability and reusability are significant advantages of magnetic catalysts in industrial processes. The recycling use of the Fe₃O₄@g-C₃N₄–SO₃H was performed in the model reaction (**2a**), and the results indicated that it was easy to collect the nanocatalyst due to its magnetic properties. After the reaction completion, water (10 mL) was added to the reaction mixture, and the nanocomposite was recovered with the aid of an external magnet. This recovered nanocatalyst was washed with 5 M HCl solutions and reused up to 5 cycles, and the results are shown in Fig. 2. The XRD data and FTIR spectra showed no changes in the structure and morphology of the nanocatalyst.

The tentative catalytic cycle is shown in Scheme 2. We reasoned that a plausible catalytic cycle could be readily initiated via activation of the nitroolefin with the sulfonic acid groups to generate an activated intermediate that reacts with the sodium azide via [3+2]-cycloaddition followed by the elimination of HNO₂ to afford the desired 1,2,3-triazole [65].

The catalytic activity of the $Fe_3O_4@g-C_3N_4-SO_3H$ nanocomposite for the formation of triazole derivatives compared with the earlier reported procedure and the results shown in Table 3. The data in Table 3 clearly showed that the present method is more versatile and more straightforward, which involves short reaction time, reusable catalyst, suitable to high product yield, to furnish regioselective synthesis of triazole derivatives.

Conclusions

In summary, we have disclosed a simple, efficient, and environmentally benign heterogeneous acidic ionic system for the regioselective synthesis of 4-Aryl-NH-1,2,3-triazoles by 1,3-dipolar cycloaddition reaction of nitroolefins with NaN₃. Fe₃O₄@g-C₃N₄–SO₃H be quickly recovered by an external magnet and reused without loss of its catalytic activity. The promising aspect of the presented procedures is operational simplicity, large-scale availability, short reaction time, and good to excellent yields.

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