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Synthesis of silver–graphene nanocomposite and its catalytic application for the one-pot three-component coupling reaction and one-pot synthesis of 1,4-disubstituted 1,2,3-triazoles in water†

Noor Salam,‡§[ab] Arjyabaran Sinha,§[c] Anupam Singha Roy,‡[ab] Paramita Mondal,[ab] Nikhil R. Jana*[c] and Sk Manirul Islam‡*[ab]

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A graphene based composite with silver nanoparticles has been synthesized *via* a simple chemical route and its catalytic activity has been tested for multi-component reactions and click reaction in a one-pot approach. This silver–graphene nanocomposite shows excellent catalytic activity at room temperature for three-component couplings between aldehydes, alkynes and amines (A^3-coupling) and one-pot synthesis of 1,4-disubstituted 1,2,3-triazole *via* click reaction between *in situ* generated azides (derived from anilines or amines) and terminal acetylenes. This solid silver–graphene catalyst has been characterized by TEM, Raman, XRD and UV-Visible absorption spectra. The developed catalyst is air-stable, inexpensive, easy to prepare and can be facilely recovered and reused five times without significant decrease in activity and selectivity.

Introduction

In the past few years, an increasing number of multi-component reactions (MCRs) have been developed for the synthesis of diverse complex molecules through a combination of three or more starting materials in a one-pot reaction. Among MCRs, the coupling reaction of aldehydes, amines and alkynes (A^3-coupling) is one of the best examples, where propargylamine is obtained as the major product. Propargylamines are valuable synthetic building blocks in the synthesis of various natural products and biologically active compounds.[1,2] Catalytic three-component couplings of aldehydes, alkynes and amines are being intensely investigated in water, organic media, ionic liquid, or under solvent-free conditions to afford different propargylamines using different catalyst such as copper, silver, gold, iron, iridium, zinc and other catalysts.[3]

Similarly, copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition reaction between azides and terminal alkynes is the widely studied 'click' reaction, developed by the groups of Sharpless[4] and Meldal[5] in 2002. This reaction has been extensively applied to the synthesis of macromolecules[6,7] and the functionalization of bio-molecules.[8] The classical method for their synthesis involved thermal 1,3-dipolar cycloaddition of organic azides with alkynes.[9] Subsequently, an improved procedure involving copper(I)-catalyzed azide–alkyne 1,3-dipolar cycloaddition has been reported,[10] which provide high regioselectivity, room temperature reaction, high yields in aqueous media even at low concentrations[11] and with enlarged scope. Moreover organic azides are not so safe to handle freely because of its toxic nature. These molecules can be prepared from their corresponding amines or anilines by diazotization followed by the addition of sodium azide or by the direct displacement reaction of alkyl halide with sodium azide. Hence a one pot AAC reaction between *in situ* generated azide from its corresponding precursor and alkyne is highly desirable.

Graphene posses two-dimensional sheet-like structure which represents an interesting geometrical support for molecular catalysts with a large open surface area that is readily accessible to substrates/products with a small diffusion barrier, which is distinct from conventional high surface area porous materials and efficiently storing and shuttling electrons through the sp^2 hybrid 2D carbon network.[12] Recently, sp^2 carbon based nanostructures have been extensively studied as supports for both heterogeneous catalysis and electrocatalysis,

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[a] *Department of Chemistry, University of Kalyani, Nadia, Kalyani, 741235, W.B., India. E-mail: manir65@rediffmail.com; Fax: +91-33-2582-8282; Tel: +91-33-2582-8750*

[b] *Department of Chemistry, Aliah University, Sector-V, Salt Lake, Kolkata-99, 700 099, West Bengal, India*

[c] *Centre for Advanced Materials, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India. E-mail: camnrj@iacs.res.in; Tel: +91-33-24734971*

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‡ Present address: Department of Chemistry, Aliah University, Sector-V, Salt Lake, Kolkata-99, 700 099, West Bengal, India, Phone: +91-33-2706-2269, 2706-2271, Fax: +91-33-2367-1433, E-mail: manir65@rediffmail.com

§ These two authors contributed equally.

due to their high mechanical strength, large surface area, good electrical conductivity, and durability under harsh conditions.[13] Graphene based composite of metal and nanoparticle have been synthesized to improve the performance of electrocatalysis,[14–17] redox catalysis,[18] carbon–carbon bond formation,[19,20] photocatalytic reaction,[21] and Li-ion batteries[22]. The heterogeneous nature of catalysts offer the advantage of thermal stability and reusability.[23] Although immobilization of nano-sized metal catalyst onto insoluble supports has become a popular strategy for these types of coupling reactions,[23] present approach used graphene based support which has exceptional high surface area, good electrical conductivity and mechanical strength offering unique catalytic performance and efficiency.

Silver and its salts have been widely employed as promoters and catalysts, respectively, in organic synthesis. They shows good catalytic activity towards coupling, cycloaddition, sigmatropic rearrangement, cycloisomerization, and nitrene transfer reactions.[24] Ag nanoparticles have been immobilized on various carbon-based supports such as CNTs, graphene, graphene oxide (GO) and used for electrochemical and antibacterial applications.[25] However, the catalytic activity of these composites toward organic reactions has received less attention. Recently it is reported that silver induces 'click' azide–alkyne cycloaddition and A^3-coupling[3,26] reactions which motivated for the present study.

Here, we have investigated the silver–graphene nanocomposite as heterogeneous novel catalyst toward the 'one-pot' A^3-coupling reactions in CH_2Cl_2 and 'one pot' azide–alkyne click reaction between *in situ* generated aromatic azides from their corresponding anilines and alkynes in water at room temperature. The catalyst, composed of micron size graphene sheet attached with 10–12 nm spherical silver nanoparticles, can be dispersed in reaction media and separated by decantation or centrifuge after the end of reaction.

Experimental section

Instrumentation

FEI Technai G2 transmission electron microscope was used for transmission electron microscopic (TEM) image of sample. Amount of silver present in the composite materials was estimated by Optima 2100DV (Perkin Elmer) inductively coupled plasma atomic emission spectroscopy (ICP-AES). Solid silver–graphene composite was dissolved in HCl–HNO_3 and insoluble graphene was separated by centrifuge and supernatant was used for ICP measurement. Amount of silver was estimate between 3 and 7 wt%. XRD measurement of the samples were done by Bruker D8 Advance powder diffractometer, using Cu Kα (λ = 1.54 Å) as the incident radiation. The reaction products were analyzed using a Varian, USA, 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a flame ionization detector. All reaction products were identified by using an Agilent, USA, GC-MS (QP-5050) equipped with a 30 m HP-5 ms capillary column. NMR spectra were monitored on a Bruker AMX-400 NMR spectrophotometer using tetramethylsilane as internal standard.

Materials and reagents

[3-(2-Aminoethylamino)propyl]trimethoxysilane (AEAPS), (3-mercaptopropyl)-trimethoxysilane (MPS), tetrabutylammonium borohydride (TBAB), tetramethylammonium hydroxide 25 wt% in methanol (TMAH), graphite powder (<20 micron), hydrazine hydrate (98%) were purchased from Sigma-Aldrich and used as received. Other reagents were purchased from Merck and used as received. All solvents were also purchased from Merck, India and purified by standard procedures.

Preparation of water soluble silica coated Ag nanoparticles

At first 8.5 mg CH_3COOAg was taken in 5 mL toluene and dissolves by sonication in presence of 100 μL octylamine. Next, 50 μL oleic acid and 100 μL toluene solution of MPS (0.1 M) was added under stirring condition. Then 500 μL toluene solution of TBAB (12.5 mg) was added as reducing agent and colour of the solution changes to yellow due to the formation of Ag nanoparticles. Next, 1 mL toluene solution of AEAPS (0.1 M) was added to this solution and heated the whole solution at 65–70 °C for 15–20 min until complete precipitation occurs. Then solution was centrifuge and washed with toluene and ethanol and then solubilized in 5 mL distilled water.

Preparation of graphene oxide (GO)

GO was synthesized *via* modified Hummer's method. In the synthesis of GO at first 200 mg graphite powder and 100 mg $NaNO_3$ was mixed with 5 mL concentrated sulphuric acid and then 600 mg $KMnO_4$ was added. The temperature of the solution at this stage remains <20 °C. Then temperature of reaction mixture was increased to 35 °C and stay for half an hour. After that the solution was diluted with water and the temperature of the solution was increased to 98 °C and maintains for 15 minutes. Next, excess permanganate was reduced by adding 3% H_2O_2 solution. Then precipitate was washed with warm water several times and air dried. Finally precipitate was dispersed in water by sonication and centrifuged at 3000 rpm for 30 minutes. The supernatant was used as GO solution.

Synthesis of silver–graphene nanocomposite (Ag–G)

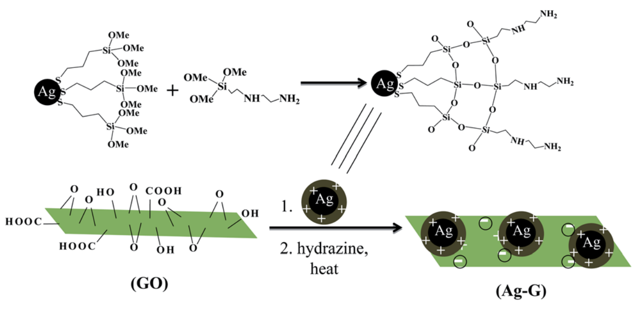
In a 30 mL GO solution (1 mg mL^{-1}), 2.5 mL of above silica coated Ag nanoparticles solution was added under stirring condition and continued for another 15 min. Next, one mL concentrated hydrazine solution was added to this solution and heated to 80 °C. After 15–20 min the precipitate was observed and the heating was continued for another 2 h. Then the precipitate was wash with water and used for reaction.

One-pot synthesis of propargylamines catalyzed by silver–graphene nanocomposite (Ag–G)

In a 50 mL RB flask, cyclohexanecarboxaldehyde (0.112 mg, 1.0 mmol), phenyl acetylene (0.112 g, 1.1 mmol), piperidine (0.094 g, 1.1 mmol), Ag–G catalyst (25 mg, 7 wt% Ag) and CH_2Cl_2 (1.0 mL) were added. The mixture was stirred at room temperature for 10 h. Part of the reaction mixture was collected at different time intervals and identified by GCMS and quantified by GC. After the completion of the reaction, the catalyst was filtered off and washed with water followed by acetone and dried in oven. The filtrate was extracted three times with ethyl acetate (3 × 20 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

One-pot synthesis of 1,2,3-triazoles from aromatic amines catalyzed by silver–graphene nanocomposite (Ag–G)

Aniline (0.5 g, 5.4 mmol) was charged into a 25 mL round bottomed flask which was then placed into an ice water bath (0 °C −5 °C). Next, 1.3 mL of concentrated HCl is diluted with 1.3 mL H_2O and added to it followed by one minute stirring. Then $NaNO_2$ (0.392 g, 5.7 mmol) dissolved in one mL of cold water was added dropwise to the reaction mixture. After stirring for 2 min, sodium azide (0.416 g, 6.4 mmol) was added and stirred for 5 min. Then phenyl acetylene (0.46 g, 4.6 mmol) and Ag–G composite (25 mg, 7 wt% Ag) were added to the reaction mixture followed by stirring at room temperature for 8 h. After the completion of reaction water layer was decanted off and the reaction mixture was dissolved in environmentally friendly ethanol. Then the catalyst was filtered off, washed with water, ethanol and acetone. The product was purified by simple crystallization from ethanol to provide corresponding triazole.



Scheme 1 Synthesis approach for silver–graphene nanocomposite (Ag–G).

Results and discussion

Synthesis strategy of silver–graphene nanocomposite (Ag–G) is shown in the Scheme 1. At first amine terminated cationic and water soluble silver nanoparticles is synthesized by established silica coating approach.[27] Then this water soluble silver nanoparticle solution is mixed with GO solution under stirring condition. At this stage cationic silver nanoparticles are attached to the anionic GO surface *via* electrostatic interaction. In addition nucleophilic attack of primary amine groups (present on silver surface) with epoxide groups of GO leads to the formation of some covalent bond formation.[28a] Next, GO is chemically reduced to graphene by hydrazine. The conversion of GO to graphene is observed *via* gradual appearance of deep black colour along with the appearance of precipitate after 10 to 15 min. Precipitated Ag–G is washed with water and dried and used for the characterization and catalytic application.

Characterization of Ag–G

Ag–G has been characterized by UV-Visible spectroscopy, XRD, TEM and Raman spectroscopy. Fig. 1a shows the UV-Visible spectra of amine terminated water soluble silica coated Ag nanoparticles, GO and Ag–G. The silica coated Ag nanoparticles show the characteristic plasmonic peak of Ag at 420 nm and GO also shows its characteristic absorbance hump around 296 nm. After the formation of Ag–G, the absorbance at 300–800 nm region increases and a new peak arises at 264 nm, indicating the formation of graphene. However, distinct plasmonic peak for Ag nanoparticles is not observed due to the low amount of Ag nanoparticles and its damping by graphene surface.[28b] Fig. 1b shows the X-ray diffraction pattern of the Ag–G. It shows the reflection at 2θ of 38.3, 43.6, 64.6 and 77.80° corresponding to the (111), (200), (220) and (311) planes of Ag, respectively and the reflection at 2θ of 23.30° due to graphene component. Raman spectra of the Ag–G shows two well documented D and G band at 1308 and 1607 cm^{-1} respectively. (Fig. 1c) The D band at 1308 cm^{-1} is attributed due to the defect or disorder in carbon atom and G band at 1607 cm^{-1} is attributed due to sp^2 in plane vibration of carbon atom. The calculated intensity ratio (I_D/I_G) of D and G band in the graphene and Ag–G are 1.86 and 2.15,

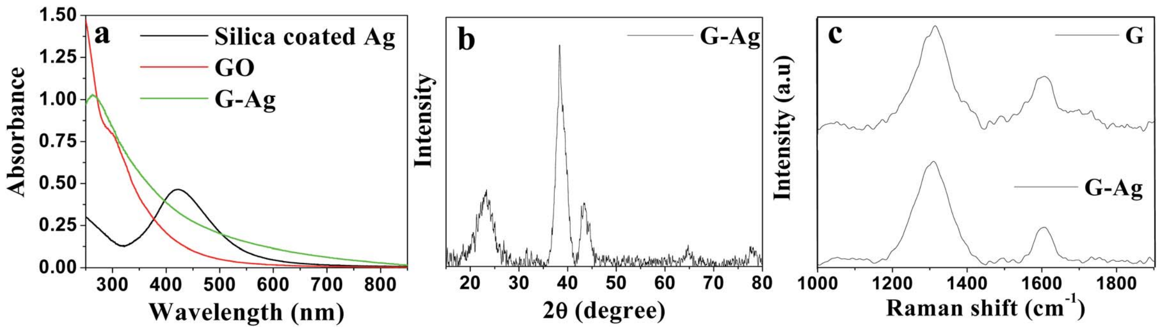


Fig. 1 (a) UV-Visible spectra of colloidal solution of silica coated cationic Ag nanoparticles, GO and Ag–G. (b) X-ray diffraction pattern of the Ag–G showing the reflections for Ag (at 2θ of 38.3, 43.6, 64.6 and 77.80 with the corresponding (111), (200), (220) and (311) planes, respectively) and graphene (at 2θ of 23.30). (c) Raman spectra of graphene and Ag–G showing two well documented D and G bands at 1308 cm^{-1} and 1607 cm^{-1}, respectively.

respectively. This increase in the intensity ratio from graphene to Ag–G indicates the decrease in size of the in plane sp^2 domain in Ag–G.[28c,d]

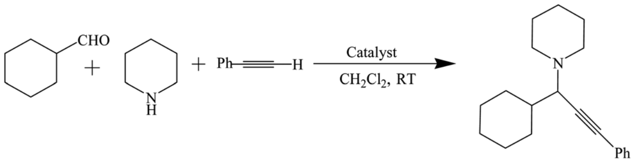
Fig. 2a–c show the low and high resolution TEM image of the Ag–G, showing their composite nature. The TEM image also clearly indicates that the Ag nanoparticles are uniformly dispersed onto the graphene plane. The presence of Ag in the Ag–G composite also confirm from the EDX spectrum (Fig 2d). Fig 2(e) shows the particles size distribution of Ag nanoparticles in the Ag–G composite and the average size of the Ag nanoparticles were 10–12 nm.

Catalytic activity of Ag–G for 'one-pot' A^3 coupling reactions

Multicomponent reactions of simple molecules provide a very versatile and efficient method to construct desired molecules. The effect of Ag–G on their catalytic activity for the A^3-coupling reaction was investigated using cyclohexanecarboxaldehyde, phenylacetylene and piperidine as a model reaction (Scheme 2).

In order to optimize the conditions of the A^3 reaction, the effect of solvent was surveyed (Table 1). Among the solvents tested CH_2Cl_2, CH_3CN, DMF, THF and solvent-free conditions all gave excellent yields of 75–98% (Table 1, entries 1, 2, 3, 4 and 9). However, solvents such as CH_3OH, toluene, H_2O and AcOEt were not suitable for the reaction and no satisfactory yields were obtained (Table 1, entries 5–8). When the amount of the Ag–G was increased to 40 mg, there was no obvious increase in the yield of the reaction (Table 1, entry 10). Thus, the optimized conditions for the A^3 reaction are 25 mg Ag–G catalyst and CH_2Cl_2 as solvent at room temperature.

To expand the scope of this A^3-coupling, various aldehydes, alkynes and amines were used as substrates under the optimized reaction conditions. From these results we found that the conditions were equally applicable to the coupling of a variety of aromatic aldehydes including heterocyclic aldehydes with piperidine, morpholine or pyrrolidine utilizing phenylacetylene, giving the corresponding propargylamines in high



Scheme 2 Schematic diagram of A^3-coupling reaction.

Table 1 The effects of various variables in the three-component coupling reaction of cyclohexanecarbaldehyde, piperidine and phenylacetylene catalyzed by the Ag–G[a]

Entry	Solvent	Yields (%)[b]
1	CH_2Cl_2	98
2	CH_3CN	85
3	DMF	80
4	THF	81
5	CH_3OH	10
6	Toluene	58
7	H_2O	50
8	AcOEt	60
9	Neat	75
10[c]	CH_2Cl_2	93
11	CH_2Cl_2	—

[a] Reaction conditions: cyclohexanecarboxaldehyde (1.0 mmol), phenylacetylene (1.1 mmol), piperidine (1.1 mmol), catalyst, CH_2Cl_2(1 mL), room temperature for 10 h. [b] GC yield based on cyclohexanecarboxaldehyde. [c] Ag–graphene – 40 mg.

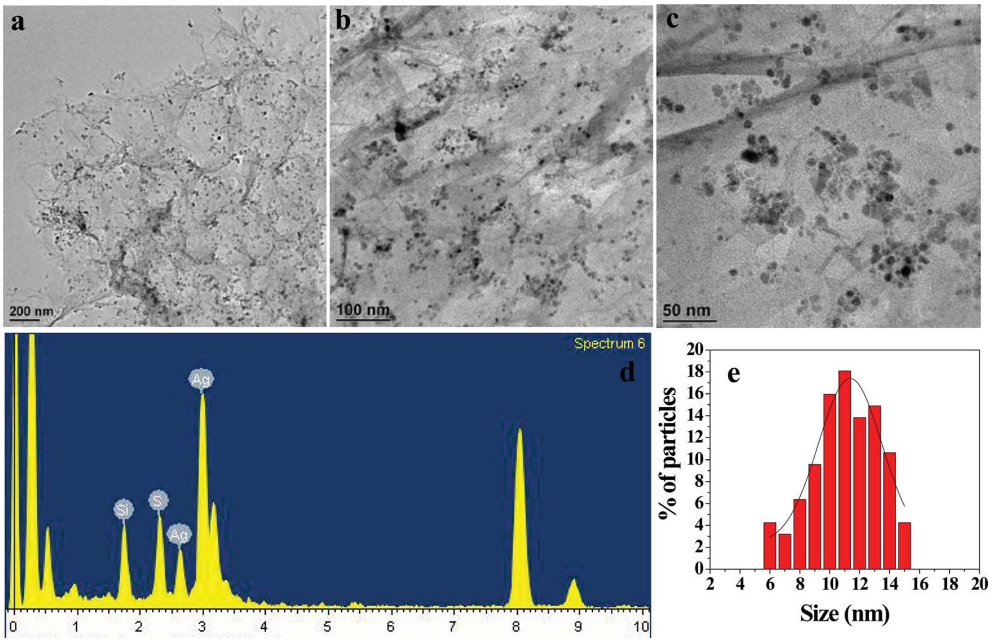


Fig. 2 (a)–(c) are the low and high resolution TEM image of Ag–G. (d) EDX spectra of the Ag–G composite and (e) the particles size distribution curve of the Ag nanoparticles in Ag–G composite.

Table 2 The three-component (A^3) coupling reaction catalyzed by the Ag–G[a]

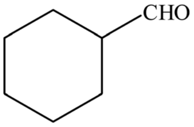
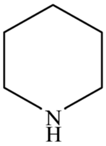
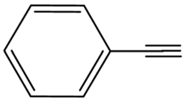
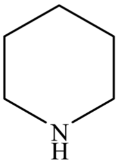
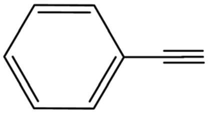
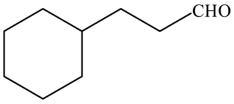
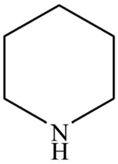
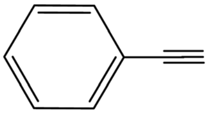
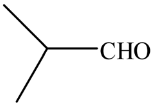
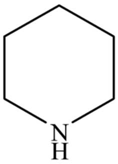
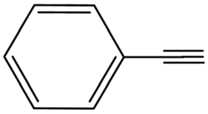
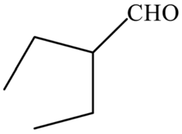
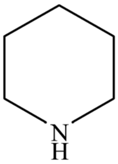
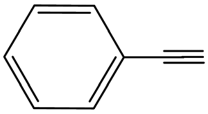
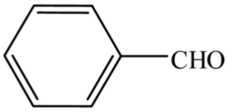
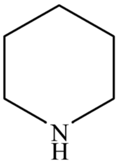
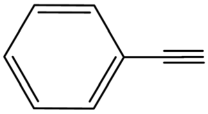
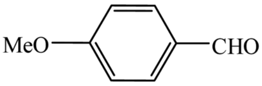
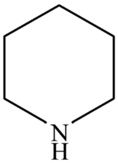
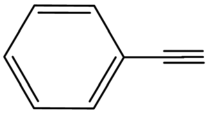
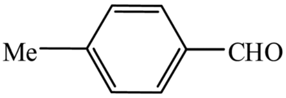
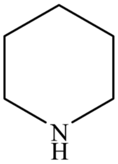
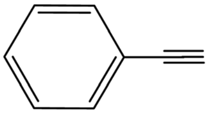
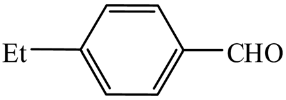
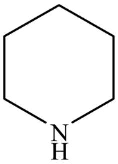
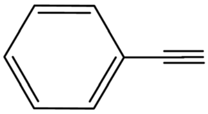
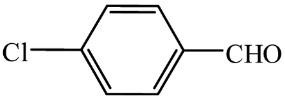
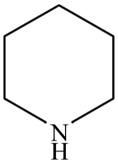
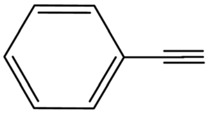
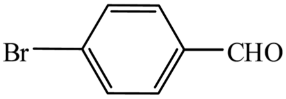
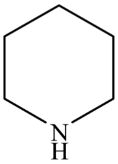
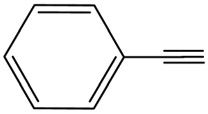
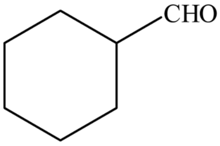
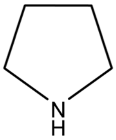
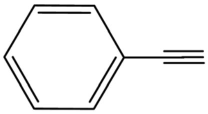
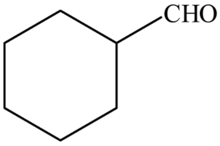
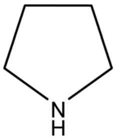
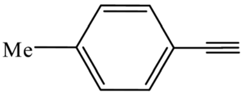
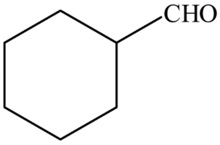
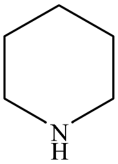
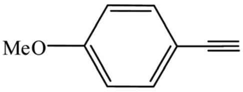
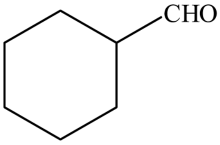
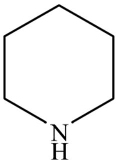
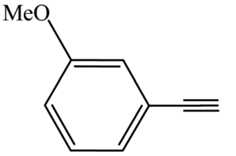
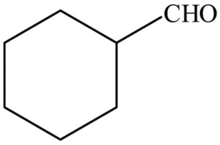
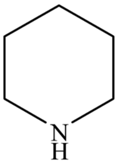
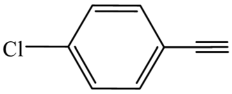
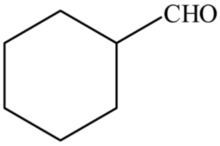
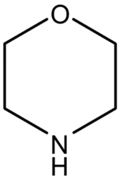
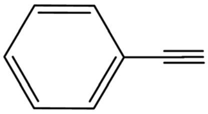
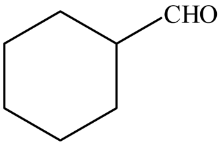
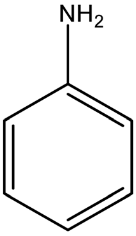
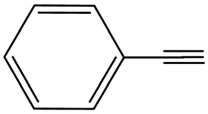
Entry	Aldehyde	Amine	Alkyne	Temperature (°C)	Time (h)	Yields[b] (%)
1				RT	10	98
2	HCHO			RT	11	93
3				RT	24	96
4				RT	12	94
5				RT	12	89
6				60	24	86
7				60	24	80
8				60	24	70
9				60	24	73

Table 2 (*Contd.*)

Entry	Aldehyde	Amine	Alkyne	Temperature (°C)	Time (h)	Yields^b (%)
10				40	24	82
11				40	24	84
12				RT	12	93
13				RT	24	93
14				RT	24	90
15				RT	24	86
16				RT	24	70
17				RT	15	82
18				RT	12	71

[a] Reaction conditions: aldehyde (1.0 mmol), alkyne (1.1 mmol), amine (1.1 mmol), catalyst (0.1 mol%), CH_2Cl_2(1 mL). [b] Isolated yield. Products were identified by comparison of their ^{1}H-NMR spectral data those reported in the literature.

yields in room temperature. The results are summarized in Table 2.

Both aromatic and aliphatic aldehydes, including those bearing functional groups such as alkoxy, chloro and bromo additions, were able to undergo the corresponding three-component-coupling. Under the optimized conditions, aliphatic aldehydes such as cyclohexanecarboxaldehyde, formaldehyde, 3-cyclohexylpropanal, iso-butyraldehyde and 2-ethylbutanal all give both higher conversions and greater yields at room temperature within 10–24 h (Table 2, entries 1–5). However, aromatic aldehydes were less reactive than aliphatic aldehydes, and the reaction could proceed at 60–40 °C in yields of 70–86% (Table 2, entries 6–11). Aryl aldehydes with electron-donating groups (entries 7–9) reacted smoothly; however, 4-methoxybenzaldehyde and 4-alkylbenzaldehyde with electron-rich groups bound to the benzene ring, reacts slowly and required a longer reaction time at high temperature. Electron-withdrawing groups (entries 10–11) displayed high reactivities; reactions were completed at a lower temperature and gave higher conversions. Good yields were observed when cyclic dialkylamines such as pyrrolidine and morpholine and also aromatic amine were used (entries 12, 17 and 18).

We also found that a variety of terminal aromatic alkynes with substituted groups in *para*- and *meta*-positions could be effectively reacted under the present reaction conditions (Table 2, entries 13–16). Note that the reactions proceeded smoothly to give the corresponding propargylamines in a good yield. The presence of electron-rich groups on the benzene ring (entries 13–15) increased the reactivities of the alkynes whereas electron-withdrawing groups (entry 16) on the benzene decreased the yield.

Catalytic activities of Ag–G for 'one-pot' azide–alkyne click reaction

In continuation of our interest in 'one-pot' azide–alkyne click reaction, we were in search of a high-yielding, catalytic, cheap and environmentally benign reagent for this reaction and considered Ag–G as a choice. Thus, when phenyl azide obtained from aniline under diazotisation method and phenyl acetylene were treated with Ag–G in water at room temperature, the 1,2,3-triazole was obtained (Scheme 3).

As water is the most easily available, economical and environment friendly solvent in the world, we first attempted to perform the so called 'click' reaction in water medium for a representative reaction between phenyl azide formed *in situ* from aniline and phenyl acetylene at 70 °C using 25 mg Ag–G and the reaction was successful leading to the formation the corresponding triazole with 97% yield. To standardize the reaction condition in water, a series of experiments varying time and temperature for the representative reaction were carried out. The results are summarized in Table 3.

The best yield was obtained using 25 mg Ag–G for 8 h at room temperature (Table 3, entry-3). No product was obtained in the absence of catalyst (Table 3, entry-7). In a typical experimental procedure aniline was first diazotized using conc. HCl, $NaNO_2$ in water at 0–5 °C followed by the addition of sodium azide to form phenyl azide. After 5 minutes stirring, phenyl acetylene and catalyst was added to the reaction mixture which was stirred for 8 h (TLC). After the reaction was over water was decanted and the solid product was recrystallized from environment friendly ethanol to provide the pure product. Thus the use of huge amount of hazardous organic solvent in the work-up and column chromatography stage was skipped.

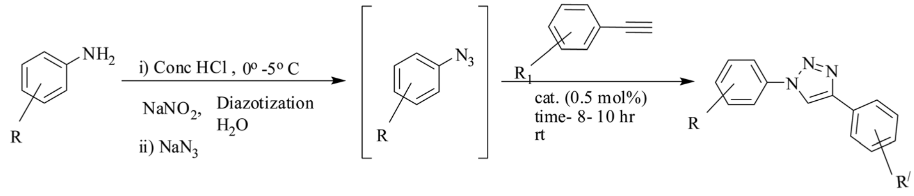
A variety of electronically different anilines was studied in the reaction with phenylacetylene in Table 4. The results indicated that benzyl, alkyl, and aryl azides reacted quickly with phenylacetylene and the corresponding triazoles were obtained in high yields at room temperature or 40 °C within 6–8 h.

Longer reaction times (10 h) were required for organic azides containing substituents at the 2-position (entries 2 and 5). The triazoles derived from electronically neutral aniline and electronically rich 4-methoxyaniline was obtained in high yields after 8 h (entries 1 and 3). Both the electron donating (4-OCH_3,

Table 3 The effects of solvent on the one pot 'click' reaction catalyzed by Ag–G[a]

Entry	Catalyst amount (mg)	Temperature (°C)	Time (h)	Yield[b] (%)
1	25	70	8	97
2	25	50	8	97
3	25	rt	8	96
3	25	rt	10	96
4	25	rt	6	81
5	40	rt	8	97
6	20	rt	8	92
7	—	rt	8	—

[a] Conditions: aniline (1 equiv.); phenyl acetylene (1.2 equiv.); solvent (5 mL). [b] Isolated yields.

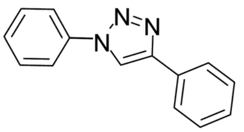
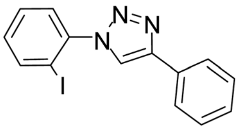
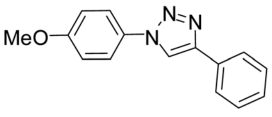
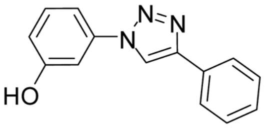
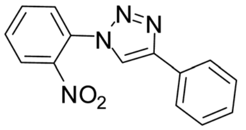
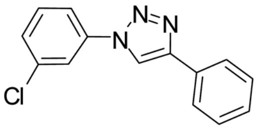
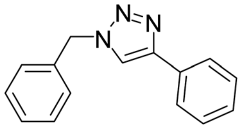


R= H, 4-OMe, 2-NO_2, 3-OH, 2-I, 3-Cl, 4- CO_2H...etc

R_1 =H, 4-OMe, 4-F, 4-Ph, 4-CN.....etc

Scheme 3 Synthesis of triazoles from anilines by one pot two step click reaction in water medium at room temperature catalyzed by Ag–G.

Table 4 One-pot 'click' reaction between anilines and phenyl acetylene catalyzed by Ag–G[a]

Entry	R	Product	Time	Yield[b] (%)
1	H		8	96
2	2-I		10	85
3	4-OMe		8	98
4	3-OH		9	93
5	2-NO$_2$		9	91
6	3-Cl		9	89
7	PhCH$_2$–		8	94

[a] Conditions: aniline (1 equiv.); phenyl acetylene (1.2 equiv.); solvent (5 mL); 50 mg catalyst at room temperature for 8 h. [b] Isolated yields.

3-OH) and electron withdrawing groups (2-NO$_2$) are compatible with the reaction condition and they also do not show any significant influence on the outcome of the reaction (entries 3–4). All the *ortho*, *meta* and *para* substituted anilines reacted almost uniformly with phenyl acetylene (entries 2–6). Benzyl azide formed *in situ* from benzyl amine also undergoes through reaction with phenylacetylene to produce the corresponding 1-benzyl-4-phenyl-1,2,3-triazole (entry 7).

Using the optimized conditions, the one-pot click reaction was further expanded to a broader range of various substituted organic anilines and other terminal alkynes in order to evaluate the scope and limitations of the method, as outlined in Table 5.

In general, the reactions are very clean and high yielding. Aniline with an electron withdrawing group was more reactive in comparison to those with an electron donating group. Both electron donating (OMe) and electron withdrawing (CN, F) groups containing acetylenes react equally with various azides to form the corresponding product (entries1–4). The heteroaryl substituted acetylene, 2-ethynyl pyridine reacted clearly with benzyl azide formed *in situ* from benzyl amine to form 2-(1-benzyl-1*H*-(1,2,3) triazole-4-yl)-pyridine (entry 6).

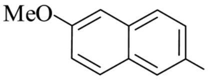
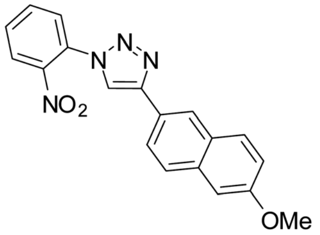
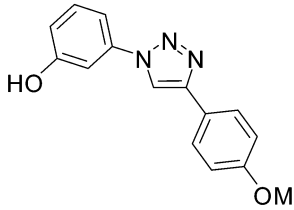
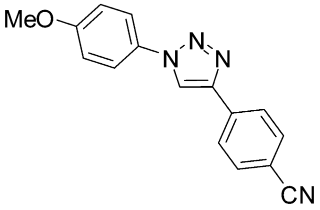
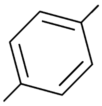
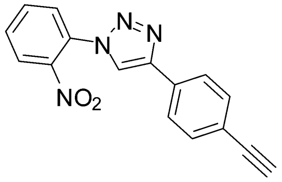
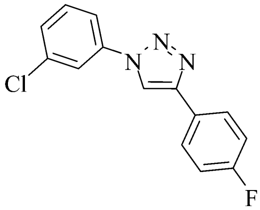
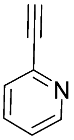
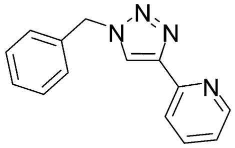
The high activity arises from the synergistic effect of GO, explained as follows: (1) GO has high adsorption ability towards reactants *via* π–π stacking interactions. This provides a relatively high concentration of reactants molecule which is closer to the silver nanoparticles on GO, leading to highly efficient contact between them; and (2) electron transfer from the GO to silver nanoparticles increases the local electron concentration, facilitating the uptake of electrons by reactants molecules.[29]

The controlled experiments (Table 6) have shown that the A^3 coupling and 'click' reaction both do not take place in the absence of the catalyst. Silver metal, silver oxide and silver salts are often utilized for coupling reactions. The silver metal itself does not show any catalytic activity in A^3 coupling reaction but in click reaction it show low conversion. Fresh silver wire-gauge washed by dil. HNO$_3$ acid shows low reactivity and gives trace amount of products. Water-soluble or partially soluble salts such as AgNO$_3$ and Ag$_2$O are all found to catalyze the A^3 coupling reaction with low conversion (36–43%) and click reaction with similar conversion (39–50%).

In comparison with homogeneous catalyst, heterogeneous catalyst shows better activity and selectivity. Additionally, the supported catalyst is expected to have several advantages over the homogenous one. The immobilized catalyst can be removed easily from the reaction mixture by a simple filtration, and it is more easily handled. We have also varied the silver concentration in this catalyst (Table 6, entries 7 and 8). From the experimental results it is seen that Ag–G composite with higher silver concentration gave the highest conversion. The possible reason might be explained on the basis of the highly and uniformly dispersed silver (having high surface area) on the surface of graphene (Fig. 1 d–f) and a synergistic effect that comes from graphene (exhibiting a certain catalytic activity, Table 1), which allow more molecules to be in contact with the surface of Ag nanoparticle.

The silver–graphene nanocomposite exhibited better catalytic activity than pure silver which indicates that the catalytic activity of silver can be remarkably improved by combining it with graphene sheets. The enhancement in catalytic activity can be attributed to three factors: (i) graphene has conducting properties and provides high migration efficiency of electrons, which plays an important role in enhancing the catalytic activity for these reactions, (ii) as compared with silver and graphene, the silver–graphene composite can offer an environment to prevent aggregation of silver on graphene and obstruct loss of activity. Silver–graphene-nanocomposite has a higher surface area which can provide more active sites for adsorption of reactants; (iii) graphene is not only a support, but also acts as catalyst for the reaction. Nevertheless, the novel properties of silver–graphene as a catalyst lead us to believe that silver–graphene composite will find application in various catalytic fields.

Table 5 One-pot 'click' reaction between various substituted anilines and terminal alkynes catalyzed by Ag–G[a]

Entry	R	R_1	Time	Product	Yield[b] (%)
1	2-NO_2		10		87
2	3-OH	4-OMe	8		92
3	4-OMe	4-CN	8		90
4	2-NO2		8		84
5	3-Cl	4-F	9		89
6	$PhCH_2$–		9		88

[a] Conditions: aniline (1 equiv.); phenyl acetylene (1.2 equiv.); solvent (5 mL); 50 mg catalyst at room temperature. [b] Isolated yields.

Comparison with other reported system

One-pot A^3-coupling reactions *via* various aldehydes, alkynes and amines and also one pot click reaction of aniline with phenylacetylene under heterogeneous conditions over a variety of catalysts has been studied (Table 7). Table 7 provides a comparison of the results obtained for our present catalytic system with those reported in the literature.[30–37]

From Table 7, it is seen that present catalyst exhibited higher yields compared to the other reported system.[30–37] Reactions conducted at room temperature, shorter reaction time was required for these reactions and most importantly above coupling reactions occurred in water using our silver–graphene catalyst.

Recycling of catalyst

For a heterogeneous catalyst, it is important to examine its ease of separation, recoverability and reusability. The reusability of

Table 6 Effect of silver source on the 'one-pot' A^3 coupling[a] and 'click' reaction[b,c]

		A^3 coupling reaction	Click reaction
Entry	Silver source	Yield (%)	Yield (%)
1	None	No reaction	No reaction
2	Ag metal	0	24
3	$AgNO_3$	43	50
4	Ag_2O	36	39
5	Fresh silver wire-gauge	Trace	Trace
6	Graphene	20	Trace
7	Ag–G (3 wt % Ag)	64	61
8	Ag–G (7 wt% Ag)	98	96

[a] Reaction conditions: cyclohexanecarboxaldehyde (1.0 mmol), phenylacetylene (1.1 mmol), piperidine (1.1 mmol), catalyst (25 mg), CH_2Cl_2(1 mL), room temperature for 10 h. [b] GC yield based on cyclohexanecarboxaldehyde. [c] Reaction conditions: aniline (1equiv.); phenyl acetylene (1.2 equiv.); solvent (5 mL); 25 mg catalyst at room temperature for 8 h.

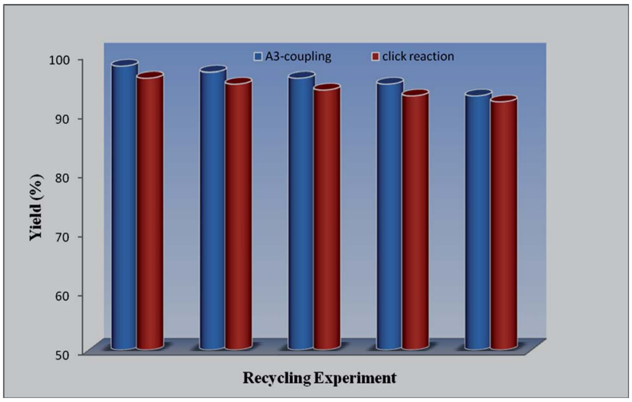


Fig. 3 Recycling activity of the Ag–G catalyst.

silver–graphene composite was investigated in 'one-pot' A^3-coupling reactions *via* cyclohexanecarboxaldehyde, phenyl acetylene and piperidine and one pot click reaction of aniline with phenyl acetylene under the optimized reaction conditions. After each run, ethyl acetate was added to dilute the reaction mixture and the organic layer was dried with anhydrous Na_2SO_4 by vacuum. The filtrate was concentrated and the resulting residue was purified. After a simple wash using ethyl acetate and dried, the catalyst was reused for the next run and almost consistent activity was observed for next five consecutive cycles (Fig. 3). TEM image (Fig. S2†) of the reused catalyst shows that the Ag nanoparticles were intact in the graphene surface but size of the particles increases due to aggregation of the particles in several reactions. Raman spectra of the reused catalyst (Fig. S1†) also shows the similar two well documented D and G band of graphene. So the catalyst can be efficiently recycled and reused for repeating cycles without appreciable decrease in product yield.

Heterogeneity test

To examine whether silver was being leached out from the solid support to the solution, experiment has been carried out in the one- pot three-component coupling reaction with our supported silver–graphene composite. A typical filtration test was performed in the one- pot three-component coupling reaction of aldehydes, amines and alkyne (A^3-coupling) to investigate whether the reaction proceeded in a heterogeneous or a homogeneous fashion. For the rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture after 4 h and the filtrate was allowed to react up to the completion of the reaction (6 h). In this case no change in conversion was observed, which suggests that the catalyst is heterogeneous in nature. No evidence for leaching of silver or decomposition of the complex catalyst was observed during the catalytic reaction. Furthermore, after separation of the catalyst,

Table 7 Comparison of catalytic activity of the present catalyst in the A^3 coupling and 'click' reactions with other reported catalyst systems

Reaction	Catalyst	Reaction conditions	Yield (%)	Ref.
A^3 coupling raction	NHC silver complexes	Dioxane, 100 °C, 12 h	81	30
	[Ag(L)(NO_3)]	$CHCl_3$, RT, 8 h	82	31
	Polymer-supported NHC–Ag(I)	CH_2Cl_2, RT, 24 h	92	32
	Nano-Ag_2O	$CHCl_3$, RT, 10 h	79	33
	Ag–G	CH_2Cl_2, RT, 10 h.	98	This study
Click reaction	Silver acetate complex	Phenyl acetylene, benzyl azide, caprylic acid, PhMe, 90 °C	79	34
	$Cu(MeCN)_4PF_4$ and silver acetylide	Pyridine, azide, 24 h, RT	75	35
	Silver(I)acetate complex (ligand: 2-diphenylphosphino-*N*,*N*-diisopropylcarboxamide)	Phenyl acetylene, benzyl azide), caprylic acid, PhMe, 48 h, RT.	95	36
	Ag_2CO_3	Phenyl acetylene, NMP, ethyl 2-isocyanoacetate, 80 °C	89	37
	Ag–G	Aniline, phenyl acetylene, water, RT, 8 h	96	This study

analysis of the filtrate by ICP indicated that no silver metal had leached out from the catalyst surface. These studies clearly demonstrated that silver was intact to a considerable extent with the heterogeneous support and there is no considerable amount of leaching during reactions.

Conclusion

In summary, we have successfully developed a new graphene based composite with silver nanoparticle as heterogeneous catalyst. The resulting catalyst showed enhanced catalytic activity with efficient recycling for the A^3 coupling reaction and one pot synthesis of 1,2,3-triazole from anilines at room temperature. Such a wide scope demonstrated by the catalyst has not been reported earlier and this procedure provides a convenient route to a variety of substituted 1,2,3-triazoles and propargylamines. Moreover, these heterogeneous nanocatalysts are stable showing no silver leaching and aggregation, and can be recycled multiple times without loss of catalytic activity and highly desirable to address the environmental concerns and thus we believe that this protocol will find a useful application in green organic synthesis. Further investigation on mechanistic studies of this catalyst for the above mention reactions are going on in our laboratory.

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