Synthesis of gold nanoparticles decorated on sulfonated three-dimensional graphene nanocomposite and application as a highly efficient and recyclable heterogeneous catalyst for Ullmann homocoupling of aryl iodides and reduction of *p*-nitrophenol

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Gold nanoparticles were decorated onto sulfonated three-dimensional graphene (3DG-SO₃H) through spontaneous chemical reduction of HAuCl₄ by 3DG-SO₃H. This nanocomposite exhibited excellent catalytic activity for the synthesis of symmetric biaryls via the Ullmann homocoupling of aryl iodides in an aqueous medium. Additionally, this nanocomposite was used as a catalyst for the reduction of *p*-nitrophenol to *p*-aminophenol. The catalyst could be used more than six times successively without significant deactivation.

KEYWORDS

gold, heterogeneous catalyst, homocoupling, reduction, three-dimensional graphene

1 | INTRODUCTION

Graphene exhibits a unique combination of physical and chemical properties such as large specific surface area, low density, superior electrical conductivity, excellent thermal stability with oxidation resistance temperature, high thermal conductivity, remarkable mechanical strength and excellent optical transmittance, and is readily chemically functionalized.^[1-14] Moreover, it shows interesting electrochemical properties, including wide electrochemical potential windows, low chargetransfer resistance, low cost of fabrication and excellent electrochemical activity.^[15-17] However, graphene sheets tend to undergo irreversible restacking arising from the strong π - π interactions and van der Waals forces, which tremendously compromises the superiority of the inherent high specific surface area, high conductivity and mechanical strength of individual graphene sheets.^[18–21]

Many attempts have been made to tackle this challenge. One effective way is to engineer a graphene material in which individual graphene sheets are bonded together to construct three-dimensional porous networks, alleviating the restacking of individual graphene sheets. Three-dimensional graphene (3DG) is commonly produced using sol-gel chemistry, which involves the reducing of graphene oxide (GO) to form a highly crosslinked graphene hydrogel, followed by freeze or supercritical drying.^[22,23] 3DG has excellent properties, including an ultrahigh surface-to-volume ratio, high surface area, high porosity, low density, good electric conductivity, strong mechanical strength and fast mass and electron transport kinetics, which make it an ideal material for supercapacitors, catalysts, electrochemical biosensors and anodes in lithium ion batteries.^[24]

Additionally, the low water and organic dispersibility of graphene materials has led to many attempts to increase the solvent dispersibility of graphene. Recently, a facile route to isolated and water-soluble graphene involved the sulfonation of graphene with *p*-sulfobenzenediazonium salt.^[25-29] When graphene sheets incorporate SO₃⁻ moieties, the graphitic sheets will separate from one another to some distance due to electrostatic repulsion.^[30]

Gold nanoparticles (Au NPs) have been demonstrated in past decades to be efficient catalysts for various reactions, such as oxidation of alcohols, secondary amines and carbon monoxide, hydrogenation of olefins and nitroarenes, formation of nitrogen-containing compounds, etc.^[31] In recent research, Au NP catalysts have been utilized in carbon–carbon coupling reactions. These coupling reactions have been established as convenient and general approaches for the production of biaryls. Biaryl scaffolds are ubiquitous building blocks in many biologically active compounds, commercial dyes, agrochemicals, natural products, conducting materials and pharmaceutical organic compounds.^[32]

In conjunction with our research aimed at the preparation of metal–graphene composite catalysts for organic reactions,^[33–35] herein we report a novel protocol for the Ullmann homocoupling reaction catalysed by Au NPs@3DG-SO₃H composite in aqueous solution. The preparation of the Au NPs@3DG-SO₃H nanocomposite is described in Scheme 1. GO as a starting material was synthesized from commercial graphite using the modified Hummers method.^[36] The 3DG was assembled with GO sheets by hydrothermal treatment with the assistance of thiourea.^[37] The 3DG-SO₃H nanocomposite was synthesized by anchoring sulfonic acid groups on 3DG. Then, Au NPs were decorated onto the 3DG-SO₃H through spontaneous chemical reduction of HAuCl₄ by 3DG.

2 | EXPERIMENTAL

2.1 | Preparation of GO

Graphite powder (2.5 g) was first treated with a mixture of 12.5 ml of concentrated H_2SO_4 with 2.5 g of $K_2S_2O_8$ and 2.5 g of P_2O_5 . The mixture was kept at 80 °C for 6 h. Subsequently, the mixture was cooled to room temperature and diluted with 500 ml of deionized (DI) water and left overnight. The mixture was then filtered and washed with DI water to remove the residual acid. The product was dried under ambient conditions overnight.

The pre-oxidized graphite was then subjected to oxidation using the Hummers method. The pre-treated graphite powder was put into cold (0 °C) concentrated H₂SO₄ (125 ml). Then KMnO₄ (15 g) was added gradually under stirring, and the temperature of the mixture was kept below 20 °C by cooling. The mixture was then stirred at 35 °C for 4 h and then diluted with DI water (250 ml). Because adding water to concentrated sulfuric acid medium releases large amounts of heat, the dilution was carried out in an ice bath to keep the temperature below 50 °C. After adding all of the 250 ml of DI water, the mixture was stirred for 2 h, and then an additional 750 ml of DI water was added. Shortly thereafter, 20 ml of 30% H₂O₂ was added to the mixture and the colour of the mixture changed to brilliant yellow and it began bubbling. The mixture was filtered and washed with 0.5 M HCl to remove metal ions, followed by 500 ml of DI water to remove the acid. The resulting GO was dried in air.^[36]

2.2 | Preparation of 3DG

The 3DG was synthesized by hydrothermal treatment of GO suspension with the assistance of thiourea. Firstly, thiourea (1 g) was added to dispersed GO (0.1 g, 100 ml), and then the mixture was sealed in a Teflon-lined stainless steel autoclave and maintained at 180 °C for 4.5 h. After that, the graphene assembly was dipped into DI water for 24 h to remove of the residual thiourea. Finally, vacuum freeze-drying was used to afford the 3DG structure.^[37] The loading of sulfur was determined to be 1.82 mmol g⁻¹ from elementary analysis (CHNS).

2.3 | Preparation of 3DG-SO₃H

A 4-sulfobenzenediazonium salt was used for sulfonation, which was prepared from the reaction of sulfanilic acid (2 mmol), NaNO₂ (2.2 mmol), HCl solution (1 M, 10 ml) and water (20 ml) in an ice bath. The diazonium salt solution was added to a dispersion of 3DG (40 mg, 20 ml) in an ice bath under stirring, and was kept in an ice bath for





2 h. Then, the mixture was washed with H₂O–EtOH (1:1). Also, the acid capacity of the functionalized solid carbon was measured according to standard acid–base titration of ion-exchanged materials in which 50 mg of catalyst was suspended into 50 ml of NaCl (2 M) for 24 h^[38] (acidity of 0. 71 mmol g⁻¹)). The loading of sulfur was determined to be 2.65 mmol g⁻¹ from elementary analysis (CHNS).

2.4 | Preparation of Au@3DG-SO₃H

 $3DG-SO_3H$ (200 mg) was dispersed in 20 ml of water. Then, 0.065 ml of HAuCl₄ (0.039 M) was added to the $3DG-SO_3H$ suspension under stirring and kept for 2 h at room temperature with constant stirring. The resulting mixture was washed with DI water and ethanol, and dried at room temperature. Inductively coupled plasma analysis gave the actual gold content as 0.20 wt% for the Au NPs@3DG-SO₃H nanocomposite.

2.5 | General procedure for Ullmann reaction

Aryl iodide (2 mmol), K_3PO_4 (6 mmol), water (4 ml) and Au NPs@3DG-SO₃H nanocomposite (1 mol% Au) were mixed in a 10 ml round-bottom flask. The resulting mixture was refluxed at 100 °C, and the reaction monitored by TLC. After the completion of the reaction, the reaction mixture was cooled to room temperature and ethyl acetate was added to the flask. The organic phase was dried over anhydrous MgSO₄ and filtered. The crude reaction mixture was concentrated under vacuum. The residue was purified by silica gel TLC using *n*-hexane–ethyl acetate as eluent to afford the pure product.

2.6 | General procedure for reduction of *p*-Nitrophenol (*p*-NP)

An amount of 30 ml of *p*-NP (0.12 mM) was mixed with 30 ml of a freshly prepared aqueous NaBH₄ solution (0.17 M). Then, Au NPs@3DG-SO₃H nanocomposite (1 mol% Au) was added to the resulting solution, and the reaction conversion was determined using UV–visible spectroscopy.

2.7 | Analytical data

Compounds 2a,^[39] 2b,^[39] 2c,^[39] 2d,^[40] 2e,^[41] 2f^[39] and 2 g^[39] are known compounds and have been reported previously.



1,1'-Biphenyl (**2a**). White solid; m.p. 65–66 °C (lit.^[39] 67–69 °C). ¹H NMR (300 MHz, DMSO- d_6 , δ , ppm): 7.68– 7.65 (m, 4H), 7.47 (t, J = 7.7 Hz, 4H), 7.39–7.34 (m, 2H).



4,4'-Dimethyl-1,1'-biphenyl (**2b**). White solid; m.p. 117–119 °C (lit.^[39] 118–120 °C). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.52–7.49 (m, 4H), 7.28–7.25 (m, 4H), 2.41 (s, 6H).



4,4'-Dimethoxy-1,1'-biphenyl (**2c**). White solid; m.p. 170–172 °C (lit.^[39] 173–175 °C). ¹H NMR (300 MHz,



FIGURE 1 Raman spectra of 3DG, 3DG-SO₃H and Au NPs@3DG-SO₃H



FIGURE 2 TGA plots of 3DG, 3DG-SO₃H and Au NPs@3DG-SO₃H

DMSO-*d*₆, δ, ppm): 7.54–7.51 (m, 4H), 7.00–6.96 (m, 4H), 3.76 (s, 6H).



FIGURE 3 XRD patterns of 3DG, 3DG-SO₃H and Au NPs@3DG-SO₃H

1,1'-([1,1'-Biphenyl]-4,4'-diyl)bis(ethan-1-one) (2d). White solid; m.p. 192–194 °C (lit.^[40] 194–195 °C). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.10–8.07 (m, 4H), 7.76–7.73 (m, 4H), 2.69 (s, 6H).



4,4'-Dimethyl-1,1'-biphenyl (**2f**). Oil.^[39] ¹H NMR (300 MHz, DMSO- d_6 , δ , ppm): 7.30–7.19 (m, 6H), 7.05–7.2 (m, 2H), 1.97 (s, 6H).

3 | **RESULTS AND DISCUSSION**

Raman spectroscopy is a useful tool for the characterization of carbon materials and provides information on the structure, quality and electronic properties of graphene materials. The Raman spectra of 3DG, 3DG-SO₃H and Au NPs@3DG-SO₃H are shown in Figure 1. The intensity ratio of G-band and D-band (I_D/I_G) is a general parameter, reflecting the carbon hybridization state of materials and the degree of disorder.^[42] I_D/I_G decreased from 1.07 for 3DG to 1.04 for 3DG-SO₃H,



FIGURE 4 SEM image of (a) 3DG, (b) 3DG-SO₃H and (c) Au NPs@3DG-SO₃H; corresponding quantitative EDS elemental mapping of (d) au, (e) S and (f) N

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which can be explained the linkage of the arylsulfonic acid on 3DG and the increasing sp² carbons on 3DG-SO₃H compared to 3DG. After decoration with Au NPs, I_D/I_G increased to 1.11 that indicated the probable chemical interaction or bonding between the Au NPs and 3DG.^[43]

Thermogravimetric analysis (TGA) plots of 3DG, 3DG-SO₃H, and Au NPs@3DG-SO₃H are shown in

Figure 2. The TGA curve of Au NPs@3DG-SO₃H nanocomposite shows high thermal stability. The total weight lost was only 7.5% at temperatures below 350 °C. Additionally, the rate of weight loss for the Au NPs@3DG-SO₃H nanocomposite increased giving 3DG-SO₃H composite at temperatures greater than 400 °C. This result shows the catalytic activity of Au NPs in the oxidative degradation processes.



FIGURE 5 TEM images of au NPs@3DG-SO₃H nanocomposite

TABLE 1 Nitrogen adsorption-desorption analysis results for 3DG, 3DG-SO₃H and Au NPs@3DG-SO₃H

	3DG	3DG-SO ₃ H	Au NPs@3DG-SO ₃ H
Surface area $(m^2 g^{-1})$	86.70	28.09	84.41
Average pore volume (cm ³ g ⁻¹)	0.22	0.09	0.21
Average pore size (nm)	14.8	13.3	13.9



FIGURE 6 Nitrogen adsorption-desorption isotherms of 3DG, 3DG-SO₃H and Au NPs@3DG-SO₃H

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The X-ray diffraction (XRD) patterns of 3DG, 3DG-SO₃H and Au NPs@3DG-SO₃H are shown in Figure 3. The broad peak at $2\theta = 20-30^{\circ}$ of the graphite plane [0 0 2] is observed in the pattern of 3DG that indicated the framework of 3DG is composed of few-layer stacked graphene sheets.^[44] The weak peak at $2\theta = 37.90^{\circ}$ corresponds to the [1 1 1] lattice plane of Au(0). Also, the peaks at $2\theta = 44^{\circ}$ and 64° correspond to the stainless steel sample holder of the powder diffractometer.

(a)

25

CPS

The three-dimensional morphology of 3DG was confirmed using scanning electron microscopy (SEM) characterization (Figure 4). 3DG, 3DG-SO₃H and Au NPs@3DG-SO₃H exhibit typical three-dimensional porous networks. Additionally, energy-dispersive X-ray spectroscopy (EDS) mapping shows that the elements Au, S and N are found to be uniformly dispersed on the whole surface of the Au NPs@3DG-SO₃H nanocomposite (Figure 4d–f).

Transmission electron microscopy (TEM) images of the Au NPs@3DG-SO₃H nanocomposite are shown in Figure 5. The cross-linked graphene sheets are also folded or crinkled, as is evident from the TEM images. The surface of 3DG-SO₃H is covered with a good dispersion of Au NPs with an average size of *ca* 20 nm. Additionally, Au NPs are not found outside of the 3DG-SO₃H sheets.

Nitrogen sorption isotherms were used to investigate the surface areas and pore structures of the as-prepared composite. The Brunauer-Emmett-Teller surface area, average pore volume and average pore size are summarized in Table 1. After sulfonation, the surface area markedly decreased from 86.70 to 28.09 m² g⁻¹ that can be attributed to the sulfonic acid groups which are capable of hydrogen bonding, promoting intermolecular interactions between neighbouring sheets, and resulting in a reduction in the free volume.^[45] After decoration of Au NPs on 3DG-SO₃H, the surface area increased to 84.41 m² g⁻¹, which can be attributed the Au NPs acting as spacers in the 3DG network thereby preventing and hydrogen bonding agglomeration between neighbouring sheets.^[35] As shown in Figure 6, the nitrogen sorption isotherms of the three materials are of type IV.

The chemical composition of the Au NPs@3DG-SO₃H nanocomposite was characterized using X-ray photoelectron spectroscopy (XPS). As shown in Figure 7a, peaks corresponding to Au 4f, C 1 s, N 1 s, O 1 s and S 2p are observed in the XPS full spectra. The N 1 s core level spectrum can be deconvoluted into four component peaks at binding energy of about 398.64, 399.77, 400.68 and 402.05 eV, corresponding to pyridinic N, pyrrolic N, quaternary N and *N*-oxide of pyridinic nitrogen, respectively (Figure 7b).^[46] The core level region of S 2p includes four components (Figure 7c). The contributions at binding



FIGURE 7 (a) Full range XPS spectrum of Au NPs@3DG-SO₃H nanocomposite; (b) N 1 s, (c) S 2p and (d) Au 4f core level region XPS spectra of au NPs@3DG-SO₃H nanocomposite

energies of around 163.61 and 164.57 eV can be attributed to the bonding sulfur in C—S_n—C (n = 1 or 2) bonds and conjugated —C=S— bonds (should be from thiophenetype), respectively. The other two contributions at higher and lower binding energies of around 167.97 and 161.48 eV can be assigned to the (—SO₃) and reduced (—SH) sulfur moieties, respectively.^[47] The core level region of Au 4f for the Au NPs@3DG-SO₃H nanocomposite shows two peaks at 84.01 and 87.68 eV which are attributed to the binding energy of Au 4f_{7/2} and Au 4f_{5/2}, respectively (Figure 7d). This result shows the spontaneous reduction of HAuCl₄ on 3DG surface, which involved the pervious spontaneous reduction of HAuCl₄ on graphene sheets.^[31]

The catalytic activity of the Au NPs@3DG-SO₃H composite as a catalyst was tested in the Ullmann homocoupling reaction. To optimize the reaction conditions, the homocoupling of iodobenzene was used as a model reaction in water as solvent at 100 °C with K₃PO₄ as the base and with a catalyst loading of 1 mol% of Au (Table 2). Under these conditions, we found the homocoupling reaction proceeds well, affording a promising high yield (93%) of the corresponding biphenyl (Table 2, entry 1). Various types of bases such as K₂CO₃, Cs₂CO₃ and KOH were tested, and they showed low efficiency and afforded low yields (Table 2, entries 1–4). Additionally, the loading of gold was optimized. An amount of 2 mol% of gold did not change the yield;

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however, the yield decreased when the amount of gold was reduced to 0.5 mol% (Table 2, entries 5 and 6). The effect of temperature on the reaction was studied. Several experiments were performed at 80, 100 and 120 °C (Table 2, entries 1, 7 and 8). The optimal reaction temperature is 100 °C (Table 2, entry 4). It is also noteworthy that, when this reaction was carried out with 3DG or $3DG-SO_3H$, we failed to isolate any coupled product (Table 2, entries 9 and 10).

Having obtained the optimal reaction conditions, we set out to explore the scope of the reaction with various aryl iodides. Aryl iodides bearing electron-donating groups (p-Me and p-OMe) reacted to give higher yield than aryl iodides possessing electron-withdrawing groups (p-COMe and p-NO₂) (Table 3, entries 2–5). The hindered substrate (2-iodotoluene) converted to the corresponding homocoupling product with moderate yield (Table 3, entry 6). Furthermore, it was observed that Au NPs@3DG-SO₃H could also act as an excellent catalyst for the homocoupling of 1-iodonaphthalene to yield 1,1'binaphthyl with 92% conversion (Table 3, entry 7). Under the same reaction conditions, the homocoupling of bromobenzene and aryl bromide bearing electron-donating and electron-withdrawing groups failed to form homocoupled products (Table 3, entries 8-10).

Reusability is an important characteristic of heterogeneous catalysis which should be examined in catalytic reactions. Therefore, we performed a reusability test for

TABLE 2 Effect of various bases on Ullmann coupling of iodobenzene^a

	La Conditions	2a	
Entry	Base	Temperature (°C)	Yield (%) ^b
1	K ₃ PO ₄	100	93
2	K ₂ CO ₃	100	21
3	Cs ₂ CO ₃	100	58
4	КОН	100	74
5 ^c	K ₃ PO ₄	100	94
6 ^d	K ₃ PO ₄	100	59
7	K ₃ PO ₄	80	62
8	K ₃ PO ₄	120	93
9 ^e	K ₃ PO ₄	100	Trace
$10^{\rm ff}$	K ₃ PO ₄	100	Trace

 a Iodobenzene (1.0 mmol), base (3.0 mmol), Au NPs@3DG-SO_3H (1.0 mol% Au), H_2O (4 ml).

^bGC yield; *n*-dodecane used as an internal standard.

^cAu NPs@3DG-SO₃H (2.0 mol% gold).

^dAu NPs@3DG-SO₃H (0.5 mol% gold).

^e3DG (50 mg).

^f3DG-SO₃H (50 mg).



 TABLE 3
 Homocoupling of aryl halides catalysed by Au NPs@3DG-SO₃H^a

	R + X Au NPs@3DG-SO ₃ H (1		
Entry	Aryl halide	Product	Yield (%) ^b
1	1a la	2a	93
2	l 1b	2b	91
3			92
4	U Id	O 2d O	86
5	O ₂ N 1e	NO ₂ O ₂ N 2e	83
6	I If	2f	78
7	I 1g	2g	92
8	Br 1h	2a	Trace
9	Br 1i	2b	Trace
10	O ₂ N Br 1j	2e	Trace

 a Aryl halide (2.0 mmol), K_3PO_4 (3.0 mmol), Au NPs@3DG-SO_3H (1 mol%), H_2O (4 ml), 100 °C, 18 h. b Isolated yield.

the Au NPs@3DG-SO₃H composite in the Ullmann homocoupling of iodobenzene under the optimized conditions. After reaction completion, the catalyst was collected by centrifugation. By adding a new batch of iodobenzene and K_3PO_4 , the recovered composite can be used directly for the next run. This recycling protocol enabled Au NPs@3DG-SO₃H to be used for six runs furnishing quantitative conversion of the substrate without loss of activity and selectivity. Figure 8a depicts results for the recovery and reusability of the Au NPs@3DG-SO₃H composite. Furthermore, no significant change was observed in the morphology of the Au NPs@3DG-SO₃H nanocomposite after the six runs, which was concluded from the TEM image in Figure 8b. The heterogeneous





FIGURE 8 (a) Recycling of Au NPs $@3DG-SO_3H$ composite in Ullmann homocoupling of iodobenzene. (b) TEM image of the composite after six runs

nature of the catalyst was examined using atomic absorption spectroscopy. The amount of gold leaching from the supported catalyst was thus determined, and the result indicated that gold concentration was less than 2.0 ppm in the reaction solution. Inductively coupled plasma analysis of the used Au NPs@3DG-SO₃H composite catalyst indicated leaching of 1.9% of gold in the Ullmann homocoupling of iodobenzene after the six cycle. Additionally, the hot filtration test (*ca* 50% conversion of



FIGURE 9 (a) UV-visible spectra of formation *p*-nitrophenolate after addition NaBH₄ solution to *p*-NP solution. (b) Time-dependent UV-visible absorption for reduction of *p*-NP in the presence of Au NPs@3DG-SO₃H nanocomposite. (c) Plot of $\ln(C_t/C_0)$ versus reaction time for reduction of *p*-NP catalysed by Au NPs@3DG-SO₃H nanocomposite

TABLE 4	Comparison of	efficiency of gold	heterogeneous	catalysts in	Ullmann	homocoupling of iodo	bezene
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Catalyst	Size of Au NPs (nm)	Conditions	Time (h)	Yield (%)	Ref.
Au NPs@3DG-SO3H	20	K ₃ PO ₄ , H ₂ O, 100 °C	18	93	This work
Au/Fe ₃ O ₄ /s-G	20-35	K ₃ PO ₄ , H ₂ O, 100 °C	48	95	[30]
AuNPs-RGO	10-20	K ₃ PO ₄ , NMP, 100 °C	6	97	[31]
Au@PMO	3–15	K ₃ PO ₄ , NMP, 100 °C	16	95	[48]
Au ₂₅ (SR) ₁₈ /CeO ₂	1.3	K ₂ CO ₃ , DMF, 130 °C	48	99.8	[49]
NAP-mg-au	5-7	K ₂ CO ₃ , DMF, 140 °C	48	92	[50]



TABLE 5Reusability of Au NPs@3DG-SO₃H nanocomposite inreduction of p-NP^a

Reaction cycle	1	2	3	4	5	6
Yield (%) ^b	98	98	97	95	95	92

 $^{\rm a}30$ ml of 0.12 mM p-NP, 30 ml of 0.17 M NaBH_4 and Au NPs@3DG-SO_3H nanocomposite (1 mol% gold).

^bYield determined by GC analysis.

iodobenzene) was used. The hot filtrates were transferred to another flask containing water at 100 °C. Upon further heating of catalyst-free solution for 16 h, no considerable progress (*ca* 3% by GC analysis) was observed. These results confirmed the heterogeneous character of the catalytically active species in this reaction.

A comparison was made of the present method with other reported heterogeneous gold catalytic systems in the Ullmann homocoupling of iodobenzene and the results are presented in Table 4. Clearly, the present method represents a simple, green (using water as solvent), highly effective, less time-consuming method for the Ullmann homocoupling reaction.

Additionally, the catalytic activity of the Au NPs@3DG-SO₃H nanocomposite was tested for the reduction of p-NP using NaBH₄ as a reducing reagent. After the addition NaBH₄ solution to *p*-NP solution, the formation *p*-nitrophenolate in the alkaline medium resulted in a maximum absorption peak wavelength shift from 315 to 400 nm (Figure 9a). After the addition of the Au NPs@3DG-SO₃H nanocomposite, the intensity of this peak reduced and a new peak at 310 nm appeared that indicated the successful reduction of p-nitrophenolate (Figure 9b). As shown in Figure 9c, a linear relationship between $\ln(C_t/C_0)$ versus reaction time was obtained, indicating the reduction followed pseudo-first order reaction kinetics. The rate constant k was calculated to be 0.116 min^{-1} .

The reusability of the Au NPs@3DG-SO₃H nanocomposite was examined in the reduction of p-NP. It was found that recovery could be successfully achieved in six successive reaction runs (Table 5).

4 | CONCLUSIONS

A novel 3-dimensional hybrid material has been developed by immobilization of Au NPs onto $3DG-SO_3H$ through spontaneous chemical reduction of $HAuCl_4$ by $3DG-SO_3H$. The as-prepared Au NPs@3DG-SO_3H nanocomposite hybrid exhibited excellent catalytic activity for the synthesis of symmetric biaryls via the Ullmann homocoupling of aryl iodides in an aqueous medium. Additionally, this nanocomposite was used as a catalyst for the reduction of *p*-NP to *p*-aminophenol.

Additionally, the catalyst was chemically stable and could be recycled at least six times in the corresponding reaction without a reduction in the catalytic activity and could be separated by simple centrifugation and reused for further reaction cycles.

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