



Hydrothermally Synthesized CuCo_2S_4 Nanosheets as an Easily Accessible and Convenient Heterogeneous Catalyst for the Sonogashira Cross-Coupling Reactions

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A high surface area and the possibility of high charge separation and transportability make the two-dimensional (2D) nanomaterials very special in many applications, particularly in the field of catalysis. The usefulness of 2D nanomaterial is positively demonstrated in this study by employing it as an efficient heterogeneous catalyst in Sonogashira cross-coupling reaction, where the later one is well known for the formation of carbon-carbon bonds. 2D nanosheets of CuCo_2S_4 are synthesized using a hydrothermal synthesis and the average thickness of the sheets is found to be in the range of 10–15 nm. The transparent nanosheets are interconnected to form thick sheets and then aggregated to form a highly open three-dimensional hierarchical structure. This study explores the Sonogashira reaction very efficiently in water/ethanol at room temperature using hydrothermally synthesized CuCo_2S_4 nanosheets as catalyst for the C-C coupling reaction for the first time. The developed method is found to be economic, green, high yields, low catalyst loading and reusability of the catalysts. This present CuCo_2S_4 nanosheet heterogeneous catalyst afford the Sonogashira coupling of various aryl halides with terminal alkynes, giving a variety of aryl acetylenes in excellent yields and can be recovered by a simple filtration and reused for at least 10 consecutive reactions with almost constant yield and activity.

Keywords: CuCo_2S_4 , nanosheet, thiospinel two-dimensional (2D), sonogashira coupling, cross-coupling reaction

INTRODUCTION

Over the past decades, two-dimensional nanosheets possess a specific perspective in nanoscience and nanotechnology. The sheet nanostructures are very important as they provide more surface area in comparison to other morphologies obtained from nanomaterials like nanoplates, nanowires, nanodiscs etc. (Liu et al., 2011; Min et al., 2012; Gunjekar et al., 2013; Chauhan et al., 2016). Therefore, remarkable development has been seen in 2D materials due to their potential applications in gas storage, sensing, catalysis, electronic applications like supercapacitors, batteries, and electrolyzer cell and hydrogen storage applications (Tan and Zhang, 2015; Chauhan et al., 2017a; Antil et al., 2019). The 2D materials which have individual properties like pure crystalline nature, tunable thickness, and extraordinary mechanical-thermal stability with high charge conductivity endowed them vital for various catalytic reactions. Moreover, the planar nature of nanosheets facilitates easy adsorption and removal of reactant species which also enhance their

reactivity. Because of unique features and outstanding performances, 2D nanomaterials are very popular and extensive research efforts have been dedicated for their development and exploration of their properties like lateral size dependent transport, crystal phase, defects, layer thickness, and surface properties (Mika et al., 2018). But still synthetic procedures for the 2D materials with desirable topographies is somewhat challenging.

Two-dimensional transition-metal chalcogenides have tremendously impacted the areas of heterogeneous catalysis in many organic transformation reactions, such as in oxidation, reduction, C-C coupling, C-S coupling, C-N coupling, etc. Cross-coupling (C-C) reactions play the main role in organic synthesis to set up the carbon skeleton of organic molecules (Maaliki et al., 2017). Transition-metal based catalysts (such as Pd, Cu, Ni etc.) displayed remarkable efficiency for achieving these reactions. Mainly palladium (Oppolzer et al., 1991), or nickel (Beletskaya et al., 2003) complexes have been used for “cross-coupling reactions.” Sonogashira reaction is the most general, reliable, and effective method for the building of C(sp²)-C(sp) bonds by cross-coupling of terminal alkyne and aryl halide (Tykwinski, 2003; Nicolaou et al., 2005; Chinchilla and Nájera, 2007). This reaction has been successfully used in the synthesis of natural products (Toyota et al., 2000), biologically active compounds (Cosford et al., 2003), materials showing photophysical properties (Mongin et al., 2002); polymeric materials (Li et al., 1999), and polyalkynylated molecules (Mongin et al., 1998). Sonogashira reactions occurs in the presence of Pd(OAc)₂ (Oppolzer et al., 1991), Palladium complexes such as Pd(PPh₃)₄ (Nicolaou et al., 2005), [PdCl₂(PPh₃)₂] (Nicolaou et al., 2001) and copper (I) iodide as a co-catalytic salts. As the Palladium is expensive, hence nowadays researchers are exploring the methods which can replace the costly metals with the cheaply available metals such as Nickel (Beletskaya et al., 2003), Copper etc. (Thathagar et al., 2004). Because antecedently copper salts were used in the catalytic reactions with the palladium complexes (Nicolaou et al., 2005), recent attention has been focused on employing copper-only or copper based catalytic systems in Sonogashira coupling. Ma et al. reported first time the coupling reaction of aryl halides and terminal alkynes in the presence of Copper iodide and *N,N*-dimethylglycine hydrochloride salt (Ma and Liu, 2004). Rothenberg et al. also reported Sonogashira coupling using copper nanoclusters (Thathagar et al., 2004). The literature studies on the various organic reactions catalyzed over transition metal oxide/chalcogenide nanosheets have clearly demonstrated that these materials reduce the reaction barrier of many organic reactions (coupling reactions, oxidation-reduction, polymerization, cycloaddition, and condensation processes) and control of the reaction products (Raza et al., 2016). These studies also unrevealed why 2D nanosheet morphology of transition metal chalcogenides are very popular in heterogeneous catalysis. The synergy effect of reactant molecules with catalyst surface and activity allow some reactions to catalyzed with different pathways and amended their product selectivity (Ng and Raiteses, 2015; Zhou et al., 2017). Very recently, various homo-coupling and cross-coupling reactions were widely studied over 2D nanosheets of WS₂ (Raza et al., 2016) and

Pd-doped WS₂ (Raza et al., 2017) with remarkable reactivity and permanence.

Herein, we report an effective approach of hydrothermally synthesized CuCo₂S₄ two-dimensional nanosheets for cross-coupling reactions of terminal alkynes and aryl halides. The CuCo₂S₄ nanosheets work as a heterogeneous catalyst with exceptional performance (yield up to 95%). 2D CuCo₂S₄ nanosheets were applied without any exfoliation, surface modification or without the introduction of any foreign expensive metal particles (Pt, Pd, Ru) or without the addition of any co-catalysts under very mild conditions (water /ethanol, 25°C). In addition, all reaction condition like the variation in the solvent mixture, temperature, catalyst loading, and reaction mechanism was investigated thoroughly. Furthermore, durability of the catalyst was examined by running continuous 10 cycles of used catalyst, where the catalyst showed retentivity of its properties suggesting the great strength and high reactivity toward cross-coupling reactions. It was found that the introduction of electron-donating and electron-withdrawing groups in aryl halide didn't affect the efficiency of catalyst and product was obtained with 100% selectivity. However, yield of the reactions decreases in the order of I > Br > Cl. Apart from CuCo₂S₄, two more thiospinel nanosheet samples by varying the Cu amount were synthesized following the similar synthesis method, viz. Cu_{0.5}Co_{2.5}S₄ and Co₃S₄ to examine the effect of Cu incorporation into the original Co₃S₄ lattice, where CuCo₂S₄ was found to be the best catalyst among them.

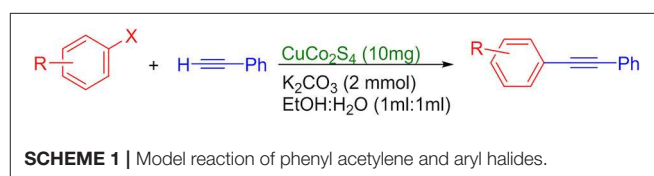
MATERIALS AND METHODS

Materials

Copper (II) sulfate pentahydrate (CuSO₄·5H₂O), cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99.5%), copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99.0%) were purchased from Sigma Aldrich USA. Thiourea (CH₄N₂S, 99%), ethylene glycol (C₂H₆O₂) and ethylenediamine (C₂H₈N₂) were purchased from Thomas Baker, India. Double distilled water was used in all experiments. 4-Bromoanisole, benzyl bromide, 4-bromotoluene, 4-*tert*butyl bromo benzene, bromo benzene, 4-nitro bromo benzene, iodo benzene, chloro benzene, phenyl acetylene, 4-bromo aniline, sodium sulfate and sodium chloride were purchased from Spectrochem. Absolute ethanol and isopropanol (99%) were procured from Fischer India, KOH from Rankem, India. All chemicals were used as received without any further purification.

Synthesis of CuCo₂S₄ Nanosheets

2D nanosheets of CuCo₂S₄ (mixed metal thiospinel) was synthesized by using a simple hydrothermal technique as



reported by our group earlier (Chauhan et al., 2017b, 2019). In a typical procedure, metal nitrate precursor of cobalt and copper, i.e., Co(NO₃)₂·6H₂O and Cu(NO₃)₂·3H₂O were dissolved in 30 ml of distilled water in a molar ratio 2:1. After stirring the solution for 10 min, 4 mmol of thiourea was added to this solution and solution further stirred for 15 min. Now

ethylenediamine (2 ml) was added into this solution and the solution color changed to brown. The whole solution was transferred to a 50 ml teflon lined autoclave. The autoclave was sealed and kept at 200°C for 12 h. The reaction vessel was allowed to cool up to room temperature. The obtained black powder product was washed with distilled water and ethanol

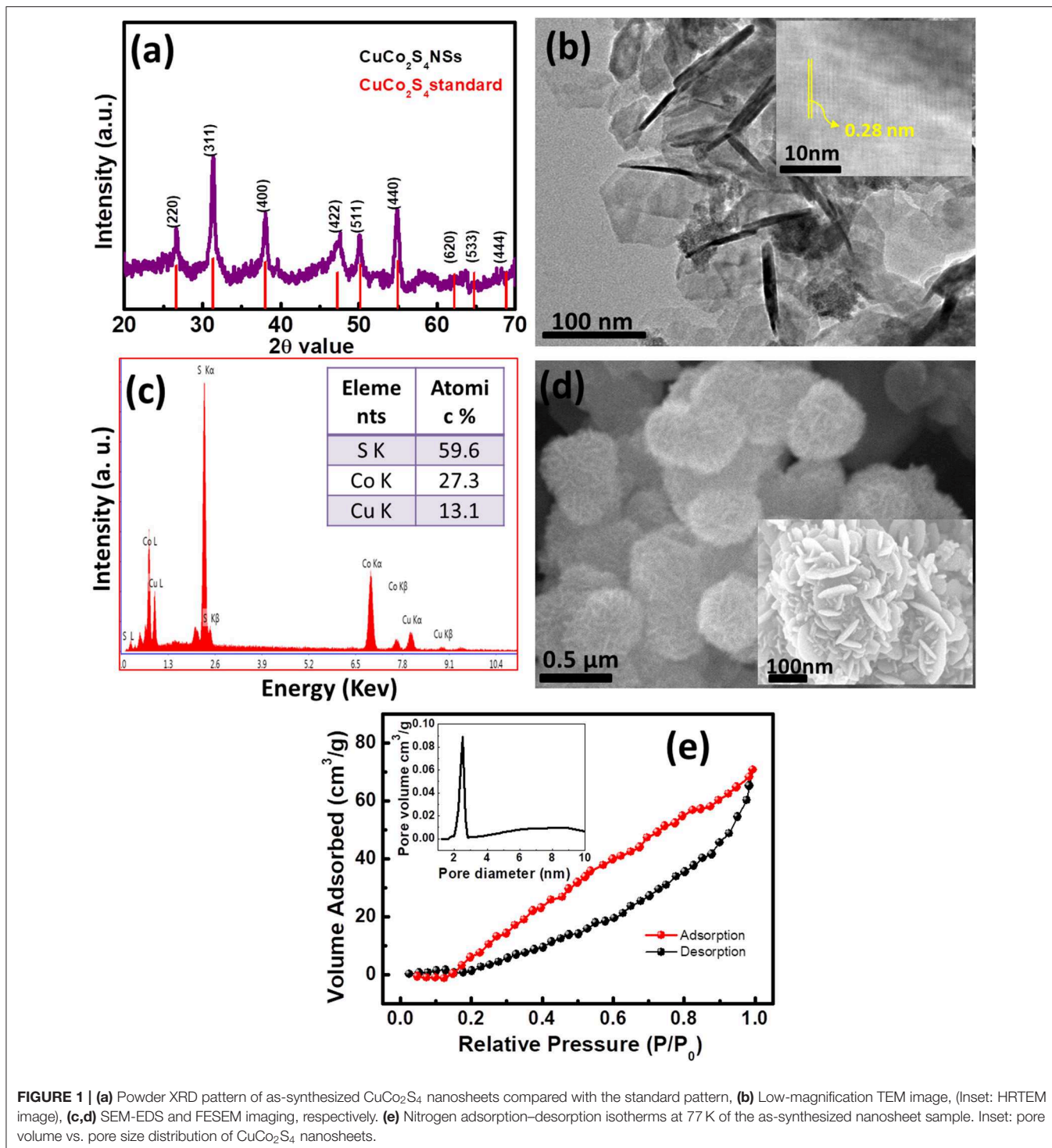


FIGURE 1 | (a) Powder XRD pattern of as-synthesized CuCo₂S₄ nanosheets compared with the standard pattern, (b) Low-magnification TEM image, (Inset: HRTEM image), (c,d) SEM-EDS and FESEM imaging, respectively. (e) Nitrogen adsorption-desorption isotherms at 77 K of the as-synthesized nanosheet sample. Inset: pore volume vs. pore size distribution of CuCo₂S₄ nanosheets.

for 3 times. The product was dried at 50°C for 6 h and stored for further studies. Nanosheets of Co₃S₄ and Cu_{0.5}Co_{2.5}S₄ were also synthesized following the method similar to that mentioned for CuCo₂S₄ nanosheets. No Cu salt was added during the synthesis of Co₃S₄. In the case of Cu_{0.5}Co_{2.5}S₄, 2.5 mmol of Co(NO₃)₂·6H₂O and 0.5 mmol of Cu(NO₃)₂·3H₂O were used during the reaction.

Characterization

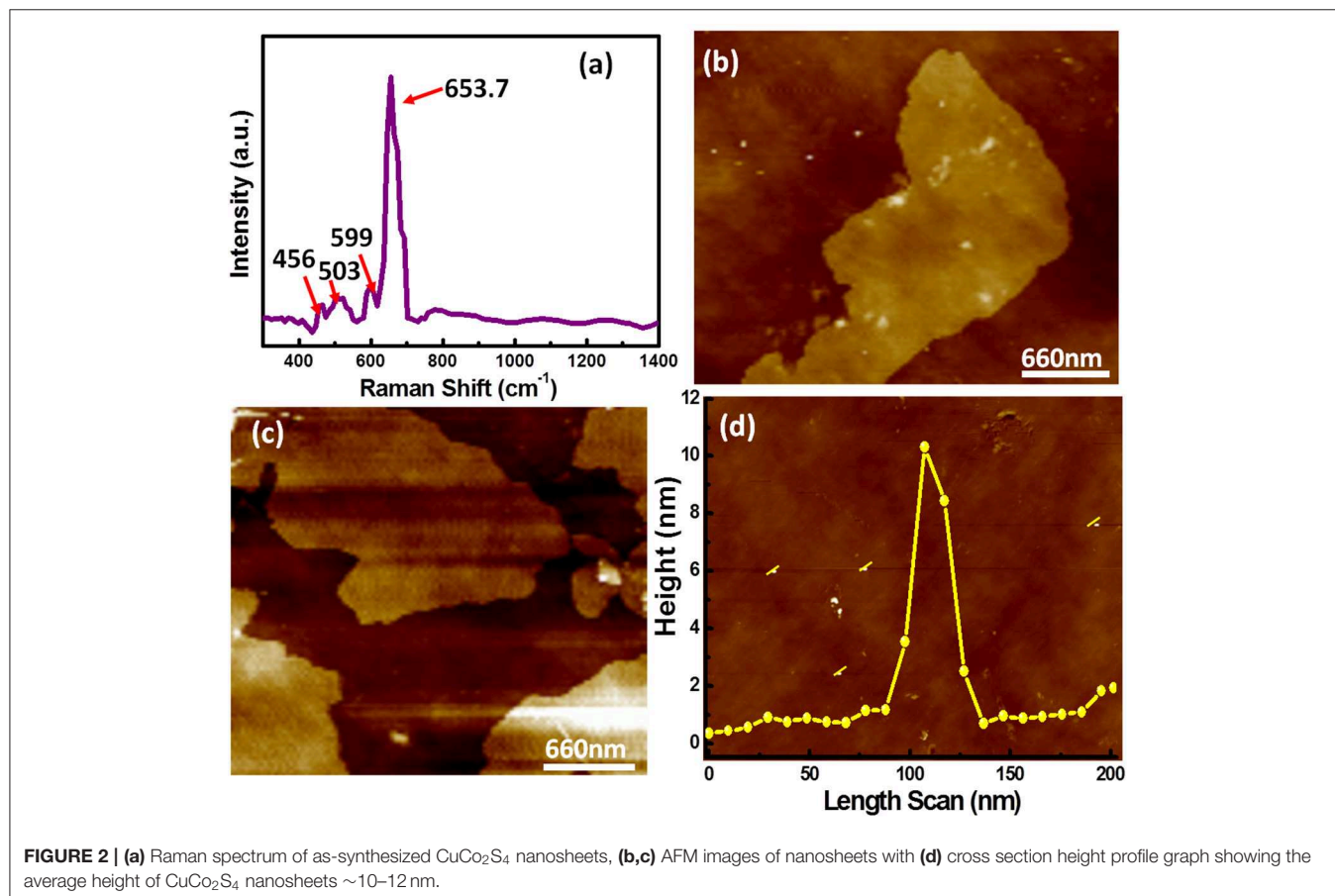
X-Ray Diffraction (XRD) patterns of thiospinel species were obtained at 298K using a Bruker D8 Advance diffractometer system using monochromatized Cu K α radiation source. Scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) measurements have been performed by using a JEOL JSM 6610 operating at 20 kV, EDAX was accomplished at a resolution of 135.2 eV. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and selected area electron diffraction (SAED) study have done by using a Philips Technai G230 transmission electron microscope with an accelerating voltage of 200 kV equipped with an energy dispersive X-ray spectroscopy (EDAX) attachment. To analyze the thickness of nanosheets AFM images were obtained by using a Bruker multimode 8 scanning probe microscope through tapping mode analysis. ¹H (proton) NMR spectra was recorded on Bruker Avance 400 MHz NMR spectrometer and CDCl₃ was used as

a solvent. Chemical shifts are reported in parts per million shift (δ -value) from (CDCl₃) (87.24 ppm for ¹H) as an internal standard. Signal patterns are indicated as s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet; bs, broad singlet; bm, broad multiplet. Mass of samples was detected using Agilent high resolution liquid chromatography and mass spectrometer (G6530AA) with mass accuracy >2 ppm.

Catalytic Reactions

All the catalytic reactions were carried out in round bottom flask. The catalytic activity of CuCo₂S₄ nanosheets was investigated in the synthesis of various diphenylacetylenes. Primarily, the catalytic reaction of nanomaterial was investigated in a model reaction of phenylacetylene and aryl halides to obtain diphenylacetylene using 10 mg of catalyst in water/ethanol mixture at 25°C (**Scheme 1**). The reaction did not proceed in the absence of the catalyst.

In order to study the efficiency of the nanocatalyst, a variety of aryl halides substrates and phenylacetylene were used to obtain various diphenylacetylenes. It is noteworthy that all the reactions proceeded smoothly and generated diphenylacetylenes in good yields (70–95%) within 150–300 min of reaction time. Furthermore, present nanosheet is found to be the best catalytic system in terms of activity, selectivity, and greenness of the



protocol, with negligible waste or by-product generation from the reaction mixture.

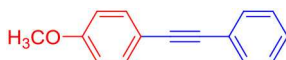
General Procedure for the Synthesis of Diphenylacetylenes. A mixture of aryl halide (1 mmol), phenylacetylene (1 mmol), catalyst (10 mg), K₂CO₃ (2.0 mmol.), ethanol (1.0 mL) and water (1.0 mL) were taken in a 10 mL round-bottomed flask and stirred at room temperature for 3–5 h. After completion of the reaction (monitored by TLC), the product was extracted in Et₂O (2 × 5 mL). The ethereal layer was dried over Na₂SO₄ and the solvent removed under reduced pressure. The crude product, thus isolated, was purified by recrystallization. All compounds were characterized by NMR and mass (see **Supplementary Material**).

NMR and mass data of the synthesized compounds in Sonogahira cross-coupling reaction.

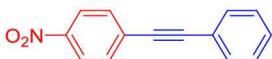
Diphenylacetylene, white solid; reported m.p. 60–62°C; observed m.p. 60°C; ¹H NMR: (CDCl₃ 400 MHz) δ 7.33–7.35 (m, 6H), 7.55–7.53 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 131.73, 128.48, 128.39, 123.37, 89.50 LCMS (ES)-calculated 178.08 found 179.06 Isolated yield: 95%.



(4-Methoxyphenyl)phenylacetylene, light yellow solid; reported m.p. 57–61°C; observed m.p. 59°C; ¹H NMR: (CDCl₃ 400 MHz) δ 3.77 (s, 3H), 6.76–6.78 (m, 2H), 7.35–7.36 (m, 3H), 7.38–7.39 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 159.71, 133.16, 131.55, 128.42, 128.05, 123.68, 115.46, 114.10, 89.48, 88.17, 55.40. LCMS (ES)- calculated 208.09 found 209.09 Isolated yield: 92%.



(4-Nitrophenyl)phenylacetylene, light yellow solid; reported m.p. 120–122°C; observed m.p. 121°C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 8.22–8.20 (d, 1H), 8.10–8.08 (d, 2H), 7.70–7.65 (m, 3H), 7.56–7.55 (m, 1H), 7.39–7.38 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 147.10, 132.72, 132.37, 131.94, 130.10, 129.38, 128.64, 125.11, 123.75, 94.80, 87.63. LCMS (ES)- calculated 223.06 found 223.09. Isolated yield: 85%.



1-methyl-4-(phenylethynyl)benzene, white solid; reported m.p. 118–122°C; observed m.p. 120°C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.53–7.50 (m, 4H), 7.36–7.32 (m, 5H), 2.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 141.40, 136.45, 131.65, 129.25, 128.87, 128.75, 128.48, 128.32, 126.44, 123.55, 91.89, 89.04, 21.64. LCMS (ES)- calculated 192.09 found 193.1005 Isolated yield: 82%.



RESULTS AND DISCUSSION

A novel hydrothermal synthesis protocol was used as per our earlier report for the synthesis of mixed-metal thiospinel CuCo₂S₄ nanosheets. The crystalline phase purity of the as-synthesized material was characterized by using powder X-ray measurements. **Figure 1a** depicts the powder XRD pattern of the as-prepared sample which matches well with the standard diffraction pattern obtained for CuCo₂S₄. The peak intensity at $2\theta = 31.6$ for (311) plane is maximum which suggested more growth of nanosheets toward the corresponding particular *hkl* values. The diffraction pattern also suggested spinel structure of CuCo₂S₄ NSs, in which all divalent metal ions (Cu²⁺) occupy the tetrahedral voids and all trivalent metal ions (Co³⁺) occupy the octahedral voids. It was reported earlier that, the octahedral coordinated site of thiospinel system are more responsible for certain catalytic activities, therefore cobalt ions plays a major role in the superior reactivity of CuCo₂S₄ (Liu et al., 2015; Chauhan et al., 2017b). The morphology of the as-synthesized material was analyzed by using transmission electron microscopy (**Figure 1b**). It reveals general sheet structure of as-prepared thiospinel sample. All nanosheets are interconnected to other adjacent sheets because of agglomeration. A few sheets lying parallel to the surface were near to transparency which specifies ultrathin nature of nanosheets. Inset of **Figure 1b** is the HRTEM image which clearly shows the lattice fringes of the nanosheets with $d = 0.54$ nm indicating the presence of largely (311) planes. FESEM imaging shows that nanosheets were not free or in isolated form. The high-magnification FESEM image in the inset (**Figure 1d**) shows that these two dimensional nanosheets are assembled and give rise to a bulkier 3D hierarchical flower like open structure. Furthermore, the ratio among the elements present in the thiospinel system was examined by using energy dispersive studies (EDS, **Figure 1c**). The ratio of Cu, Co and S is found to be close to that of 1:2:4, which supported the

TABLE 1 | CuCo₂S₄ catalyzed synthesis of diphenylacetylenes and its derivatives in one pot reaction.

Entry	Aromatic halides	Product	Time (min)	% Yield
1	Iodo benzene	Diphenylacetylene	180	95
	Bromo benzene		180	90
	Chloro benzene		210	80
2	4-Iodotoluene	1-methyl-4-(phenylethynyl)benzene	180	82
	4-Bromotoluene		200	81
	4-Chloro toluene		240	69
3	4-Iodoanisole	(4-Methoxyphenyl)phenylacetylene	190	92
	4-Bromoanisole		200	90
	4-Chloro anisole		240	75
4	4-Nitro Iodo benzene	(4-Nitrophenyl)phenylacetylene	200	85
	4-Nitro bromo benzene		240	83
	4-Nitro chloro benzene		270	70

formation of stoichiometric thiospinel CuCo₂S₄. Surface area, pore volume and pore size distribution used to be important parameters of a catalyst material. A high surface area as well as sufficient pore volume with narrow pore size distribution are highly essential to be an efficient catalyst. Hence we have carried out specific BET measurement to analyze the surface area and pore volume/pore distribution (Figure 1e). The isotherm is found to be adsorption on mesoporous solids proceeds via

TABLE 2 | Optimization study for variation of various solvents, base, time and temperature in the synthesis of diphenylacetylenes.

Entry	Variation in solvents	Base	Time (min)	Temperature	Conversion ^a
1	Water	K ₂ CO ₃	180	RT	60
2	Ethanol	K ₂ CO ₃	180	RT	50
3	THF	K ₂ CO ₃	180	RT	trace
4	Toluene	K ₂ CO ₃	180	RT	trace
5	Acetonitrile	K ₂ CO ₃	180	RT	20
6	DMF	K ₂ CO ₃	180	RT	30
7	Isopropanol	K ₂ CO ₃	180	RT	35
8	Water/ethanol	K ₂ CO ₃	180	RT	95
9	Water/ethanol	Na ₂ CO ₃	180	RT	50
10	Water/ethanol	KOH	180	RT	30
11	Water/ethanol	TEA	180	RT	40
12	Water/ethanol	NaOAc	180	RT	35
13	Water/ethanol	NaOH	180	RT	25
14	Water/ethanol	K ₂ CO ₃	180	60	70
15	Water/ethanol	K ₂ CO ₃	180	90	Trace
16	Water/ethanol	K ₂ CO ₃	30	RT	40
17	Water/ethanol	K ₂ CO ₃	60	RT	60
18	Water/ethanol	K ₂ CO ₃	90	RT	80
19	Water/ethanol	K ₂ CO ₃	120	RT	85
20	Water/ethanol	K ₂ CO ₃	150	RT	90
21	Water/ethanol	K ₂ CO ₃	240	RT	95

Reaction condition: Iodo Benzene (1 mmol), phenyl acetylene (1 mmol), base (2 mmol), catalyst, solvent (5 ml) and temperature (25°C). ^aIsolated yield.

multilayer adsorption of a combination of Type IV and V with H3 hysteresis loop. The present nanosheets exhibited 31 m²/g of specific BET surface area and 0.09 cm³/g of pore volume. A sharp mesoporous size distribution is found at 2.5 nm as seen in the inset of Figure 1e. Thus, these significant surface properties of the as-synthesized CuCo₂S₄ nanosheets demonstrate its possibility to be a good catalyst.

As prepared CuCo₂S₄ thiospinel nanosheets were further analyzed by using Raman spectroscopy (Figure 2a). The vibrational modes in the Raman spectrum of thiospinel were obtained because of lattice vibration of tetrahedral and octahedral cations. The higher frequency vibrational modes (A_{1g}) were affected directly via metal cations present in the octahedral voids while other lower frequency modes (F_{2g}, E_g) generated due to metal ion in tetrahedral voids. CuCo₂S₄ have five allowed transitions for normal spinel system. All the peaks present below 653 cm⁻¹ are corresponds to the stretching frequency of bond between octahedral coordinated metal cation and sulfur (Co-S). The vibrational mode present at 653.7 cm⁻¹ resembles to stretching frequency related to the bonding between the anions (S-S). There are no evidence of bonding between tetrahedral coordinated copper ions and sulfur (Nie et al., 2016). The surface topology and average thickness of the CuCo₂S₄ nanosheets were examined by atomic force microscopy (AFM) measurements. The AFM study of nanosheets defines the uniformity of the sheets, which also confirmed from the TEM images of nanosheets. The AFM topographic image of CuCo₂S₄ nanosheets shown in Figures 2b,c together with the sheets thickness profiles (Figure 2d) taken from the much diluted sample. The AFM analysis effectively ensure the aggregated nature of nanosheets however when we have thoroughly analyzed very diluted sample of nanosheets it discloses that the average thickness of single nanosheets was approximately 10–12 nm (Chauhan et al., 2017b).

Catalytic Application of CuCo₂S₄ Nanosheets

In order to explore C-C coupling reaction such as Sonogashira reaction, we focused our attention toward the CuCo₂S₄ catalyst

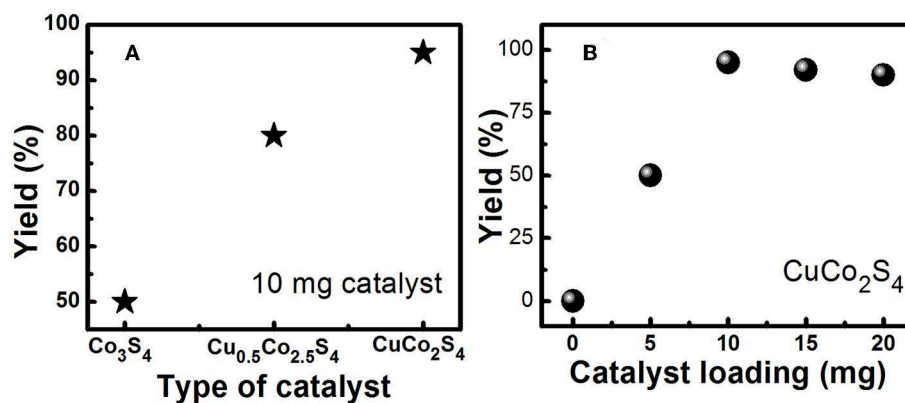


FIGURE 3 | (A) Optimization study for variation of catalyst (10 mg catalyst, 2 mmol K₂CO₃, 5 ml solvent, 180 min, 25°C). (B) Optimization study for variation of catalyst loading (CuCo₂S₄ catalyst, 2 mmol K₂CO₃, 5 ml solvent, 180 min, 25°C).

due to its easy separation, inexpensiveness and recyclability for various reactions. Its catalytic activity in the Sonogashira reaction was investigated under mild conditions. The obtained results are summarized in **Table 1**.

The coupling of iodobenzene with phenylacetylene was first chosen as the model reaction for optimization of the reaction conditions, and the effects of the concentration of catalyst, temperature, time, type of base and solvent on the reaction were examined. The results are shown in **Table 2**. Firstly, different solvents were employed in this reaction using K₂CO₃ as a base and in the presence of 10 mol% of catalyst. We can see that the water/ethanol system is best of among all tried solvents and it is greener and environmentally friendly. Reaction temperature is another parameter that considerably could affect the reaction. Therefore, its effect was also examined by performing the model reaction at room temperature (25°C), 60 and 90°C. According to the results shown in **Table 2**, the reaction can be carried out optimally at 25°C resulting in higher conversion into desirable product. On increasing the temperature there is a degradation of catalyst (color change from black to green). Same way, the types of base used in these reactions also affect their yields. The substrate conversions and product yields (%) are calculated as reported earlier (Deori et al., 2015). So, in the next step, various types of organic and inorganic bases were investigated. K₂CO₃ conduct the reaction effectively. Thus, considering more availability of K₂CO₃ and its lower price, it was chosen as the optimum base for the reaction. As it is mentioned in the experimental section, two more nanosheet samples, viz. Co₃S₄ and Cu_{0.5}Co_{2.5}S₄ were synthesized and now these two are too loaded as catalyst for the Sonogashira reaction as shown in **Figure 3A**. We found that the activity of the catalyst is increasing with the increase of copper amount in the catalyst. We also varied the loading amount of catalyst (5, 10, 15, and 20 mg) as shown in **Figure 3B**. Low yield is observed for 5 mg of catalyst loading, and the yield became maximum for 10 mg of catalyst loading. After that there is saturation in the reaction and no further increase in yield was observed on increasing the catalyst loading. Hence 10 mg of Cu_{0.5}Co_{2.5}S₄ nanosheet catalyst, 2 mmol K₂CO₃ base,

5 ml water/ethanol solvent, 180 min of reaction time and 25°C reaction temperature is found to be the best condition for the synthesis of diphenylacetylenes and its derivatives in one pot reaction with maximum yield.

From the optimized conditions, we have explored the Sonogashira reaction. The results are summarized in **Table 1** (Entry 1). We have introduced different types of aryl halides containing both electron-donating and electron-withdrawing groups under the defined conditions. In general, the reactivity of aryl chlorides in the coupling reactions is low and same has been observed in the present case too where yield of the reaction decreases in the order of I > Br > Cl. However, employment of these presently delivered conditions are found to be best suitable to carry out the reactions between various types of aryl chlorides as well as aryl iodides and bromides. Observing the excellent activity of the present nanosheets catalytic system under the

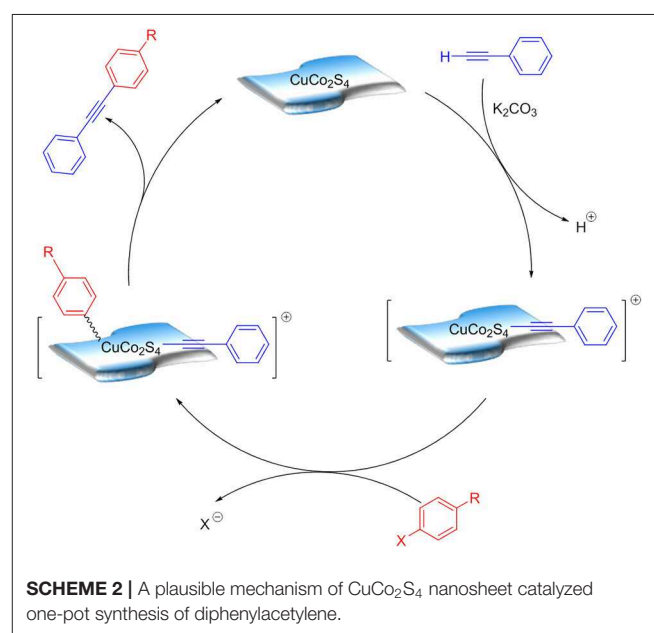


TABLE 3 | Comparison of the catalytic properties (synthesis of diphenylacetylenes) between present CuCo₂S₄ nanosheets and literature reports.

Sl. No.	Catalysts	Reaction Condition	% Yield	Literature
1.	CuCo ₂ S ₄	Room Temperature, water/EtOH	95	Current work
2.	Palladium catalyst with 2,20,7,70-tetra(4-pyridyl)-9,90-spirobifluorene,	80° 6h	91	Zhang et al., 2016
3.	Reduced graphene oxide-supported CuPd alloy nanoparticles	DMF, 120°C, 1 h	95	Diyarbakir et al., 2015
4.	<i>In situ</i> generated supramolecular ensemble 6:CuO NPs as Catalysts	3h, K ₂ CO ₃ , EtOH	90	Deol et al., 2016
5.	Iron oxide-supported copper oxide nanoparticles	100 mg catalyst, no solvent, 60 min 140°C	96	Shelke et al., 2014
6.	CuI-catalyzed	CuI, K ₂ CO ₃ , DMF, 100°C, 24 h.	82–98%	Ma and Liu, 2004
7.	Ni–Cu system	CS ₂ CO ₃ , 100°C argon atmosphere, 9h.	89%	Mukherjee et al., 2014
8.	PdCl ₂	Ligand PPh ₃ , additive, O ₂ (1 atm), solvent (1.5 mL)	82%	Zhao and Song, 2015
9.	Pd(PPh ₃) ₄	THF, 60°C for 3 h	94%	Stein et al., 2015
10.	Ni(PPh ₃) ₂ Cl ₂	dioxane/water, CuI, Et ₃ N, reflux 2 h.	78–94%	Beletskaya et al., 2003
11.	Nickel ferrite	K ₂ CO ₃ , H ₂ O and 100°C.	94	Moghaddam et al., 2015

defined reaction conditions, in the next step, the reactions of some activated alkyl halides were investigated (Table 1, Entry 2–4). In these cases too, efficient catalytic activities are seen for CuCo₂S₄ nanosheet catalyst and all the reactions were completed with 100% selectivity and very good yields as noted.

We have compared our results with those of the Pd, Ni and Cu based catalysts for the Sonogashira coupling reaction, taking the example of the reaction between iodobenzene and phenylacetylene as shown in Table 3. For example Moghaddam et al. and Beletskaya et al. prepared diphenylacetylenes in 94 and 93% using nickel based catalyst (Beletskaya et al., 2003; Moghaddam et al., 2015). Stein et al. and Zhao et al. used the palladium based catalyst for the synthesis of diphenylacetylenes in the range of 82% to 94% (Stein et al., 2015; Zhao and Song, 2015). In 2004 copper salt is used to prepare diphenylacetylene in the isolated yield of 82–98% (Ma and Liu, 2004). Till date lot of catalyst had been synthesized for Sonogashira coupling and some of them give high yields of diphenylacetylenes, however, our new CuCo₂S₄ nanosheet catalyst is found to be excellent as compared to earlier these reports (Table 3).

We propose a possible reaction mechanism of the Sonogashira reaction in Scheme 2. Firstly, K₂CO₃ base abstract the proton from the phenylacetylene and CuCo₂S₄ forms the Cu-acetylide intermediate. In the second step, there is a formation of intermediate of Cu-acetylide complex and aryl moiety with the elimination of halide ion. So, this step can be the oxidative addition step. Finally the formation of the diphenylacetylene as the desired product (reductive elimination) and regeneration of CuCo₂S₄ catalyst again. The activity of catalyst depends on

defects on the surface and high surface area as corroborated from the nanosheet's surface characterization in Figure 1e. Somewhat intrinsic properties also affect the efficiency of catalyst for the organic reaction.

To check the reusability and stability of the catalyst, the reaction of iodobenzene with phenyl acetylene was performed under the optimized reaction conditions. CuCo₂S₄ nanosheets recovered after washing with water and drying in air was reemployed in the same reaction for the second run. This process was repeated for 10 times and each time isolated yield was monitored. The conversion of reactants to product for each repeated cycle is shown in Figure 4a. These results concluded efficient recyclability of thiospinel nanosheet with the minor decrease in product yield after 10 successive cycles and the catalyst was not deactivated during the catalysis of the reactions. This negligible decrease in efficiency may be attributed to catalyst lost during successive cycles. After each test, the catalyst was recovered by centrifugation followed by washing with water and dried. For a heterogeneous catalyst it is important to retain original properties, such as crystal structure, phase, morphology, etc. Therefore, to check the structural changes in crystal structure, XRD measurement has been performed on the dried used catalysts and the obtained XRD pattern is depicted in Figure 4b. It can be seen from XRD pattern of reused CuCo₂S₄ that peak positions remain unchanged and matching well with the standard XRD pattern, which presents the structural stability of present nanosheet sample. The retention of nanosheet morphology or shape stability of the spent catalyst can be seen by examining the TEM images in Figures 4c,d.

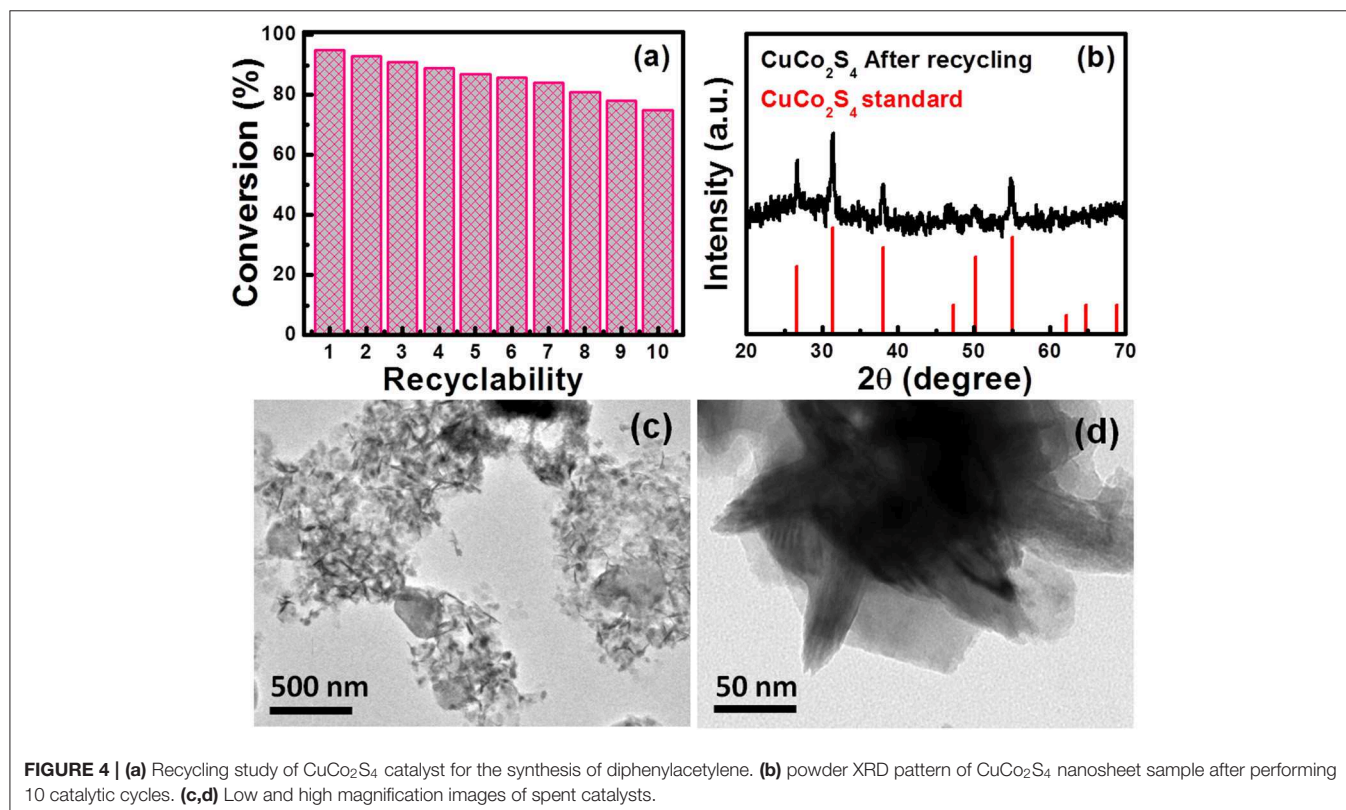


FIGURE 4 | (a) Recycling study of CuCo₂S₄ catalyst for the synthesis of diphenylacetylene. (b) powder XRD pattern of CuCo₂S₄ nanosheet sample after performing 10 catalytic cycles. (c,d) Low and high magnification images of spent catalysts.

CONCLUSIONS

Two dimensional CuCo₂S₄ nanosheets have been synthesized following a new hydrothermal approach and this material is found to be the excellent heterogeneous catalyst in the Sonogashira coupling reaction for the first time. All the reactions proceeded smoothly and diphenylacetylenes were synthesized in good yields (70–95%) within 150–300 min of reaction time. This catalyst is economic, greener and works under milder condition. Further durability of the catalyst was also examined by reusing the catalyst for continuous 10 cycles where it shows only ~20% decline in the activity. In addition, this catalytic reaction procedure can be applied in pharmaceutical industries, because of the benefits of total removal of the thiospinel catalyst without any loss in their (product) strength and activity from the reaction media.

DATA AVAILABILITY STATEMENT

All datasets generated for this study are included in the article/**Supplementary Material**.

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AUTHOR CONTRIBUTIONS

The experiments were conceived by SD. Synthesis and characterization of nanosheets was done by MC. KS performed all organic catalysis reactions. The results were interpreted and the paper written by KS, MC, and SD.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmats.2019.00273/full#supplementary-material>

NMR and Mass data for all the coupling products are given in supporting file.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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