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FULL PAPER

Copper nanoparticles supported on polyaniline-functionalized multiwall carbon nanotubes: An efficient and recyclable catalyst for synthesis of unsymmetric sulfides using potassium ethyl xanthogenate in water

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A new and powerful polyaniline-functionalized carbon nanotube-supported copper(II) nanoparticle catalyst was successfully prepared and evaluated as a heterogeneous catalyst for the one-pot synthesis of unsymmetric thioethers by coupling of aryl, alkyl and benzyl halides using potassium ethyl xanthogenate as source of sulfur in water. All of these reactions gave the desired products in good to excellent yields. The catalyst is available, air-stable and can be reused several times without significant loss in its catalytic activity.

KEYWORDS

copper(II), potassium ethyl xanthogenate, nanocatalyst, polyaniline, unsymmetric thioethers

1 | INTRODUCTION

Transition metal-catalyzed cross-coupling is one of the most widely employed reactions in the formation of C─S bonds, in which the construction of symmetric and unsymmetric sulfides is particularly noteworthy due to their importance in pharmaceutical and biological molecules and chemical materials.[1–3]

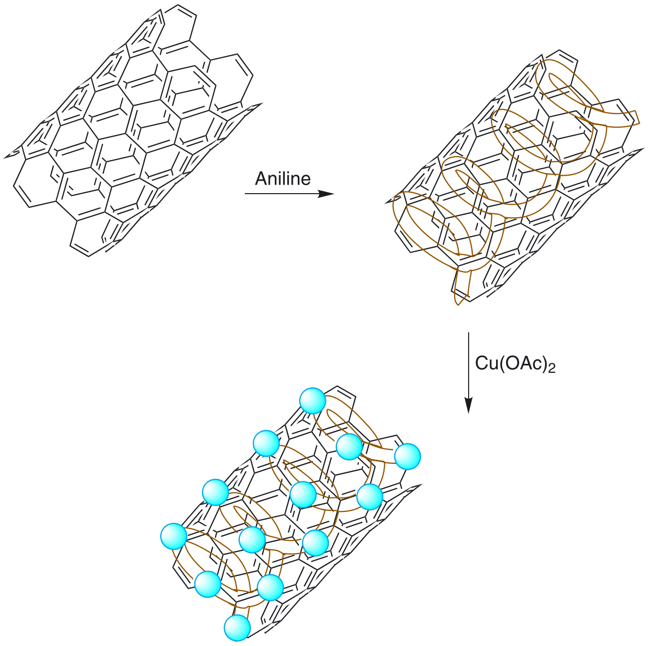
The cross-coupling reactions of aryl halides with thiols using transition metal catalysts including palladium,[4] cobalt,[5] nickel,[6] indium,[7] copper[8] and iron[9] salts are some of the most common methods for the synthesis of these important materials. However, these reactions require unstable and toxic thiols, high temperatures, expensive and toxic solvents, long time for completion the reactions and the use of homogeneous catalysts that can not be separated and recovered simply. Therefore finding safe sources instead of odorous thiols, new support materials for heterogeneous catalysts, green solvents, inexpensive ligands and mild conditions is a necessary issue for the development of catalytic methods in scale-up operations.

Recently, thiourea,[10] potassium thiocyanate,[11] thiolates,[12] carbon disulfide,[13] sulfur powder,[14] thioimide,[15] sodium thiosulfate[16] and ethyl xanthogenate[17,18] have been reported as sulfur sources in C─S bond formation. However, these reactions are often conducted in dimethylformamide (DMF) at a high temperature. Moreover, the scope of the substrate is also limited in some cases.

In recent years, nanocatalysis has appeared as a stable, efficient and attractive alternative to usual catalysis because the nanoparticles have a high surface-to-volume ratio, which increases their activity and selectivity, though at the same time maintaining the inherent characteristics of a heterogeneous catalyst.[19–21]

Among nanomaterials, carbon nanotubes, the elegant empty tubular carbon design of nanometric range, are noteworthy options for the synthesis of nanocatalysts due to their appealing mechanical properties and structural specifications.[22] It has been reported that many heterogeneous catalysts employ surface-modified carbon nanotubes as supports.[23–28]

Attaching of polymers like polyaniline to carbon nanotubes is an interesting and developing area of research.[22] Lately the preparation of identical tubular composite of polyaniline and multiwall carbon nanotubes (MWCNTs) has been reported.[29] This functionalization with polyaniline



SCHEME 1 Preparation of heterogeneous catalyst Cu(II)-PANi-MWCNT

help to disperse metallic particles in the carbon nanotubes.[30] Especially, the immobilization of copper nanoparticles on polyaniline-functionalized carbon nanotubes permits a higher dispersity and stability of the particles and further use of the particular activity of the catalyst.[31]

However, to the best of our knowledge, there is no report in the literature describing polyaniline-functionalized MWCNT-supported copper(II) nanoparticles (Cu(II)-PANi-MWCNT) as a nanocatalyst for the synthesis of unsymmetric sulfides from potassium thioacetate with aryl, alkyl and benzyl halides in water. In continuation of our interest in the development of new catalysts for C─S bond formation reactions,[11,32] we report synthesis of Cu(II)-PANi-MWCNT (Scheme 1) as a new, effective, recyclable and heterogeneous nanocatalyst for the synthesis of unsymmetric thioethers in water. This catalyst can be recovered and recycled for up to six consecutive runs without important loss in its efficiency.

2 | RESULTS AND DISCUSSION

The Cu(II)-PANi-MWCNT catalyst employed for C─S coupling was synthesized according to a procedure in the literature.[29] PANi-MWCNT composites were first synthesized by the in situ polymerization of aniline in the presence of a carbon nanotube suspension. Cu nanoparticles dispersed on PANi-MWCNT support were prepared by adding $Cu(OAc)_2{\cdot}H_2O$ salt to PANi-MWCNT composites in a suspension of tetrahydrofuran–water (1:1) (Scheme 1). PANi-MWCNT composites were characterized by Lee et al.[29] The Cu(II)-PANi-MWCNT catalyst was characterized using transmission electron microscopy (TEM; Figure 1a,b), inductively coupled plasma (ICP) atomic emission spectrometry, energy-dispersive X-ray spectroscopy (EDX; Figure 1d) and thermogravimetric analysis (TGA).

Also TEM micrograph of the catalyst taken after sixth recycle (Figure 2) shows no significant change in the morphology of the nanocatalyst, and therefore it can be realized that the catalytic activity is preserved after recycling. As shown in

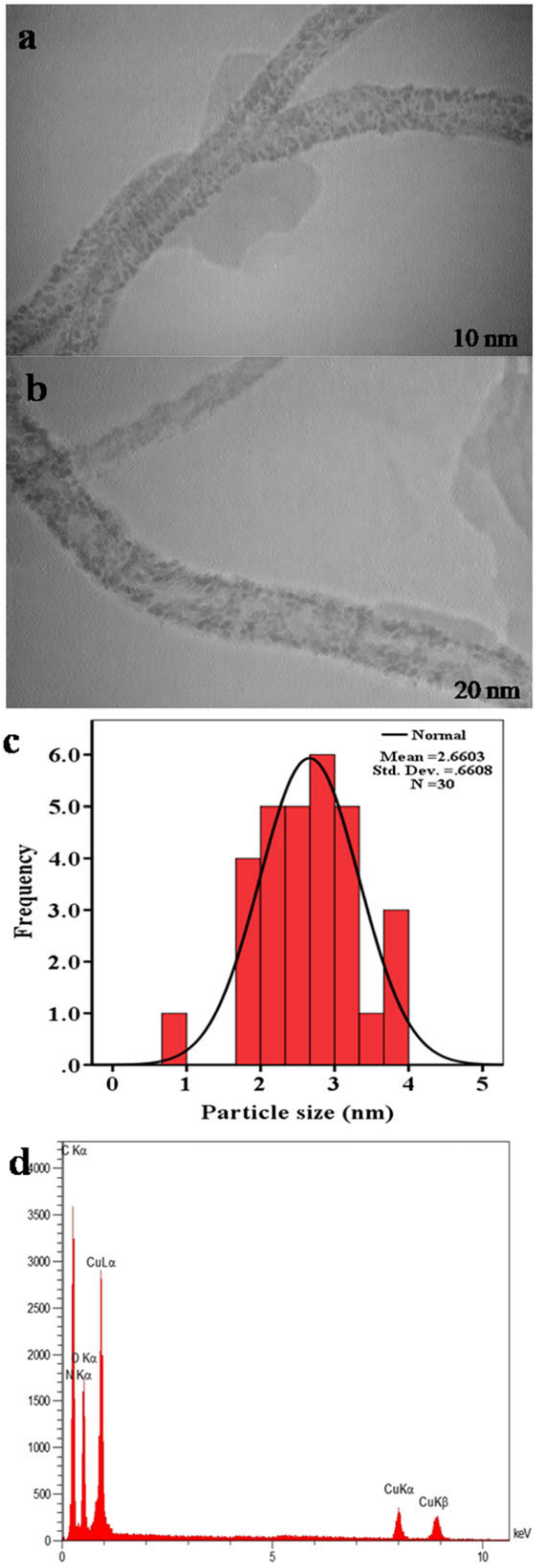


FIGURE 1 (a, b) TEM images of Cu(II)-PANi-MWCNT catalyst. (c) Particle size distribution of catalyst. (d) EDX spectrum of catalyst

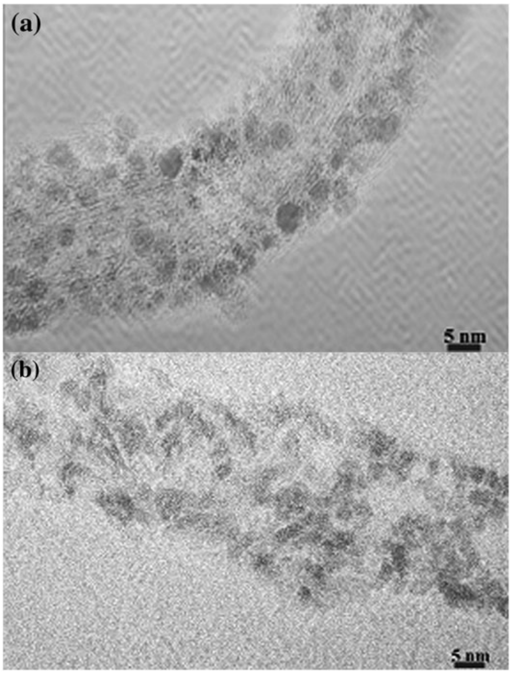


FIGURE 2 TEM images of catalyst (a) after first run and (b) after sixth run

Figure 3, the TGA curve of catalyst shows three different mass loss stages. The first mass loss, at around 25–150 °C, is due to water and organic solvent residues and moisture absorbed onto the catalyst. The second stage of weight loss occurs between 200 and 550 °C and then there is a smooth mass loss until 800 °C These TGA results indicate that the thermal stability of the catalyst is considerable.

After the characterization of the composite, the catalytic activity of the Cu(II)-PANi-MWCNT catalyst was examined in the coupling reaction of 4-iodotoluene with potassium ethyl xanthogenate in the presence of 15 mol% copper nanocatalyst and 30 mol% cetyltrimethylammonium bromide (CTAB) at 80 °C in water. After 12 h, KOH and phenyl iodide were added to the reaction mixture and the resulting mixture was further heated for 15 h which afforded 95% of an unsymmetric diaryl thioether, phenyl(*p*-tolyl)sulfane.

Initially, a C(aryl)─S coupling between 4-iodotoluene and potassium ethyl xanthogenate was conducted to give *O*-ethyl *S*-4-methoxyphenylcarbonodithioate. Then, this carbonodithioate was hydrolyzed in the presence of KOH. Finally the generated thiolate reacted with iodobenzene to form second C(aryl)─S bond to give phenyl(*p*-tolyl) sulfane[33] (Scheme 2).

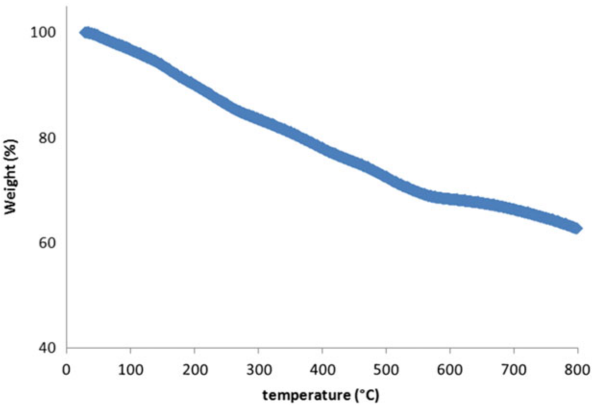
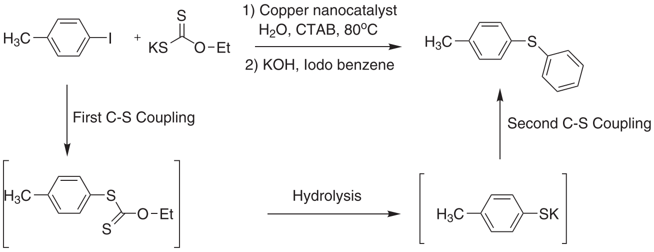


FIGURE 3 TGA curve of Cu(II)-PANi-MWCNT catalyst

To optimize reaction conditions, we examined the effects of bases and additives on this reaction. Among the studied bases, KOH was the best and the corresponding product is obtained in 95% yield (Table 1, entry 1). Also, among the studied additives CTAB was the best (Table1, entries 1–4). Then other solvents were investigated for the reaction (Table1, entries 5–8). As evident from Table 1, water was the best solvent. The amount of copper(II) complex was also studied. A 15 mol% loading of copper(II) was found to be optimal, since a lower yield was obtained when the amount of complex is decreased (Table 1, entry 14). Finally, the time of reaction was investigated (Table 1, entries 15 and 16). Time of 12 h for first step and 15 h for second step were best (Table 1, entry 1).

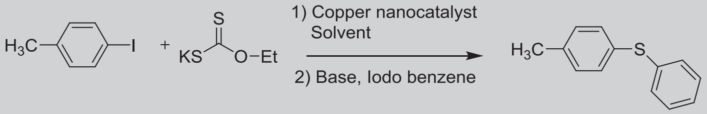
After determining the optimized conditions, the Cu(II)-PANi-MWCNT complex was used as a catalyst for this methodology with aryl halides containing electron-donating or electron-withdrawing substituents, alkyl halides and benzyl bromide. The obtained results are summarized in Table 2. On the whole, all the reactions gave corresponding products (Table 2, pa–pq) in good to excellent yields ranging from 68 to 96%. Aryl iodides with electron-withdrawing and electron-donating substituents gave the corresponding products in high yields (Table 2, entries 1–7). One-pot thioetherification of various aryl bromides bearing either electron-withdrawing groups or electron-donating groups was also carried out using potassium ethyl xanthogenate in some hours longer and produces various aryl sulfides in good yields (Table 2, entries 8–12). The yields of the coupling between Ar─I and Ar─Br are good (Table 2, entries 13–17). Also, we investigated the synthesis of various sulfides using alkyl halides. These reactions proceed well to produce the corresponding sulfides in good yields (Table 2, entries 18–23). The coupling reactions of phenyl iodide and phenyl bromide with benzyl bromide in the presence of potassium ethyl xanthogenate proceed well to produce the corresponding unsymmetric sulfides in excellent yields (Table 2, entries 24 and 25).

We also studied the recyclability and reusability of this catalyst utilizing the reaction of 4-iodotoluene with potassium ethyl xanthogenate and iodobenzene under optimum conditions as a model reaction (Table 3). After each



SCHEME 2 Formation of phenyl(*p*-tolyl)sulfane using copper nanocatalyst

TABLE 1 Optimization of conditions for synthesis of phenyl(*p*-tolyl)sulfane[a]

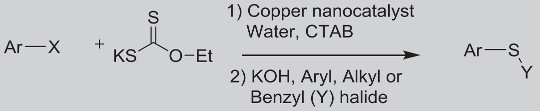


Entry	Base	Solvent	Additive	Catalyst (mol%)	Time (h)	Yield (%)[b]
1	KOH	H_2O	CTAB	15	12/15	95
2	KOH	H_2O	TBAB	15	12/15	89
3	KOH	H_2O	TBAI	15	12/15	73
4	KOH	H_2O	TBAF	15	12/15	78
5	KOH	H_2O–DMSO (1:1)	CTAB	15	12/15	91
6	KOH	H_2O–DMF (1:1)	CTAB	15	12/15	90
7	KOH	H_2O–CH_3CN (1:1)	CTAB	15	12/15	82
8	KOH	H_2O–EtOH (1:1)	CTAB	15	12/15	76
9	K_2CO_3	H_2O	CTAB	15	12/15	52
10	Na_2CO_3	H_2O	CTAB	15	12/15	45
11	*t*-BuOK	H_2O	CTAB	15	12/15	48
12	K_3PO_4	H_2O	CTAB	15	12/15	59
13	KOH	H_2O	CTAB	20	12/15	95
14	KOH	H_2O	CTAB	10	12/15	86
15	KOH	H_2O	CTAB	15	15/18	95
16	KOH	H_2O	CTAB	15	10/12	84

[a] Reaction conditions: 4-iodotoluene (1.0 mmol), potassium ethyl xanthogenate (1.0 mmol), idobenzene (1.0 mmol), base (3.0 mmol), CTAB (30 mol%), solvent (3 ml), 80 °C and aerobic conditions.

[b] Isolated yield.

TABLE 2 Scope of coupling reactions of aryl halides with potassium ethyl xanthogenate, and aryl, alkyl or benzyl halides[a]



Entry	Ar	X	Ar′/alkyl/benzyl	X′	Product	Time (h)	Yield (%)[b]
1	*p*-$CH_3OC_6H_4$	I	C_6H_5	I	pa	12/15	95
2	*p*-$NO_2C_6H_4$	I	C_6H_5	I	pb	8/15	92
3	*p*-$CH_3COC_6H_4$	I	C_6H_5	I	pc	8/15	90
4	*p*-$CH_3C_6H_4$	I	C_6H_5	I	pd	12/15	95
5	*o*-$CH_3C_6H_4$	I	C_6H_5	I	pe	12/15	94
7	*o*-$NO_2C_6H_4$	I	C_6H_5	I	pf	9/15	91
8	*p*-$CH_3OC_6H_4$	Br	C_6H_5	Br	pa	20/24	74
9	*p*-$NO_2C_6H_4$	Br	C_6H_5	Br	pb	18/24	70
10	*p*-$CH_3COC_6H_4$	Br	C_6H_5	Br	pc	18/24	71
11	*m*-$CH_3OC_6H_4$	Br	C_6H_5	Br	pg	20/24	70
12	Naphthalene	1-Br	C_6H_5	Br	ph	20/24	73
13	*p*-$CH_3OC_6H_4$	Br	C_6H_5	I	pa	20/15	81
14	*p*-$NO_2C_6H_4$	Br	C_6H_5	I	pb	18/15	79
15	*p*-$CH_3OC_6H_4$	I	C_6H_5	Br	pa	12/24	75
16	*p*-$NO_2C_6H_4$	I	C_6H_5	Br	pb	8/24	69
17	*p*-$CH_3COC_6H_4$	I	Naphthalene	1-Br	pi	8/24	68
18	C_6H_5	Br	CH_3	I	pj	20/1	85
19	*p*-$CH_3C_6H_4$	Br	CH_3	I	pk	20/1	88
20	*p*-BrC_6H_4	I	CH_3	I	pl	12/1	92
21	C_6H_5	Br	CH_3CH_2	Br	pm	20/2	89
22	*p*-$NO_2C_6H_4$	Br	CH_3CH_2	Br	pn	18/2	87
23	*p*-$CH_3COC_6H_4$	Br	CH_3CH_2	Br	po	20/2	86
24	C_6H_5	I	Benzyl	Br	pp	12/2	96
25	C_6H_5	Br	Benzyl	Br	pp	20/2	89

[a] Reaction conditions: aryl halide (1.0 mmol), potassium ethyl xanthogenate (1.0 mmol), aryl, alkyl or benzyl halide (1.0 mmol), copper nanocatalyst (15 mol%), KOH (3.0 mmol), CTAB (30 mol%), solvent (3 ml), 80 °C and aerobic conditions.

[b] Isolated yield.

TABLE 3 Recyclability of catalyst under optimum reaction conditions[a]

Entry	Cycle	Yield (%)[b]
1	1	95
2	2	95
3	3	94
4	4	94
5	5	93
6	6	93

[a]Reaction conditions: 4-iodotoluene (1.0 mmol), potassium ethyl xanthogenate (1.0 mmol), idobenzene (1.0 mmol), KOH (3.0 mmol), copper nanocatalyst (15 mol%), CTAB (30 mol%), H_2O (3 ml), 80 °C and aerobic conditions.

[b]Isolated yield.

run, the catalyst was recovered by centrifugation, followed by washing with water and ethyl acetate and then was dried. The activity of the catalyst remains almost the same after being reused sixth times.

It seems the substituent effects in this protocol are not very important. A plausible pathway for the synthesis of sulfides with xanthogenate has been reported by Akkilagunta and Kakulapati.[17]

In order to determine the absolute amount of the copper species dissolved in solution caused by leaching, the reaction of 4-iodotoluene with potassium ethyl xanthogenate and iodobenzene was carried out under the optimum conditions and the catalyst was removed from the reaction mixture by hot filtration after 12/7.5 h (at this time, almost 50% conversion). After elimination of the catalyst, the reaction was continued and no more product conversion was seen and no copper metal was identified in the solution using ICP analysis. Also, a TEM image of recycled catalyst after six runs was taken (Figure 2b), which does not show major changes in the morphology or the size of the catalyst (2–3 nm; Figure 1c). This confirms the preservation of the catalytic activity of the catalyst after recycling.

The catalytic activity of the Cu(II)-PANi-MWCNT catalyst was compared with that of other copper nanoparticles that have been reported before.[17,33] This demonstrates that the reaction time is shorter and the protocol is green for the present copper catalyst compared to other copper nanoparticles.

3 | CONCLUSIONS

We successfully prepared polyaniline-functionalized MWCNT-supported copper(II) nanoparticles and developed an efficient and green procedure for the synthesis of unsymmetric sulfides using potassium ethyl xanthogenate in good yields and with a broad range of functional group tolerance. This catalyst could be recovered by centrifugation and reused six times without an important loss in its activity. The reaction proceeded in a short period of time without expensive metal and unclean smell of thiols.

4 | EXPERIMENTAL

4.1 | General

MWCNTs were purchased from Neutrino Co. (www.neunano.com; diameter of 10–20 nm, length of 30 μm, purity >95%). All reagents and solvents were purchased from Merck or Aldrich and used without further purification. TEM images were obtained with an EM208S at an accelerating voltage of 100 kV. The metal content of the complex was measured using ICP analysis (Varian vista-mpx). GC was performed using a BEIFIN 3420 gas chromatograph equipped with a Varian CP SIL 5CB column (30 m, 0.32 mm, 0.25 mm). TGA of the catalyst was conducted using a laboratory-made TGA instrument. The EDX analysis (SEM, MIRA3 TESCAN) was engaged for characterization of the catalyst. ^{1}H NMR and ^{13}C NMR spectra were recorded with $CDCl_3$ as solvent. Chemical shifts were measured in ppm using tetramethylsilane as an internal standard. Also, GC–MS was conducted using an Agilent 7890A-5975C instrument. Column chromatography was carried out on columns of silica gel 60 (70–230 mesh).

4.2 | Preparation of PANi-MWCNT

PANi-MWCNT composites were prepared according to a previously reported procedure.[29] A round-bottom flask containing HCl solution (2 M, 100 ml) and MWCNT (1 g) was sonicated for half an hour at room temperature. Then were added a stoichiometric amount of aniline monomer and two drops of $FeSO_4$ (5%) in this suspension. An aqueous solution of ammonium persulfate (1 g of $(NH_4)_2S_2O_8$ in 20 ml of deionized water) was then added. This reaction mixture was continuously stirred in an ice bath for 1 h and then brought up to room temperature and stirred for another 3 h. At the end of this time, the obtained PANi-MWCNT was separated by centrifugation and washed with distilled water and ethanol and dried at 80 °C.

4.3 | Preparation of Cu(II)-PANi-MWCNT

To a round-bottom flask equipped with a magnetic stirrer bar and containing 100 ml of THF–H_2O (1:1) was added PANi-MWCNT (100 mg). The reaction mixture was suspended using ultrasonication for 30 min, and following that was stirred for another 30 min. $Cu(OAc)_2{\cdot}H_2O$ (0.03 g) was added to the solution and the reaction mixture was stirred for 12 h at room temperature. Then the obtained black solid was separated by centrifugation and washed several times with distilled water, and dried in vacuum overnight at 60 °C.

4.4 | General procedure for synthesis of unsymmetric sulfides

An aryl halide (1.0 mmol) and potassium ethyl xanthogenate (1.0 mmol) were added to a mixture of water (3 ml), Cu(II)-PANi-MWCNT (15 mol%) and CTAB (30 mol%) in a glass flask under vigorous stirring. The reaction mixture was stirred at 80 °C until the aryl halide was consumed (12 h), as determined by GC. Then KOH (3 mmol) and second aryl halide (1.0 mmol) were added. The mixture was heated at 80 °C until the second aryl halide was consumed (15 h), as determined by GC. At the end of the reaction, the catalyst was separated by centrifugation, washed with ethyl acetate, ethanol and water, vacuum dried and kept for a subsequent reaction. Then ethyl acetate was added to the reaction mixture and the organic layer was extracted using saturated brine solution. The solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography.

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