

Cite this: *Green Chem.*, 2020, 22, 651Received 3rd December 2019,
Accepted 3rd January 2020

DOI: 10.1039/c9gc04137k

rsc.li/greenchem

Highly dispersed Ni₂P nanoparticles on N,P-codoped carbon for efficient cross-dehydrogenative coupling to access alkynyl thioethers†

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An ultrafine Ni₂P (a metal-rich interstitial phosphide compound) nanoparticles with a narrow size distribution homogeneously dispersed on N,P-codoped carbon was developed for efficient synthesis of alkynyl thioethers *via* base- and ligand-free cross-dehydrogenative coupling (CDC) of terminal alkynes and thiols using atmospheric air as the oxidant under mild conditions. A remarkable catalytic performance with good functional group compatibility, broad substrate scope and high stability is accomplished. Pyridinic N atoms are identified as basic sites for facilitating the activation of terminal alkynes *via* hydrogen bonding interactions and play a key role in the success of this base- and ligand-free CDC reaction.

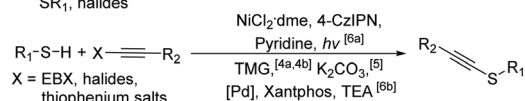
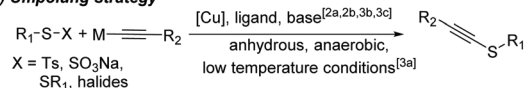
Alkynyl thioethers are extremely versatile and essential building blocks in organic synthesis and act as intermediates for the synthesis of sulfur-rich functional polymers.¹ To date, various methods have been developed for the synthesis of alkynyl thioethers, including (i) an umpolung strategy *via* the prefunctionalization of either thiols or alkynes to sulfenyl halides² and disulfides,³ or ethynyl benziodoxolone (EDX) reagents,⁴ (alkynyl)-dibenzothiophenium triflates⁵ and haloalkynes,⁶ followed by the reaction with coupling partners (Scheme 1a) and (ii) an electrophilic alkynylthio transfer strategy, in which an alkyne is firstly converted to a highly active electrophile as an alkynylthio transfer reagent with subsequent reaction with nucleophiles to give C–S bond compounds (Scheme 1b).⁷ In these two strategies, the prefunctionalization process of either terminal alkynes or thiols is necessary and the coupling process should be carried out in the presence of transition-metal (Pd,^{6b} Cu,^{2a,b,3a,b} and Ni^{6a}) catalysts with the

assistance of ligands or mediated by bases (K₂CO₃,⁵ pyridine,^{6a} tetramethylguanidine (TMG),^{4a,b} triethylamine (TEA),^{6b} or triethylenediamine (DABCO)^{7b}), which usually cause some issues of the formation of unstable intermediates or undesirable side-products, and require harsh reaction conditions.^{3a,7a}

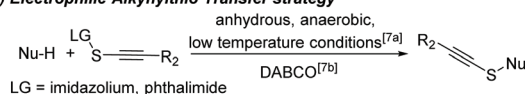
Besides, transition-metal catalyzed cross dehydrogenative coupling (CDC) of unactivated alkenes with thiols or disulfides represents the most straightforward and efficient method to access alkynyl thioethers, as shown in Scheme 1c, and has been frequently employed for the construction of C–X (X = C, N, and O) bonds.⁸ However, to date, only sporadic reports are available for the synthesis of C–S bonds, most likely due to the poison effect of sulphur atoms on metals. In this context, Cu-based catalysts have been successfully applied for such a transformation with one exception of using a precious metal Rh complex.^{9a} Nonetheless, the use of sophisticated and expensive organic

Previous work:

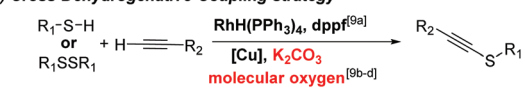
a) Umpolung strategy



b) Electrophilic Alkynylthio Transfer strategy



c) Cross-Dehydrogenative Coupling strategy



This work:



- Base- and ligand-free, atmospheric air as oxidant, mild conditions
- High activity, broad substrate scope ● Easy separation and recyclable

Scheme 1 Strategies for the synthesis of alkynyl thioethers.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9gc04137k

ligands (dppf),^{9a} and bases (K₂CO₃)^{9b-d} under a molecular oxygen atmosphere is necessary for the success of this reaction.^{9b-d} Much worse, in these cases, poor compatibilities of functional groups, low selectivity to the targeted products, and difficulty of product–catalyst separation significantly limited their practical applications. Therefore, the synthesis of alkynyl thioethers by the coupling of alkynes with thiols or disulfides still remains a significant challenge.

Herein, we developed a stable inexpensive heterogeneous metal-rich interstitial nickel phosphide catalyst (denoted as Ni₂P@NPC-800), in which ultrafine Ni₂P nanoparticles (NPs) with a narrow size distribution were homogeneously dispersed on N,P-codoped biomass-derived porous carbon. The resultant catalyst Ni₂P@NPC-800 shows excellent catalytic activities for the synthesis of alkynyl thioethers *via* base- and ligand-free cross dehydrogenative coupling of alkynes and thiols using air as the sole oxidant under mild conditions (for details of comparison with previous studies see Table S2†). To the best of our knowledge, this is the first case of expedient synthesis of alkynyl thioethers *via* cross dehydrogenative coupling of alkynes and thiols catalyzed by a stable Ni catalyst. High catalytic activity and excellent selectivity accompanied by good tolerance to functional groups, broad substrate scope and strong stability were accomplished under mild reaction conditions, highlighting the practicability of this protocol for accessing important building blocks, alkynyl thioethers.

Ultrafine and highly dispersed Ni₂P NPs on biomass-derived porous carbon were prepared by a sequential hydrothermal and pyrolysis process according to our previous reports, as shown in Fig. 1a (see details in the ESI†).¹⁰ The as-prepared catalysts were denoted as Ni₂P@NPC-*T*, where *T* represents the pyrolysis temperature. The Ni content in the cata-

lysts was determined to be 3.05–4.96 wt% by coupled plasma optical emission spectrometry (ICP-OES) (Table S1†).

The high-resolution transmission electron microscopy (HR-TEM) images (Fig. 1b and c) of the catalyst Ni₂P@NPC-800 show that small Ni₂P NPs with a narrow size distribution (3.2 ± 0.7 nm) are uniformly dispersed on the graphitic carbon material. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Fig. S1a†) with energy-dispersive X-ray (EDX) mapping (Fig. S1b–1f†) clearly shows a homogeneous distribution of Ni, P, N, C and O over the entire carbon framework. Powder X-ray diffraction (PXRD) patterns (Fig. 1d) show the formation of a single Ni₂P phase on graphitic carbon, which is in good agreement with HR-TEM observation. N 1s and P 2p XPS analysis (Fig. 1f and g) verifies that N and P atoms were co-incorporated into the carbon framework. High resolution deconvolution analysis reveals the presence of N atoms as pyridinic-, pyrrolic-, graphitic-, and oxidized-N species, while P–C, P–O, and Ni–P species were formed from P atoms. Ni 2p XPS (Fig. 1e) further confirms the formation of metal-rich interstitial Ni₂P NPs, while a certain amount of Ni²⁺ species was also detected most likely due to the inevitable partial oxidation of Ni₂P NPs on the surface.¹¹ N₂ adsorption/desorption measurements demonstrate that the catalyst Ni₂P@NPC-800 prepared by this strategy possesses hierarchical micro-, meso-, and macro-pores with a high specific surface area and large pore volume, as shown in Fig. S3 and Table S1.†

With the as-prepared catalysts in hand, we initiated our investigation using phenylacetylene (**1a**) and *para*-chlorobenzenethiol (**3a**) as coupling partners to test their feasibility, as shown in Table 1. Initially, we performed the reaction in the presence of Ni₂P@NPC-800 (8 mol% of Ni) as a catalyst and 10 mol% K₂CO₃ as a base at 70 °C in DMF (0.1 M) under an air atmosphere; full conversion of **1a** with 77% GC yield of the targeted product **2a** accompanied by the formation of a diene (**4a**) in 23% yield after 6 h was achieved (Table 1, entry 1). The GC yield of **2a** could be enhanced to 84% by increasing the ratio of **1a/1b** from 1/1.1 to 1/1.5 (entry 2), while no obvious effect was observed upon further increasing the ratio to 1/2 (entry 3). Delightfully, we found that the GC yield of **2a** was markedly improved to 95% together with 5% of **4a** when the reaction was carried out in the absence of a base under otherwise identical conditions. Subsequently, other factors, such as solvents (entries 5–7), reaction temperatures (entries 9 and 10), and reaction times (entry 8), were intensively investigated for their effect on the reaction efficiency. The reaction in DMSO as the solvent showed comparable reactivity to that in DMF (entry 5), whereas a considerably lower reactivity with the formation of **4a** as the major product was observed in THF or CH₃CN as the solvent (entries 6 and 7). Reactivity as a function of reaction time showed that the reaction could complete within 4 h at 50 °C (entry 8). Besides, lowering the reaction temperature from 70 to 50 °C had a negligible effect on the reactivity and selectivity to **2a** (entry 9), however, a further decrease to room temperature led to a significant drop in the reactivity (entry 10). In comparison, the catalyst Ni₂P@NPC-700

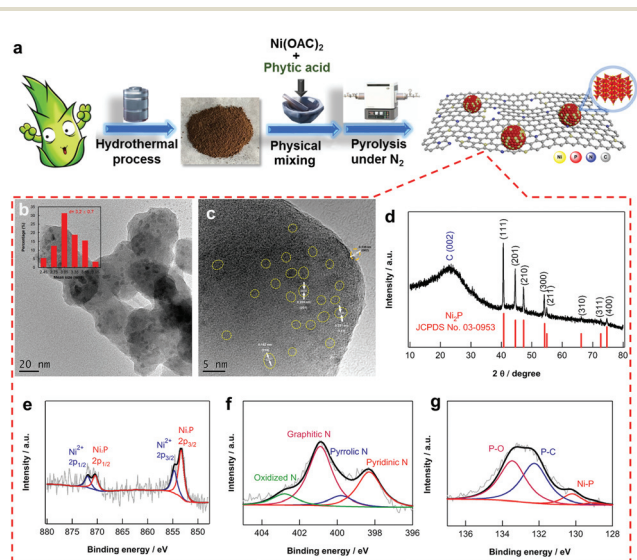
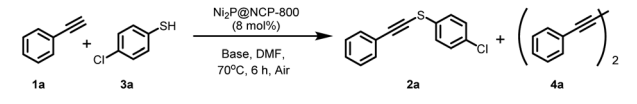


Fig. 1 (a) Illustration of the preparation of the catalyst; (b) and (c) HR-TEM and size distribution of Ni₂P@NPC-800; (d) powder XRD pattern of Ni₂P@NPC-800; (e–g) high-resolution XPS spectra of Ni 2p, N 1s, and P 2p of Ni₂P@NPC-800.

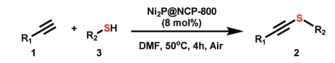
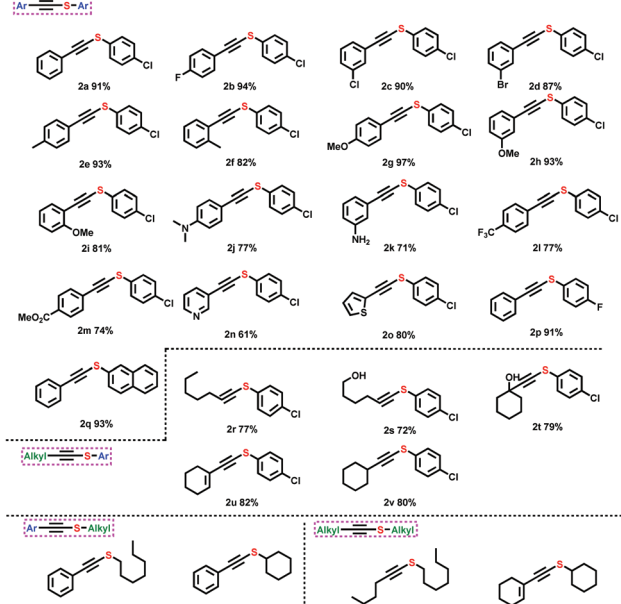
Table 1 Optimization of reaction conditions^a


Entry	1a/1b (molar ratio)	Solvent	T [°C]	Conv. ^b [%]	GC yield ^b [%]	
					2a	4a
1 ^c	1/1.1	DMF	70	100	77	23
2 ^c	1/1.5	DMF	70	100	84	16
3 ^c	1/2	DMF	70	100	87	17
4	1/1.5	DMF	70	100	95	5
5	1/1.5	DMSO	70	100	91	4
6	1/1.5	THF	70	61	11	50
7	1/1.5	CH ₃ CN	70	77	9	68
8 ^d	1/1.5	DMF	70	100	96	4
9 ^d	1/1.5	DMF	50	100	95	5
10	1/1.5	DMF	RT	31	13	18
11 ^e	1/1.5	DMF	50	53	40	13
12 ^f	1/1.5	DMF	50	100	93	7
13 ^g	1/1.5	DMF	50	0	0	0
14 ^h	1/1.5	DMF	50	21 ^k	0	0
15 ⁱ	1/1.5	DMF	50	0	0	0
16 ^j	1/1.5	DMF	50	0	0	0

^a Reaction conditions: phenylacetylene (0.2 mmol), catalyst (8 mol% of Ni), solvent (2 mL), air atmosphere. ^b Determined by GC based on the consumption of phenylacetylene. ^c K₂CO₃ (10 mol%) was used. ^d 4 h instead of 6 h. ^e Ni₂P@NPC-700, 4 h. ^f Ni₂P@NPC-900, 4 h. ^g NPC-800, 4 h. ^h Under an Ar atmosphere, 4 h. ⁱ Ni(OAc)₂ instead of Ni₂P@NPC-800, 4 h. ^j No catalyst, 4 h. ^k (4-Chlorophenyl)(styryl)sulfane was detected by GC-MS.

showed a relatively lower activity, while a comparable reactivity was observed for the catalyst Ni₂P@NPC-900 (entries 11 and 12) compared with that of Ni₂P@NPC-800 under otherwise identical conditions. In addition, a set of control experiments either in the absence of a catalyst or air, or in the presence of NPC-800 without Ni loading or nickel salts as the sole catalyst were performed, and all showed negligible or no reactivity (entries 13–16). From these observations, we can safely conclude that the catalyst Ni₂P@NPC-800 and an air atmosphere were indispensable for the success of the reaction.

After identifying the optimized reaction conditions, we then explored the generality of this protocol for the synthesis of alkynyl thioethers, and the results are compiled in Table 2. Firstly, a set of functional group substituted phenylacetylenes were tested to couple with 3a under the optimized conditions. Phenylacetylenes bearing either electron-donating groups (–Me, –OMe, –NH₂, and –NMe₂) or electron-withdrawing groups (–CF₃ and –CO₂Me) were efficiently coupled to give their corresponding alkynyl thioethers in 71–97% yields. Comparatively, a relatively higher yield was achieved for phenylacetylenes with electron-donating substituents (1e, 1g, 1h) than those with electron-withdrawing ones (1l and 1m). The steric effect was clearly observed, for example, *ortho*-methyl (1f) or methoxyl (1i) substituted phenylacetylene exhibited a lower reactivity than the *para*- or *meta*-substituted one. Halogen substituents (F, Cl, and Br) are compatible with the present conditions, affording the corresponding alkynyl

Table 2 Substrate scope for the synthesis of alkynyl thioethers^{a,b}



^a Reaction conditions: alkyne (0.2 mmol), thiol (0.3 mmol) Ni₂P@NPC-800 (8 mol% Ni), DMF (2 mL), air atmosphere, 50 °C, 4 h. ^b Isolated yields are reported.

thioethers in 87–94% yields. Noteworthy, amino-substituted phenylacetylenes (1j and 1k), which were problematic substrates in previously reported protocols due to easy oxidation and coordination of the metal centers with N atoms,¹² could also be transformed into alkynyl thioethers in 77% and 71% yields, respectively. Besides, heterocyclic substituted acetylenes, such as 1n and 1o, were also smoothly converted into the desired products in good yields. Next, aliphatic terminal alkynes (1r–1v), including those containing a hydroxyl group (1s and 1t) and conjugated with a C=C bond (2u), are suitable for the reaction leading to the formation of the targeted alkynyl thioethers in 72–82% yields. Moreover, other substituted benzene thiols (3p and 3q) or alkyl thiols (3w and 3x) also work well to construct C–S bonds in decent to high yields. Remarkably, more challenging coupling of aliphatic terminal alkynes with aliphatic thiols was also realized with this protocol to deliver the corresponding alkynyl thioethers (2y and 2z) in satisfactory yields.

Subsequently, we investigated the recyclability of the catalyst Ni₂P@NPC-800 for the benchmark reaction under the optimized conditions. The catalyst was used 6 times consecutively with negligible changes in activity, indicating its strong stability (Fig. S7†). Separation of the catalyst from solution at approximately 45% conversion of 1a via hot filtration stopped the formation of 2a, suggesting that irreversibly leached nickel species (if any) have a minor contribution to the reactivity (Fig. S8†). Taken together, all the results strongly indicate the intrinsic role of heterogeneous Ni₂P@NPC-800 in catalysis.

To gain insight into the reaction pathway, a set of control experiments were carried out. The compound distribution for the benchmark reaction as a function of reaction time under the optimized reaction conditions (Fig. 2) reveals that 1,2-bis(4-chlorophenyl)disulfane (5a) was rapidly produced with the quick consumption of 3a at the initial reaction stage (within 1 h), while only a small amount of the desired product 2a was generated during this period. Subsequently, the gradual formation of 2a *via* the coupling of 1a and 5a dominated the reaction until complete consumption of 1a. So we assume that 5a most likely acts as the real intermediate for the coupling and has been frequently employed for the coupling of alkynes to construct C–S bonds.³ To prove this assumption, *p*-chlorobenzethiol (3a) was subjected to the standard conditions (Scheme 2, eqn (a)), and 5a was obtained in 99% yield as determined by GC. More interestingly, 3a could be quantitatively converted into 5a in the absence of the catalyst Ni₂P@NPC-800 under otherwise identical conditions (Scheme 2, eqn (b)). Furthermore, the coupling reaction of phenylacetylene (1a) with 5a instead of 3a as the coupling partner under the standard conditions also gave a comparable yield (93% *vs.* 95% in Table 1, entry 9) of 2a (Scheme 2, eqn (c)). Taking all results together, it was proved that the coupling reaction indeed proceeds firstly *via* the formation of disulfane as a nucleophile for the subsequent reaction with an alkyne to produce the desired alkynyl thioether.

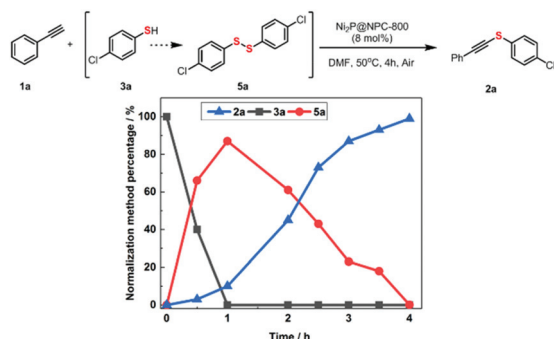
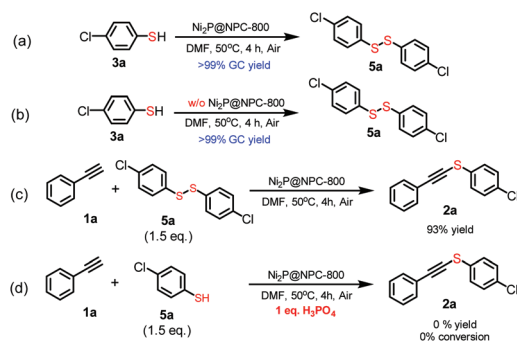


Fig. 2 The compound distribution for the benchmark reaction as a function of reaction time under the optimized reaction conditions.



Scheme 2 Control experiments.

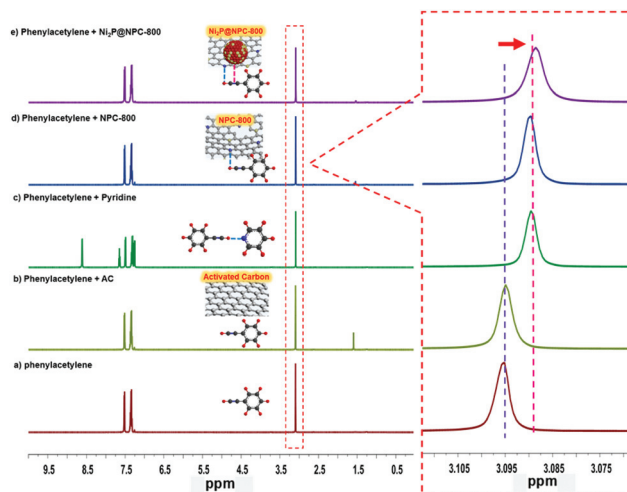
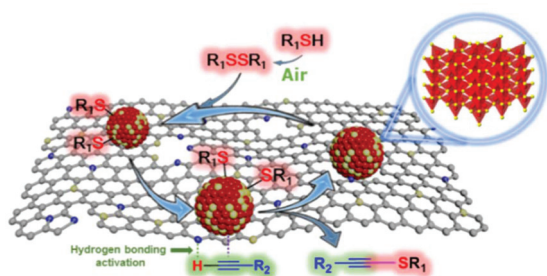


Fig. 3 ¹H NMR experiments for studying the role of N-doping.

Previous studies showed that a base (inorganic or organic) is basically required in CDCs to initiate the reaction *via* activating either a thiol or terminal alkyne.^{9b-d} However, this is not the case in our present catalysis, and an outstanding catalytic performance was achieved in the absence of a base, as shown in Table 2. We further attempted to elucidate the role of the catalyst. Control experiments discussed above reveal that a thiol could be readily oxidized into disulfane without a catalyst under air in DMF at 50 °C (Scheme 2, eqn (a)). So, ¹H NMR experiments were conducted to investigate how the catalyst activates the terminal alkyne (Fig. 3). Taking phenylacetylene (1a) as an example, an obvious chemical shift of terminal alkynyl hydrogen to high field was observed when 1a was added into the CDCl₃ solution containing Ni₂P@NPC-800 for 10 min, which might be due to the hydrogen bonding interaction between the alkynyl hydrogen and Ni₂P NPs or N atom-doped carbon.¹³ A similar but slightly lower shift was also observed using NPC-800 instead of Ni₂P@NPC-800 with the same treatment. In sharp contrast, no visible chemical shift was detected using activated carbon (AC) without N-doping, indicating that N atoms did play a role in the interaction with the alkyne. As was previously reported,^{10,14} N atoms, specifically pyridinic species, in N-doped carbon could serve as basic sites to interact with and/or activate some molecules. To prove this, pyridine, to mimic the N species in the carbon material, was mixed with 1a in CDCl₃ solution, and an almost identical shift to that in NPC-800 was observed, further confirming the role of N atoms as basic sites to interact with alkyne in the catalyst Ni₂P@NPC-800.^{10e,14} In addition, no reactivity was observed when the benchmark reaction was performed under the optimized conditions, but the addition of a stoichiometric amount of H₃PO₄ as a poisoning agent deactivating the N sites (Scheme 2, eqn (d)). Therefore, these experimental results clearly reveal the key role of N atom-doped carbon as basic sites to activate the alkyne *via* hydrogen bonding interactions, thereby facilitating the reaction.



Scheme 3 Proposed mechanism for the synthesis of alkynyl thioethers via the CDC strategy.

Taking all control experiments and our previous work into account, we proposed a plausible mechanism for the reaction, as presented in Scheme 3. Initially, the thiol was rapidly converted into disulfane in the presence of an air atmosphere, which in turn underwent oxidative addition to Ni₂P NPs to form the intermediates.^{9a,d} Next, the terminal alkyne was adsorbed and activated *via* hydrogen bonding between N atoms in carbon and terminal alkynyl hydrogen. In this step, N atoms as basic sites not only boost the selective absorption of the alkyne on the surface of the catalyst, but also activate the C_{sp}-H bond of the terminal alkyne.^{10,13} Finally, the desired product was obtained *via* reductive elimination and the entire catalytic cycle was simultaneously completed.

Conclusions

In conclusion, a stable heterogeneous Ni₂P nanoparticles on N,P-codoped carbon was developed for the synthesis of alkynyl thioethers *via* the cross-dehydrogenative coupling of alkynes and thiols under base- and ligand-free conditions. A broad range of alkynes and thiols could be efficiently coupled into their corresponding alkynyl thioethers in good to high yields with good tolerance to various functional groups. The catalyst can be readily recovered for successive recycling. N-dopants in the catalyst were identified to play a key role in the success of the reaction. To the best of our knowledge, this is the first case of accessing alkynyl thioethers catalyzed by a stable heterogeneous Ni-based catalyst, and also represents one of the most straightforward and efficient methods for the synthesis of alkynyl thioethers in a cost-effective and environmentally friendly manner.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors would like to acknowledge the financial support from the Key Technology R&D Program of Shandong Province (2019GGX102075), Open Projects of the State Key Laboratory of

Physical Chemistry of the Solid Surface (Xiamen University) (No. 201808), and the 13th-Five Key Project of the Chinese Academy of Sciences (Grant No. Y7720519KL). Y. Y. also acknowledges the support from the Royal Society (UK) for a Newton Advanced Fellowship (NAF\R2\180695).

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