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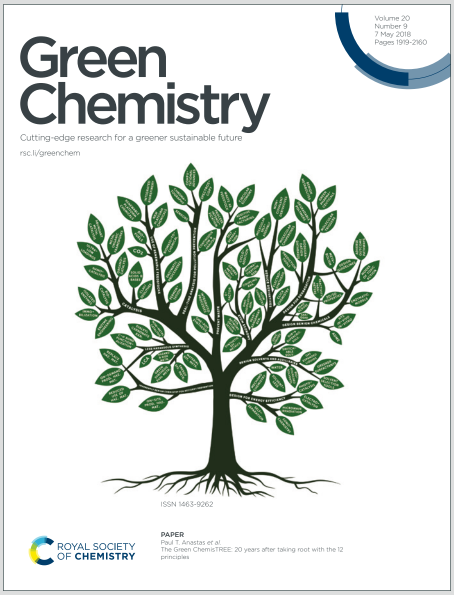

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PAPER
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The Green ChemisTREE: 20 years after taking root with the 12 principles

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COMMUNICATION

Highly Dispersed Ni_2P Nanoparticles on N,P-codoped Carbon for Efficient Cross-Dehydrogenative Coupling to Access Alkynyl Thioethers

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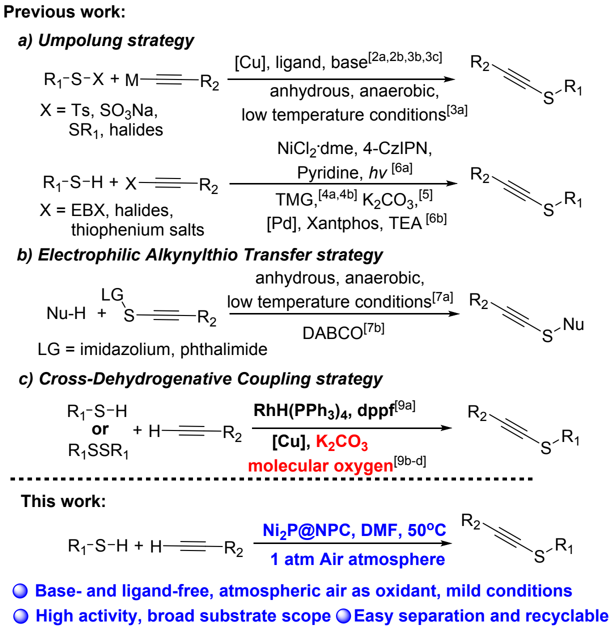
An ultrafine Ni_2P (a metal-rich interstitial phosphide compound) nanoparticles with narrow size distribution homogeneously dispersed on N,P-codoped carbon was developed for efficient synthesis of alkynyl thioethers via cross-dehydrogenative coupling (CDC) of terminal alkynes and thiols with base- and ligand-free using atmospheric air as oxidant under mild conditions. A remarkable catalytic performance with good compatibility of broad substrate scope and high stability are accomplished. Pyridinic N is identified as basic sites for facilitating activation of terminal alkyne via hydrogen bonding interaction and plays a key role for the success of this base- and ligand-free CDC reaction.

Alkynyl thioethers are extremely versatile and essential building blocks in organic synthesis and intermediates for synthesis of sulfur-rich functional polymers.[1] Up to now, various methods have been developed for preparation of alkynyl thioethers, including (i) umpolung strategy via the prefunctionalization of either thiols or alkynes to sulfenyl halides,[2] disulfides,[3]or ethynyl benziodoxolone (EDX) reagents,[4] (alkynyl)-dibenzothiophenium triflates,[5] haloalkynes[6], followed by the reaction with the coupling partners (Scheme 1a); (ii) electrophilic alkynylthio transfer strategy, in which alkyne was firstly converted to highly active electrophile as an alkynylthio transfer reagent with subsequent reaction with nucleophiles to deliver C-S bond compounds (Scheme 1b).[7] In these two strategies, prefunctionalization process of either terminal alkynes or thiols is necessary and in the presence of transition-metal (Pd,[6b] Cu,[2a, 2b, 3a, 3b] Ni[6a]) catalysis assisting with ligands or the mediate of base (K_2CO_3, [5] pyridine, [6a] tetramethylguanidine (TMG), [4a,4b] triethylamine (TEA), [6b] triethylenediamine (DABCO)[7b]), which usually cause some issues of the formation of unstable intermediates or undesirable side-products, and requirement of harsh reaction conditions[3a,7a].



Scheme 1. Strategies for the synthesis of alkynyl thioethers.

Besides, transition-metal catalyzed cross dehydrogenative coupling (CDC) of inactivated alkynes with thiols or disulfides represent the most straightforward and efficient method to access the alkynyl thioethers as shown in Scheme 1c, which have been frequently employed for construction of C-X (X = C, N, O) bonds.[8] However, only sporadic reports are available for synthesis of C-S bond to date, most likely due to the poison effect of sulphur atom on metals. In this context, Cu-based catalysts have been successfully applied for such a transformation with one exception of using precious Rh complex.[9a] Nonetheless, the assistance of sophisticated and

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x expensive organic ligands (dppf)[9a], and bases (K_2CO_3) [9b-d] in the presence of molecular oxygen atmosphere are necessary for the success of the reaction.[9b-d] More 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 from 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 Ni_2P@NPC-800), in which ultrafine Ni_2P nanoparticles (NPs) with narrow size distribution were homogeneously dispersed on N,P-codoped biomass-derived porous carbon. The resultant catalyst Ni_2P@NPC-800 shows excellent catalytic activities for synthesis of alkynyl thioethers via cross dehydrogenative coupling of alkynes and thiols using air as the sole oxidant with base- and ligand-free under mild conditions (Details of comparison with previous works see Table S2). To the best of our knowledge, this is the first case for 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 accompanying with good tolerance of functional groups, broad substrate scopes 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 Ni_2P NPs on biomass-derived porous carbon was prepared in a sequential hydrothermal and pyrolysis process according to our previous reports as shown in Figure 1a (See details in the Supporting Information).[10] The as-prepared catalysts were denoted as Ni_2P@NPC-T, where T represents the pyrolysis temperature. The Ni content in the catalysts was determined to be 3.05-4.96 wt% by the coupled plasma optical emission spectrometry (ICP-OES) (Table S1).

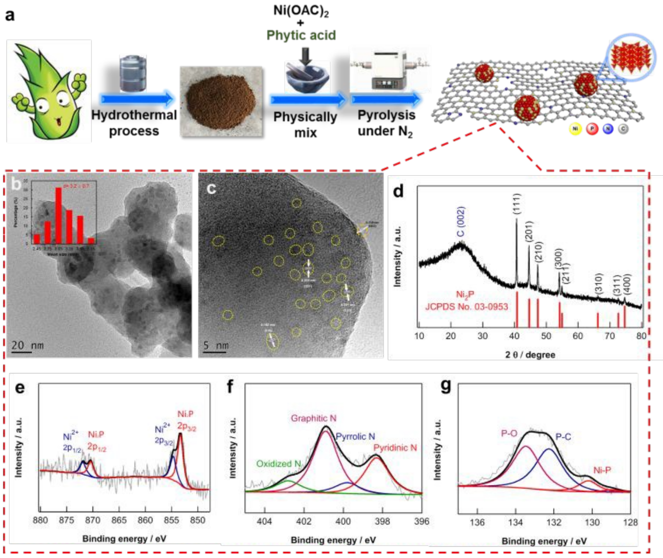

Figure 1. (a) Illustration for preparation of catalyst; (b), (c) HR-TEM and size distribution of Ni_2P@NPC-800; (d) Powder XRD pattern of Ni_2P@NPC-800; (e-g) High-resolution XPS spectra of Ni 2p, N 1s, P 2p of Ni_2P@NPC-800.

High-resolution transmission electron microscopy (HR-TEM) images (Figure 1b and c) of the catalyst Ni_2P@NPC-800 disclose that the small Ni_2P NPs with narrow size distribution (3.2 ± 0.7 nm) are uniformly dispersed on the graphitic carbon materials. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Figure S1a) with energy-dispersive X-ray (EDX) maps (Figure S1b-1f) clearly show that a homogeneous distribution of Ni, P, N, C and O through the entire carbon framework. Powder X-ray diffraction (PXRD) pattern (Figure 1d) discloses the formation of single Ni_2P phase on graphitic carbon, in good consistency with HR-TEM observation. N 1s and P 2p XPS analysis (Figure 1f and 1g) verify that N and P atoms were co-incorporated into the carbon framework. High resolution deconvolution analysis discloses that N atoms presented in pyridinic-, pyrrolic-, graphitic-, and oxidized-N species, while P-C, P-O, and Ni-P species were formed for P atoms. Ni 2p XPS (Figure 1e) further confirm the formation of metal-rich interstitial Ni_2P NPs, while a certain amount of Ni^{2+} species were also detected most likely due to the inevitable partial oxidation of Ni_2P NPs on the surface. N_2 adsorption/desorption measurements demonstrate that the catalyst Ni_2P@NPC-800 prepared in this strategy possesses hierarchically micro-, meso-, and macro-pores with high specific surface area and large pore volume as shown in Figure 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 the feasibility as shown in Table 1. Initially, we performed the reaction in the presence of Ni_2P@NPC-800 (8 mol% of Ni) as a catalyst, 10 mol% K_2CO_3 as a base at 70°C in DMF (0.1 M) under air atmosphere, full conversion of **1a** with 77% GC yield of the targeted product **2a** was achieved accompanying with the formation of diene (**4a**) in 23% after 6 h (Table 1, entry 1). The GC yield to **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 with further increasing the ratio to 1/2 (entry 3). Delightfully, we found that the GC yield to **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, 10), and reaction times (entries 8), were intensively investigated for the effect on reaction efficiency. The reaction in DMSO as the solvent showed comparable reactivity to that in DMF (entry 5), whereas a considerable lower reactivity with the formation of **4a** as major product was observed in THF or CH_3CN as solvent (entries 6 and 7). The reactivity as a function of reaction time showed that the reaction could complete with 4 h at 50°C (entry 8). Besides, the reaction temperature lowered from 70 to 50°C had a negligible effect on reactivity and selectivity to **2a** (entry 9), however, a further decrease to room temperature led to a significant drop in reactivity (entry 10). For comparison, the catalyst Ni_2P@NPC-700 showed a relatively lower activity, while a comparable reactivity was observed for the catalyst Ni_2P@NPC-900 (entries 11 and 12), compared with that of Ni_2P@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, all gave negligible or no reactivity (entries 13-16).

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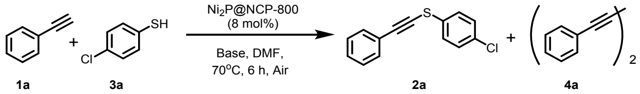
From these observations, we can safely conclude that the catalyst Ni_2P@NPC-800 and air atmosphere were indispensable for the success of the reaction.

Table 1. Optimization of reaction conditions.[a]



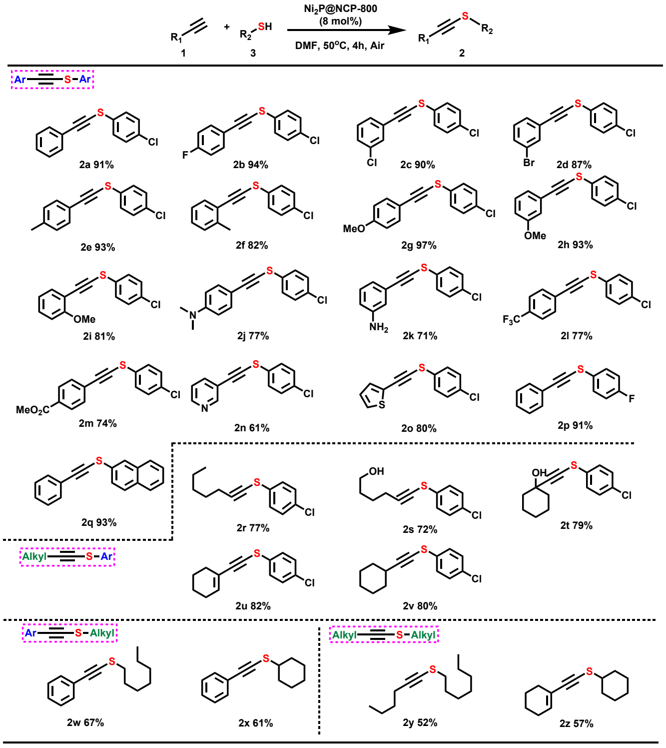
Entry	1a/1b (molar ratio)	Solvent	T [°C]	Conv. [%][b]	GC yield [%][b]	
					2a	4a
1[c]	1/1.1	DMF	70	100	77	23
2[c]	1/1.5	DMF	70	100	84	16
3[c]	1/2	DMF	70	100	87	17
4	1/1.5	DMF	70	100	95	5
5	1/1.5	DMSO	70	100	91	4
6	1/1.5	THF	70	61	11	50
7	1/1.5	CH_3CN	70	77	9	68
8[d]	1/1.5	DMF	70	100	96	4
9[d]	**1/1.5**	**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 consumption of phenylacetylene. [c] K_2CO_3 (10 mol%) was used. [d] 4 h instead of 6 h. [e] Ni_2P@NPC-700, 4 h. [f] Ni_2P@NPC-900, 4 h. [g] NPC-800, 4 h. [h] Under Ar atmosphere, 4 h. [i] $Ni(OAc)_2$ instead of Ni_2P@NPC-800, 4 h. [j] No catalyst, 4 h. [k] (4-chlorophenyl)(styryl)sulfane was detected by GC-MS.

After identifying the optimized reaction conditions, we then explored the generality of this protocol for the synthesis of alkynyl thioethers, the results are compiled in Table 2. Firstly, a set of functional groups substituted phenylacetylenes were tested to couple with **3a** under the optimized conditions. Phenylacethylenes bearing either electron-donating groups (-Me, -OMe, $-NH_2$, $-NMe_2$) or electron-withdrawing groups ($-CF_3$, $-CO_2Me$) were efficiently coupled to give their corresponding alkynyl thioethers in 71-97% yields. Comparatively, a relatively higher yield was achieved for the phenylacetylenes with electro-donating substituents (**1e, 1g, 1h**) than those with electro-withdrawing ones (**1l** and **1m**). The steric effect was clearly observed, for example, *otho*-methyl (**1f**) or methoxyl (**1i**) substituted phenylacetylene behaved a lower reactivity than that in *para*- or *meta*-position. Halogen substituents (F, Cl, and Br) are compatible with the present conditions, affording their corresponding alkynyl thioethers in 87-94% yields. Of note, the amino-substituted phenylacetylene (**1j** and **1k**), which are problematic substrates in previously reported protocols due to the easy oxidation and coordination with metal centers with N atom,[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 hydroxyl (**1s** and **1t**) group and conjugated with C=C bond (**2u**), are suitable for the reaction with formation of the targeted alkynyl thioethers in 72-82% yields. Moreover, other substituted benzenethiols (**3p** and **3q**) or alkyl thiols (**3w** and **3x**) also work well to construct the 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 their corresponding alkynyl thioether (**2y** and **2z**) in satisfactory yields.

Subsequently, we investigated the recyclability of the catalyst Ni_2P@NPC-800 for the benchmark reaction under the optimized conditions. The catalyst has been used 6 times consecutively with negligible changes of activity, indicating the strong stability (Figure S7). Separation of the solution from the catalyst 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 (Figure S8). Taken together, all the results strongly indicate the intrinsic role of the heterogeneous Ni_2P@NPC-800 in catalysis.

Table 2. Substrate scopes for synthesis of alkynyl thioethers.[a]



[a] Reaction conditions: alkyne (0.2 mmol), thiol (0.3 mmol) Ni_2P@NPC-800 (8 mol% of Ni), DMF (2 mL), air atmosphere, 50°C, 4h, [b] Isolated yields were reported.

To gain insight into the reaction pathway, a set of control experiments were carried out. The compounds distribution for the benchmark reaction as a function of reaction time under the optimized reaction conditions (Figure 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 small amount of the desired product **2a** was generated in this period. Subsequently, the gradual formation of **2a** via the coupling of **1a** and **5a** dominated the reaction till complete consumption of **1a**. So we assume that **5a** most likely acts as the real intermediate for the coupling, which has been frequently employed for the coupling of alkynes to construct C-

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S bond.[3] To prove this assumption, *p*-chlorobenzenethiol (**3a**) was subjected into the standard conditions (Scheme 2 eq. a), and **5a** was obtained in 99% yield determined by GC. More interestingly, **3a** could be quantitatively converted into **5a** in the absence of the catalyst Ni_2P@NPC-800 under otherwise identical conditions (Scheme 2 eq. b). Furthermore, the coupling reaction of phenylacetylene (**1a**) with **5a** instead of **3a** as coupling partner under the standard conditions also gave a comparable yield (93% vs 95% in Table 1, entry 9) to **2a** (Scheme 2 eq. c). Taken all results together, it was convinced that the coupling reaction indeed proceeds via the first formation of disulfane as a nucleophile for subsequent reaction with alkyne to produce the desired alkynyl thioether.

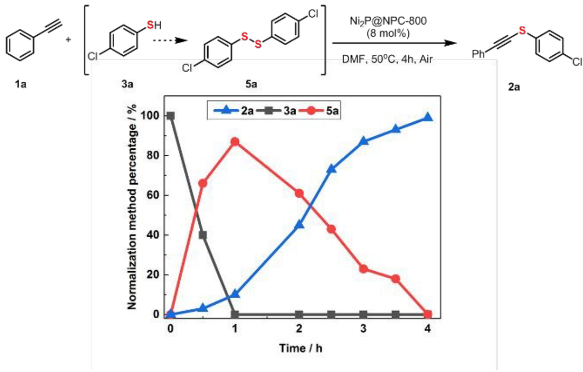
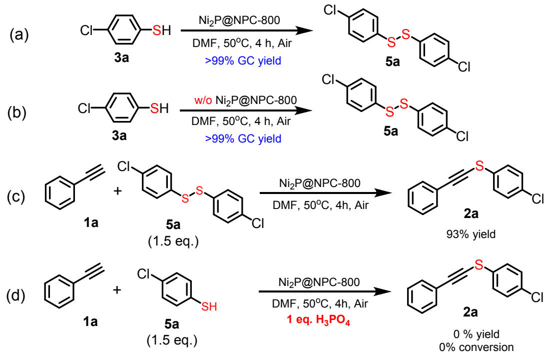


Figure 2. The compounds distribution for the benchmark reaction as a function of reaction time under the optimized reaction conditions.



Scheme 2. Control experiments.

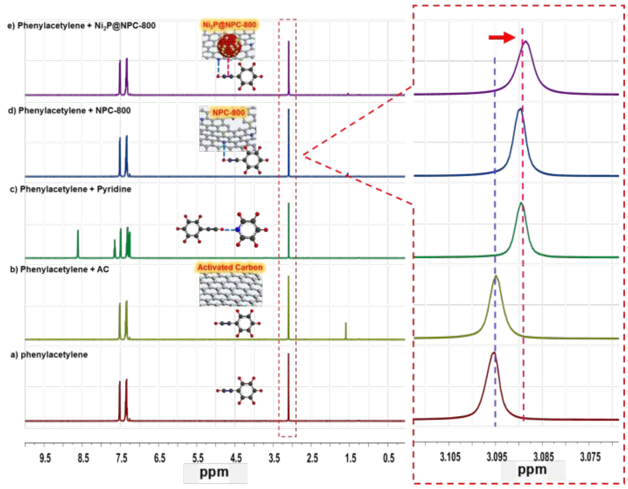
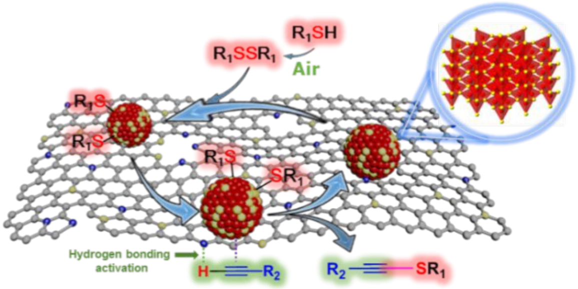


Figure 3. ^{1}H NMR experiments for study of the role of N-doping.

Previous studies show that a base (inorganic or organic) is basically required in CDCs to initiate the reaction via activating either thiol or terminal alkyne.[9b-9e] However, this is not the case in our present catalysis, and outstanding catalytic performance was achieved in the absence of base as shown in Table 2. We further attempted to elucidate the role of the catalyst. Control experiments discussed above reveal that thiol could be readily oxidized into disulfane without catalyst under air in DMF at 50ºC (Scheme 2, eq. a). So, ^{1}H NMR experiments were conducted to identify how the catalyst activate the terminal alkyne. 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 $CDCl_3$ solution containing the Ni_2P@NPC-800 for 10 min, which might due to the hydrogen bonding interaction between alkynyl hydrogen and Ni_2P NPs or N atoms doped in carbon.[13] Similar but with a slightly lower shift was also observed using NPC-800 instead of Ni_2P@NPC-800 with same treatment. In sharp contrast, no visible chemical shift was detected using activated carbon (AC) without N-doping instead, indicating that N atoms did play a role to interact with alkyne. As previously reported,[10,14] N atoms, specifically pyridinic species, in N-doped carbon could serve as basic sites to interact and/or activate some molecules. To prove it, pyridine, as mimicking N species in carbon, was mixed with **1a** in $CDCl_3$ solution, 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 Ni_2P@NPC-800.[10e,14] In addition, no reactivity was obtained when the benchmark reaction was performed under the optimized conditions, but with addition of stoichiometric amount of H_3PO_4 as a poisoning agent to deactivate N sites (Scheme 2, eq. d). Therefore, these experimental results clearly disclose that the key role of N atoms doped in carbon is as basic sites to activate alkyne via hydrogen bonding interaction, thereby facilitating the reaction.



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

Taking all control experiments and our previous works into account, we proposed a plausible mechanism for the reaction as presented in Scheme 3. Initially, thiol was rapidly converted into disulfane in the presence of air atmosphere, which underwent the oxidative addition to Ni_2P NPs to form the intermediates.[9a, 9e] 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

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not only boost the selective absorption of alkyne on the surface of catalyst, but also activate C_{sp}-H bond of terminal alkyne.[10, 13] Finally, the desired product was generated via reductive elimination and simultaneously completed the entire catalytic circle.

Conclusions

In conclusion, a stable heterogeneous Ni_2P 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 of various functional groups. The catalyst can be readily recovered for successive recycle. N-dopants in the catalyst was identified to play a key role for the success of the reaction. To the best of our knowledge, this is the first case to access alkynyl thioethers catalyzed by a heterogeneous stable Ni-based catalyst, and also represents one of the most straightforward and efficient method for synthesis of alkynyl thioethers in a cost-effective and environmentally friendly manner.

Conflicts of interest

There are no conflicts to declare.

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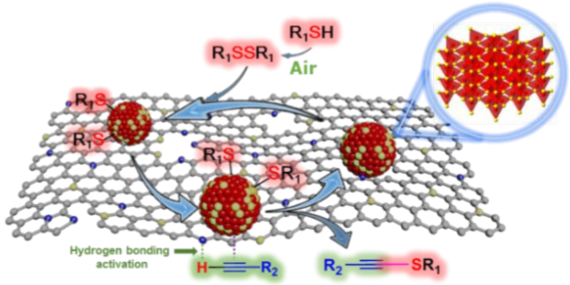

An Ni_2P nanoparticles on N,P-codoped carbon was developed for efficient synthesis of alkynyl thioethers via cross-dehydrogenative coupling (CDC) strategy under base- and ligand-free, air as oxidant conditions.