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Electrochemical Sulfenylation of Indoles with Disulfides Mediated by Potassium Iodide

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A novel electrochemical system for sulfenylation of indoles with disulfides to generate 3-sulfenylindoles via C-S bond formation mediated by potassium iodide at a low potential was developed. Iodine was electrogenerated from iodide ions at a graphite anode and showed a high catalytic activity for the electrochemical sulfenylation reactions. A variety of aromatic, heteroaromatic and aliphatic disulfides could react with 2-methlyindole to synthesize the corresponding 3-sulfenylindoles in good to excellent yields. In addition, protected and unprotected indoles with various groups, especially electron-donating groups, also performed well in the sulfenylation reactions. The transformation, which proceeded through the redox of iodine and the generation of intermediate 3-iodoindole, provided an efficient and environmentally benign protocol for the synthesis of 3-sulfenylindoles under mild conditions.
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Development of green and efficient methods for the C-S bond formation of the organosulfur compounds has gained much attention in organic synthesis and material science.[1–5] Organosulfur compounds, such as 3-sulfenylindoles, play an important role due to their therapeutic value in the treatment of HIV,[6] cancer,[7] allergies[8] and bacterial infection.[9] Over the past several years, two major synthetic strategies have been developed for preparation of 3-sulfenylindoles. One protocol was achieved by cyclization reaction of 2-alkynylanilines, 2-(gem-dibromo(chloro)vinyl)anilines or isocyanides.[10–13] Another was the direct sulfenylation of indoles via C–H functionalization, which has emerged as a highly attractive and powerful strategy to construct complicated organosulfur compounds.[14–19] A variety of sulfenylating reagents, such as *N*-thioiphthalimides, sulfonyl hydrazides, sulfinic acids, sulfonium salts, thiols and disulfides, have been employed as the important partners during the reactions. However, many of these reactions were catalyzed by transition-metal catalysts such as copper,[12] palladium,[13] cerium,[14] iron[15] or vanadium.[16] Recently, several approaches have been developed to access 3-sulfenylindoles without transition-metal catalysts. Schlosser et al. reported an efficient one-pot procedure for sulfenylation of 2-carboxyindoles with sulfenyl chlorides generated from thiols in the presence of *N*-chlorosuccinimide, but the reactions were carried out at −78°C.[20] The sulfenylation reaction of indoles with *N*-(thio)succinimides was studied by Hostier et al., but 15 equiv. of trifluoroacetic acid was needed as the promoter.[21] Bunte salts ($RSSO_3Na$) also have been utilized as the sulfenylating reagent to prepare 3-sulfenylindoles, but these salts are difficult to obtain.[22,23] Therefore, a green and sustainable method without transition-metal catalysts, harsh reaction conditions or stoichiometric amounts of oxidants for the synthesis of 3-sulfenylindoles is still highly desirable.

It is well-known that electrochemical method is an atom economical and environmentally benign strategy for formation of many organic compounds, and it can be performed under mild conditions.[24–27] In 2016, Zeng et al. reported an indirect electrochemical method to construct C-S bonds of 3-amino-2-thiocyanato-α,β-unsaturated carbonyl derivatives using 50 mol% NH_4Br as the redox mediator.[28] Subsequently the same group developed a similar methodology to generate oxindoles in the presence of 10 mol% NH_4Br.[29] During the course of this present work, Lei et al. reported a direct electrooxidation of *N*-methylindoles with thiols to synthesize 3-sulfenylindoles.[30] Their work was very interesting, but only trace amounts of 3-sulfenylindoles were obtained when aliphatic thiols were used, because high potentials might cause the over-oxidation of thiols.[31,32]

As a nontoxic, cheap and readily available catalyst, iodine has been widely applied in various organic transformations.[33–37] In recent years, iodine has been known as an important oxidation catalyst for C–S bond formation reactions, and iodine-catalyzed sulfenylation reactions in the presence of oxidants have stimulated considerable interest.[38–40] In 2016, our group developed an iodine-catalyzed protocol for the synthesis of 3-sulfenylindoles from indoles and thiols using DMSO as the oxidant.[41] It is well-known that iodine can be generated through electrochemical oxidation from iodide ions at a low potential,[42,43] and then serves as a redox mediator in indirect electrosynthesis. In continuation of our work on the development of electrochemical synthetic methodologies under mild conditions,[44–47] herein we reported an indirect electrochemical system for sulfenylation of indoles with disulfides to generate 3-sulfenylindoles mediated by potassium iodide (KI) at a low potential and over-oxidation of disulfides could be effectively inhibited. Cyclic voltammetry and electrolysis techniques were utilized in the present work to examine the electrocatalytic activity of iodine. In addition, a plausible mechanism was proposed on the basis of the identification of the intermediate.

Experimental

General remarks.—1,2-Bis(2-chlorophenyl)disulfide, 1,2-bis(3-chlorophenyl)disulfide, 1,2-bis(2-methoxyphenyl)disulfide, 1,2-bis(3-methoxyphenyl)disulfide and 1,2-didodecyldisulfane were prepared in our laboratory according to literature procedures.[48] Other chemicals and solvents were purchased from commercial suppliers and used without further purification. Gas chromatography (GC) was performed on an Agilent GC7890A system equipped with a SE-54 capillary column and a flame ionization detector (FID). ^1H (500 MHz) and ^{13}C NMR (125 MHz) were performed on a Bruker Avance III spectrometer. $CDCl_3$ was used as the solvent with tetramethylsilane (TMS) as the internal standard.

Cyclic voltammetry of sulfenylation.—Cyclic voltammetry experiments were carried out on Vertex Potentiostat/Galvanostat with an L-type graphite electrode (3 mm in diameter) in a 25 mL undivided cell. $NaBF_4$ (0.1 mol/L) was used as the supporting electrolyte in CH_3CN solution (15 mL). Another graphite rod (6 mm in diameter, 1 cm in length) was employed as the counter electrode and Ag/Ag^+ electrode (0.1 mol/L $AgNO_3$ in CH_3CN) as the reference. All the potentials in this work were referred to the Ag/Ag^+ reference electrode (E_0 = -77.5 mV vs. ferrocene redox couple).

Electrosynthesis of 3-sulfenylindoles.—The electrochemical experiment was performed on 263A Potentiostat/Galvanostat (Princeton Applied Research, USA) in a 25 mL undivided cell. Two graphite rods (6 mm in diameter, 1 cm in length) were employed as the working electrode and the counter electrode respectively. The reference electrode was Ag/Ag^+ electrode (0.1 mol/L $AgNO_3$ in CH_3CN). 2-Methylindole (**1a**, 1.0 mmol), diphenyl disulfide (**2a**, 0.5 mmol) and KI (0.05 mmol) were added into 0.1 mol/L of $NaBF_4/CH_3CN$ solution (15 mL) with stirring at 60°C. The electrolysis reactions were operated at 0.4 V.

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After completion of the reaction (monitored by GC or TLC), the resulting mixture was concentrated under reduced pressure and purified by column chromatography on silica gel using hexanes/EtOAc (100:1) as eluent to afford 2-methyl-3-(phenylthio)-indole (**3aa**) as a white solid in 94% yield.

Characterization data for products.—*2-methyl-3-(phenylthio)-1H-indole (3aa).*—Yield: 94%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 8.2 Hz, 1H), 7.21– 7.17 (m, 1H), 7.16–7.11 (m, 3H), 7.04–7.01 (m, 3H), 2.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.1, 139.3, 135.4, 130.3, 128.7, 125.5, 124.5, 122.2, 120.7, 119.0, 110.6, 99.4, 12.2.

3-((4-chlorophenyl)thio)-2-methyl-1H-indole (3ab).—Yield: 90%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.27–7.23 (m, 1H), 7.20–7.18 (m, 1H), 7.17–7.13 (m, 2H), 7.01-6.98 (m, 2H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.2, 137.9, 135.4, 130.2, 130.0, 128.7, 126.7, 122.3, 120.8, 118.8, 110.7, 98.9, 12.1.

3-((3-chlorophenyl)thio)-2-methyl-1H-indole (3ac).—Yield: 99%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.33–7.30 (m, 1H), 7.28–7.25 (m, 1H), 7.15–7.09 (m, 3H), 7.03-7.01 (m, 1H), 2.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.7, 141.5, 135.4, 134.6, 129.9, 129.7, 124.9, 124.7, 123.5, 122.3, 120.8, 118.6, 110.8, 98.1, 11.9.

3-((2-chlorophenyl)thio)-2-methyl-1H-indole (3ad).—Yield: 92%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 8.2 Hz, 1H), 7.35–7.34 (m, 1H), 7.25–7.22 (m, 1H), 7.17–7.14 (m, 1H), 7.01-6.98 (m, 1H), 6.95-6.92 (m, 1H), 6.57-6.55 (m, 1H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.7, 138.4, 135.6, 130.2, 130.1, 129.3, 126.9, 125.9, 125.2, 122.4, 120.9, 119.0, 110.7, 97.9, 12.2.

3-((4-bromophenyl)thio)-2-methyl-1H-indole (3ae).—Yield: 97%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.28–7.25 (m, 2H), 7.24–7.21 (m, 1H), 7.17–7.14 (m, 1H), 6.92-6.90 (m, 2H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.2, 138.7, 135.5, 131.6, 130.0, 127.1, 122.4, 120.9, 118.8, 118.0, 110.7, 98.9, 12.2.

3-((4-fluorophenyl)thio)-2-methyl-1H-indole (3af).—Yield: 90%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.23–7.20 (m, 1H), 7.17–7.14 (m, 1H), 7.05–7.01 (m, 2H), 6.90-6.85 (m, 2H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.8 (d, J = 242.2 Hz), 141.0, 135.4, 134.2, 130.1, 127.4 (d, J = 7.3 Hz), 122.3, 120.8, 118.9, 115.7 (d, J = 21.9 Hz), 110.6, 99.9, 12.2.

2-methyl-3-((4-nitrophenyl)thio)-1H-indole (3ag).—Yield: 82%; Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.03-8.00 (m, 2H), 7.48 (d, J = 5.7 Hz, 1H), 7.42 (d, J = 8.1 Hz, 1H), 7.28–7.24 (m, 1H), 7.19–7.16 (m, 1H), 7.12–7.10 (m, 2H), 2.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.9, 144.8, 141.7, 135.6, 129.6, 124.9, 123.9, 122.7, 121.2, 118.6, 111.0, 97.0, 12.1.

3-((4-methoxyphenyl)thio)-2-methyl-1H-indole (3ah).—Yield: 96%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.22–7.19 (m, 1H), 7.17–7.14 (m, 1H), 7.09–7.06 (m, 2H), 6.77-6.74 (m, 2H), 3.75 (s, 3H), 2.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.5, 140.6, 135.4, 130.3, 129.9, 127.9, 122.1, 120.6, 118.9, 114.5, 110.6, 100.8, 55.3, 12.1.

3-((3-methoxyphenyl)thio)-2-methyl-1H-indole (3ai).—Yield: 90%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.22–7.19 (m, 1H), 7.16–7.13 (m, 1H), 7.10–7.07 (m, 1H), 6.65-6.59 (m, 3H), 3.70 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.9, 141.2, 140.9, 135.4, 130.3, 129.5, 122.2, 120.7, 119.0, 117.9, 111.2, 110.6, 110.0, 99.2, 55.1, 12.2.

3-((2-methoxyphenyl)thio)-2-methyl-1H-indole (3aj).—Yield: 94%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H), 7.23–7.20 (m, 1H), 7.15–7.12 (m, 1H), 7.06–7.03 (m, 1H), 6.88-6.86 (m, 1H), 6.70-6.67 (m, 1H), 6.53-6.51 (m, 1H), 4.00 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.2, 141.5, 135.6, 130.5, 127.6, 125.4, 125.1, 122.2, 121.1, 120.7, 119.1, 110.6, 110.1, 97.7, 55.9, 12.2.

2-methyl-3-(p-tolylthio)-1H-indole (3ak).—Yield: 96%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.19–7.16 (m, 1H), 7.13–7.10 (m, 1H), 6.95 (s, 4H), 2.50 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.9, 135.7, 135.4, 134.3, 130.4, 129.5, 125.3, 122.1, 120.7, 119.0, 110.6, 99.9, 20.8, 12.2.

3-((4-isopropylphenyl)thio)-2-methyl-1H-indole (3al).—Yield: 90%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.59 (d, J = 7.8 Hz, 1H), 7.36 (d, J = 8.1 Hz, 1H), 7.22–7.19 (m, 1H), 7.16–7.13 (m, 1H), 7.05–7.03 (m, 2H), 7.01-7.00 (m, 2H), 2.86-2.78 (m, 1H), 2.54 (s, 3H), 1.20 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.4, 141.0, 136.1, 135.4, 130.4, 126.9, 125.7, 122.1, 120.6, 119.1, 110.6, 99.9, 33.5, 24.0, 12.2.

4-((2-methyl-1H-indol-3-yl)thio)aniline (3am).—Yield: 92%; Brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.19–7.16 (m, 1H), 7.15–7.11 (m, 1H), 7.00–6.97 (m, 2H), 6.54-6.52 (m, 2H), 3.54 (s, 2H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.1, 140.3, 135.3, 130.4, 128.6, 127.1, 121.9, 120.5, 119.0, 115.8, 110.5, 12.2.

3-((2-methyl-1H-indol-3-yl)thio)phenol (3an).—Yield: 93%; Brown solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.34 (d, J = 7.9 Hz, 1H), 7.21 (t, J = 7.4 Hz, 1H), 7.17–7.14 (m, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 6.51 (d, J = 8.1 Hz, 1H), 6.40 (d, J = 1.6 Hz, 1H), 4.70 (t, J = 8.1 Hz, 1H), 2.51 (d, J = 2.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.9, 141.4, 141.1, 135.4, 130.2, 129.8, 122.2, 120.7, 118.9, 117.9, 112.0, 111.7, 110.8, 98.8, 12.1.

2-methyl-3-(thiophen-2-ylthio)-1H-indole (3ao).—Yield: 86%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.76–7.73 (m, 1H), 7.32– 7.29 (m, 1H), 7.20–7.17 (m, 2H), 7.14–7.13 (m, 1H), 7.07–7.06 (m, 1H), 6.88–6.86 (m, 1H), 2.62 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.0, 138.7, 135.1, 129.8, 128.9, 127.2, 126.7, 122.2, 120.7, 118.8, 110.6, 103.2, 12.2.

2-methyl-3-(pyridine-2-ylthio)-1H-indole (3ap).—Yield: 95%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H),8.44-8.42 (m, 1H), 7.56 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.35-7.32 (m, 1H), 7.24–7.20 (m, 1H), 7.17–7.14 (m, 1H), 6.96–6.94 (m, 1H), 6.66 (d, J = 8.2 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.8, 149.3, 141.5, 136.6, 135.7, 130.0, 122.3, 120.8, 119.4, 119.1, 118.8, 110.8, 98.1, 12.2.

2-methyl-3-(propylthio)-1H-indole (3aq).—Yield: 82%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.74-7.71 (m, 1H), 7.31-7.28 (m, 1H), 7.22–7.18 (m, 2H), 2.64 (t, J = 5.0 Hz, 2H), 2.54 (s, 3H), 1.58–1.51 (m, 2H), 1.00 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.8, 135.2, 130.7, 121.7, 120.2, 118.8, 110.5, 102.6, 38.2, 23.2, 13.3, 12.2.

3-(dodecylthio)-2-methyl-1H-indole (3ar).—Yield: 65%; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.75-7.72 (m, 1H), 7.30-7.28 (m, 1H), 7.22–7.19 (m, 2H), 2.67 (t, J = 7.3 Hz, 2H), 2.53

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(s, 3H), 1.56–1.50 (m, 2H), 1.43–1.37 (m, 2H), 1.35–1.28 (m, 16H), 0.94 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.7, 135.2, 130.6, 121.7, 120.2, 118.8, 110.5, 102.6, 36.3, 31.9, 30.0, 29.6, 29.6, 29.6, 29.6, 29.3, 29.3, 28.6, 22.7, 14.1, 12.1.

3-(benzylthio)-2-methyl-1H-indole (3as).—Yield: 72%; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.70–7.67 (m, 1H), 7.32–7.28 (m, 1H), 7.21–7.16 (m, 5H), 6.98–6.97 (m, 2H), 3.77 (s, 2H), 2.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 141.17, 139.25, 135.28, 130.41, 129.00, 128.06, 126.55, 121.80, 120.30, 118.61, 110.50, 101.34, 40.34, 11.47.

3-(butylthio)-2-methyl-1H-indole (3at).—Yield: 52%; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.72–7.69 (m, 1H), 7.32– 7.28 (m, 1H), 7.20–7.17 (m, 2H), 2.66 (t, J = 1.5 Hz, 2H), 2.55 (s, 3H), 1.53–1.48 (m, 2H), 1.45–1.38 (m, 2H), 0.88(t, J = 1.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.70, 135.23, 130.73, 121.75, 120.19, 118.81, 110.46, 102.77, 35.90, 32.06, 21.74, 13.73, 12.18.

1-methyl-3-(phenylthio)-1H-indole (3ba).—Yield: 92%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.36– 7.34 (m, 2H), 7.24–7.21 (m, 1H), 7.21–7.19 (m, 2H), 7.17–7.15 (m, 2H), 7.11–7.08 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.7, 137.5, 135.0, 129.8, 128.6, 125.7, 124.7, 122.5, 120.5, 119.7, 109.7, 100.5, 33.1.

3-((4-chlorophenyl)thio)-1-methyl-1H-indole (3bb).—Yield: 95%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.37–7.33 (m, 2H), 7.24–7.20 (m, 1H), 7.16–7.13 (m, 2H), 7.07–7.04 (m, 2H), 3.87 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.3, 137.6, 135.1, 130.4, 129.5, 128.7, 127.0, 122.7, 120.64, 119.5, 109.8, 100.1, 33.1.

1-methyl-3-(p-tolylthio)-1H-indole (3bj).—Yield: 83%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 7.27–7.24 (m, 2H), 7.17–7.12 (m, 1H), 7.01 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 8.2 Hz, 2H), 3.74 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.5, 136.0, 134.9, 134.5, 129.9, 129.5, 126.2, 122.5, 120.4, 119.8, 109.7, 101.2, 33.0, 20.9.

3-(phenylthio)-1H-indole (3ca).—Yield: 86%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 2.6 Hz, 1H), 7.42 (d, J = 8.2 Hz, 1H), 7.28– 7.24 (m, 1H), 7.18–7.14 (m, 3H), 7.11–7.09 (m, 2H), 7.06–7.03 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.2, 136.5, 130.7, 129.1, 128.7, 125.9, 124.8, 123.1, 120.9, 119.7, 111.6, 102.9.

5-methyl-3-(phenylthio)-1H-indole (3da).—Yield: 95%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.46 (d, J = 2.5 Hz, 1H), 7.44 (s, 1H), 7.35 (d, J = 8.3 Hz, 1H), 7.20– 7.17 (m, 2H), 7.13–7.11 (m, 3H), 7.09–7.06 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.5, 134.8, 130.9, 130.4, 129.4, 128.7, 125.7, 124.7, 124.7, 119.2, 111.2, 102.0, 21.5.

3-((4-chlorophenyl)thio)-5-methyl-1H-indole (3db).—Yield: 93%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.46 (d, J = 2.6 Hz, 1H), 7.40 (s, 1H), 7.35 (d, J = 8.4 Hz, 1H), 7.16–7.13 (m, 3H), 7.05–7.03 (m, 2H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.1, 134.8, 130.9, 130.6, 130.4, 129.1, 128.8, 126.9, 124.9, 119.0, 111.3, 101.6, 21.5.

5-methyl-3-(p-tolylthio)-1H-indole (3dj).—Yield: 94%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.45–7.44 (m, 2H), 7.33 (d, J = 8.3 Hz, 1H), 7.12–7.10 (m, 1H), 7.06–7.04 (m, 2H), 7.01 (d, J = 8.2 Hz, 2H), 2.44 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.8, 134.8, 134.5, 130.7, 130.3, 129.5, 129.4, 126.0, 124.6, 119.2, 111.2, 102.6, 21.4, 20.9.

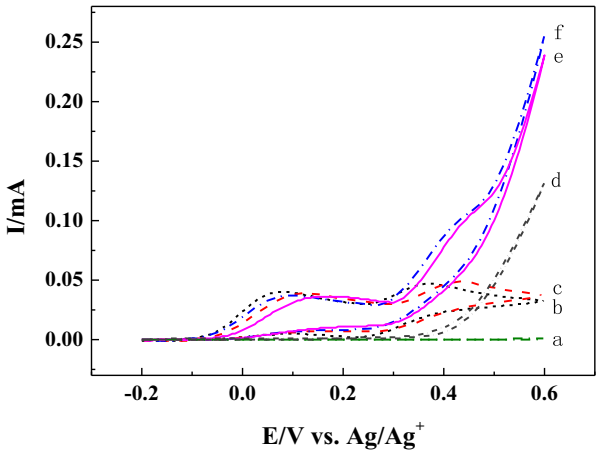

Figure 1. Cyclic voltammograms recorded in 0.1 mol/L $NaBF_4/CH_3CN$ at 50 mV s^{-1} scan rate with (a) blank solution; (b) KI (0.05 mmol); (c) KI (0.05 mmol) and **2a** (0.5 mmol); (d) **1a** (1 mmol) and **2a** (0.5 mmol); (e) KI (0.05 mmol), **1a** (1 mmol) and **2a** (0.5 mmol); (f) KI (0.05 mmol) and **1a** (1 mmol).

5-methyoxy-3-(phenylthio)-1H-indole (3ea).—Yield: 84%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.46 (d, J = 2.6 Hz, 1H), 7.33 (d, J = 8.8 Hz, 1H), 7.20 (t, J = 7.7 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 7.10–7.07 (m, 2H), 6.96–6.94 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 155.2, 139.3, 131.4, 131.3, 130.0, 128.7, 125.7, 124.7, 113.6, 112.4, 102.3, 100.8, 55.8.

1-methyl-2-phenyl-3-(phenylthio)-1H-indole (3fa).—Yield: 92%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 7.9 Hz, 1H), 7.52–7.46 (m, 6H), 7.40–7.37 (m, 1H), 7.28–7.24 (m, 1H), 7.21–7.18 (m, 2H), 7.12–7.06 (m, 3H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.9, 140.0, 137.6, 130.6, 130.5, 129.7, 128.7, 128.6, 128.2, 125.5, 124.4, 122.8, 120.9, 119.8, 109.8, 99.6, 31.7.

5-bromo-3-(phenylthio)-1H-indole (3ga).—Yield: 67%; White solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (s, 1H), 7.78 (s, 1H), 7.50 (d, J = 2.5 Hz, 1H), 7.38– 7.36 (m, 1H), 7.32 (d, J = 8.2 Hz, 1H) 7.21 (t, J = 5.2 Hz, 2H), 7.10 (t, J = 4.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.7, 135.1, 131.9, 131.0, 128.8, 126.1, 125.9, 125.1, 122.2, 114.5, 113.1, 102.8.

3-iodo-2-methyl-1H-indole (4).—Yield: 15%; Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.39– 7.38 (m, 1H), 7.28–7.25 (m, 1H), 7.22–7.17 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.3, 135.9, 130.9, 122.4, 120.6, 120.3, 110.6, 59.1, 14.5. MS (EI), m/z 260.17 [M^+, 100%].

Results and Discussion

Cyclic voltammetric study of sulfenylation.—Electrochemical sulfenylation of 2-methylindole (**1a**) with diphenyl disulfide (**2a**) mediated by KI in 0.1 mol/L $NaBF_4/CH_3CN$ solution was studied by cyclic voltammetry. As shown in curve a of Fig. 1, cyclic voltammograms were recorded in $NaBF_4/CH_3CN$ blank solution, and no redox wave was observed at potentials ranged from −0.2 V to 0.6 V. With the addition of KI (0.05 mmol) into the blank solution, two typical oxidation peaks of iodide ions were displayed at about 0.08 V and 0.37 V (curve b), which corresponded to the oxidation of iodide ion to form triiodide ion (Eq. 1) and the oxidation of triiodide ion to produce molecular iodine (Eq. 2):[49]

$$3I^- - 2e^- \rightarrow I_3^- \quad [1]$$

$$2I_3^- - 2e^- \rightarrow 3I_2 \quad [2]$$

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Table I. Optimization of electrolytic conditions[a].

Entry	KI (mol%)	Potential (V)	Electrode	Temperature (°C)	Time (h)	Conv.[b,c] (%)	Select.[c,d] (%)
1	5	0.6	Pt	60	5	99	99
2	3	0.6	Pt	60	5	42	85
3	0	0.6	Pt	60	5	trace	–
4	5	0.6	C	60	5	99	99
5	5	0.4	C	60	5	93	99
6	**5**	**0.4**	**C**	**60**	**6**	**99**	**99**
7	5	0.2	C	60	6	58	98
8	5	0.4	C	40	6	64	99
9	5	0.4	C	25	6	27	99

[a]Electrolytic conditions: **1a** (1 mmol), **2a** (0.5 mmol), 0.1 mol/L $NaBF_4/CH_3CN$ solution (15 mL), undivided cell.
[b]Conversion of **1a**.
[c]Determined by GC with peak area normalization method.
[d]Selectivity to **3aa**.

In order to investigate the catalytic ability of iodine for the electrochemical sulfenylation reaction, 0.5 mmol **2a** and 1.0 mmol **1a** were added into the above solution respectively. As a comparison with curve b, the peak currents didn't change obviously in the presence of **2a** (curve c), which revealed that **2a** showed almost no voltammetric response at the electrode. While **1a** was added to the solution, the second oxidation peak at about 0.37 V increased dramatically (curve f). It demonstrated that iodine, which electrogenerated from triiodide ion at the anode, has reacted with **1a** rather than **2a** in 0.1 mol/L $NaBF_4/CH_3CN$ solution. With the consumption of **1a**, the oxidation current of triiodide ion to iodine was greatly promoted and the reduction current decreased. When **1a** and **2a** were added into the solution simultaneously, almost the same cyclic voltammogram as curve f was observed (curve e). It suggested that an intermediate might be generated from iodine and **1a**, and then reacted with **2a** through chemical process to generate a new compound.[50,51] The conductivity of the solution decreased a little with the addition of substrates, and the oxidation peak potentials of curve e shifted positively as compared with curve f.

In addition, the oxidation currents of curves e and f increased rapidly when the potential was more than 0.5 V. To analyze the cyclic voltammograms more clearly, the experiment in 0.1 mol/L $NaBF_4/CH_3CN$ with **1a** and **2a** in the absence of the mediator KI was also carried out (curve d). As shown in curve d, the oxidation current of **1a** began to increase at about 0.4 V to form indole radical cation.[52] However, iodide ion as a nucleophilic reagent, could attack indole radical cation to produce 3-iodo-indole, and the electropolymerization of indole was inhibited effectively as shown in curves e and f.[53] Therefore, a low and suitable potential should be chosen for the electrochemical reactions.

Optimization of electrolysis conditions.—In an endeavor to achieve the optimized conditions for electrochemical sulfenylation reactions, **1a** and **2a** were chosen as the model substrates to generate the corresponding product **3aa** and the results were shown in Table I. When 0.6 V was chosen as the potential for a controlled potential electrolysis at Pt electrode (entry 1), excellent conversion of **1a** (99%) and selectivity to **3aa** (99%) were obtained in the presence of 5 mol% KI. To our delight, polymerization reaction of **1a** was not obvious. The conversion was decreased to 42% when KI was reduced to 3 mol% (entry 2), and only trace amounts of the desired product was observed in the absence of KI (entry 3). It showed that iodine played an important role in the electrochemical sulfenylation reaction. Therefore, 5 mol% KI was applied for all the substrates in the following electrochemical experiments. When inexpensive graphite rods took the place of Pt electrodes, it also showed excellent performance for the sulfenylation reaction under the similar conditions (entry 4). When the potential was reduced to 0.4 V or 0.2 V, the conversion of **1a** decreased slightly (entries 5 and 7). With the reaction time prolonged to 6 h at 0.4 V, 99% conversion and 99% selectivity were obtained (entry 6). Thus 0.4 V was chosen for the constant potential electrolysis, which was in good agreement with the results of cyclic voltammetry. The sulfenylation reactions have also been performed at 40°C and room temperature (25°C) under the above optimized conditions. However, only 64% and 27% conversions of **1a** were obtained after 6 h (entries 8 and 9), and 60°C might be better for the sulfenylation reactions.

To further study the electrolysis progress, the sulfenylation reaction of **1a** with **2a** was monitored by gas chromatography (GC) once an hour (Fig. 2). During the electrolysis, **1a** and **2a** reduced gradually and the desired product **3aa** was formed with time. After 6 h of electrolysis, the GC yield of **3aa** was 99% and the Faradic efficiency was about 87%. As we expected, **1a** and **2a** were successfully converted into **3aa** in the presence of KI at a low potential of 0.4 V.

Scope of sulfenylation of indoles with disulfides.—The general applicability of the catalytic system for sulfenylation of **1a** with various disulfide derivatives was investigated. Isolated yields of the products were obtained during the electrochemical sulfenylation of **1a** (1.0 mmol) with disulfide derivatives (0.5 mmol) in 0.1 mol/L $NaBF_4/CH_3CN$ solution (15 mL) in the presence of KI (5 mol%), as shown in Scheme 1. **3aa** was obtained from **1a** and **2a** under the optimized conditions with 94% isolated yield. It was found that diphenyl disulfides with halide groups such as chloro (*o*-, *m*-, *p*-), bromo, and fluoro on benzene ring could react with **1a** steadily and the isolated yields of 3-sulfenylindoles were higher than 90% (**3ab-3af**). 4-Nitrophenyl disulfide and **1a** could smoothly transformed

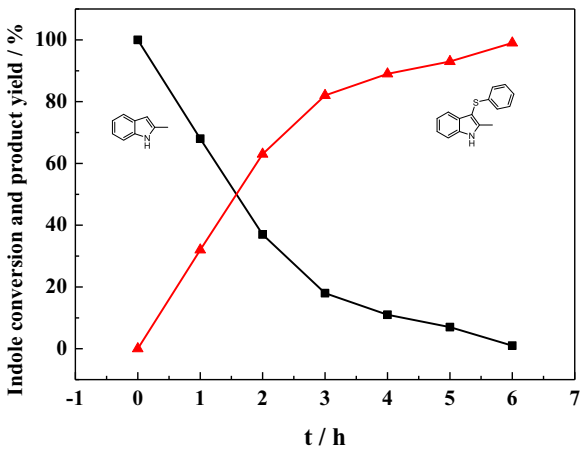

Figure 2. Effect of reaction time on indole conversion and product yield. Reaction conditions: 0.1 mol/L $NaBF_4/CH_3CN$ (15 mL), **1a** (1.0 mmol), **2a** (0.5 mmol), KI (0.05 mmol), 0.4 V, 60°C, 6 h. Conversion and yield were determined by GC with area normalization method.

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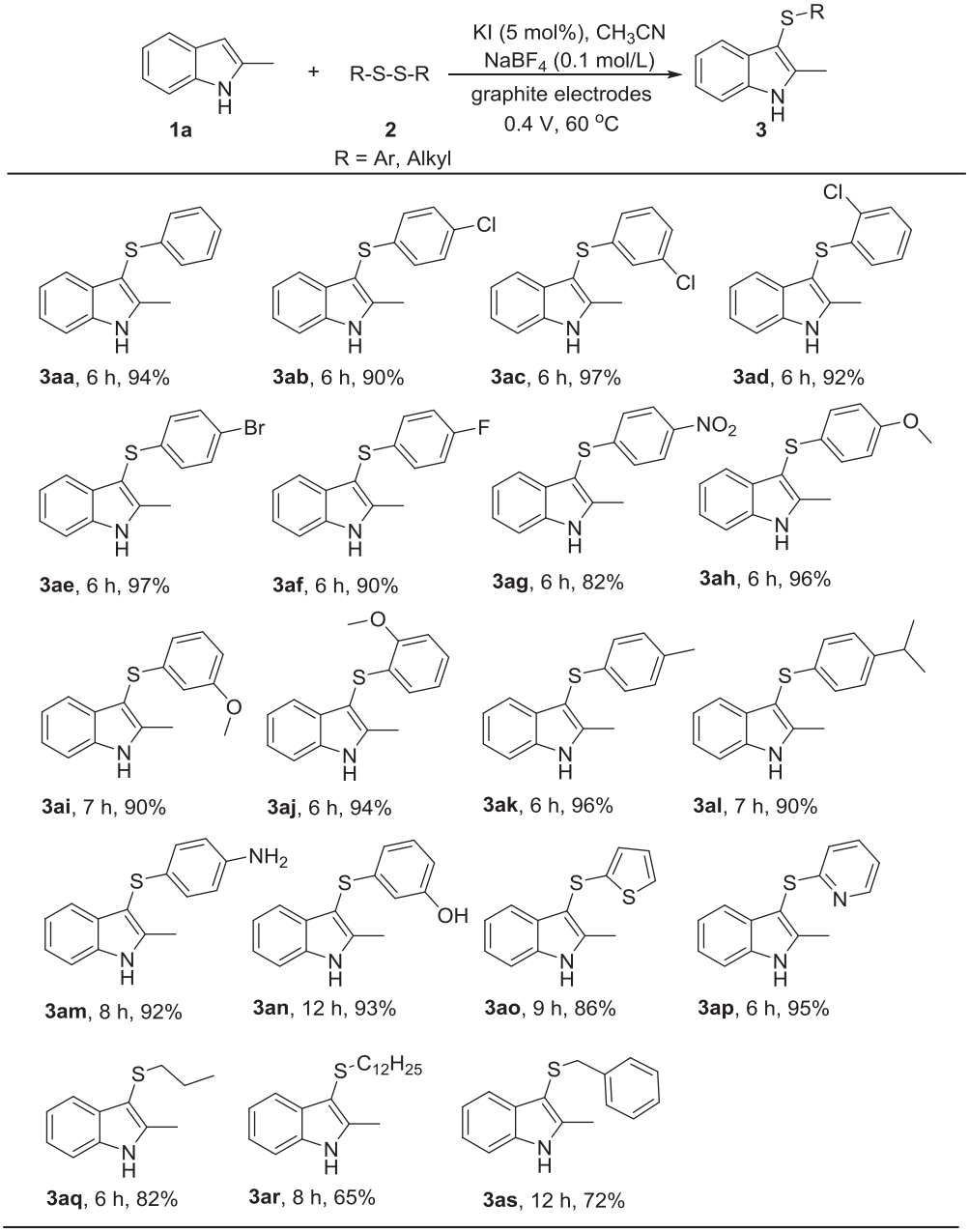

Scheme 1. Reactions of **1a** with various disulfides. The reactions were carried out with **1a** (1 mmol), **2** (0.5 mmol) and KI (0.05 mmol) in 0.1 mol/L $NaBF_4/CH_3CN$ solution (15 mL) at 60°C. Yield of isolated product 65–97%.

to the desired product **3ag** in 82% yield. Diphenyl disulfides with methoxy group in ortho, meta and para positions also underwent smooth transformations to generate the desired products in excellent isolated yields (**3ah-3aj**). Furthermore, electron-donating groups such as methyl, isopropyl, amino, and hydroxyl in para positions performed well in this transformation with the yields higher than 90% (**3ak-3an**). These results revealed that aromatic disulfides with either electron-withdrawing or electron-donating groups could react with **1a** and give the corresponding 3-sulfenylindoles in good to excellent yields. In addition, we were delighted to disclose that similar sulfenylation reactions, using heteroaromatic disulfides including 2-thienyl disulfide and 2,2'-dithiodipyridine as sulfenylating agents, were also performed successfully under present reaction conditions (**3ao-3ap**). Aliphatic disulfides, such as dipropyl disulfide, 1,2-didodecyldisulfane and 1,2-dibenzyldisulfane, also could react with **1a** to generate the desired products in good yields (**3aq-3as**).

Next, we explored the scope of indole derivatives. As shown in Scheme 2, 1-methylindole has been successfully employed in this process, and the isolated yields of products were more than 83% (**3ba-3bj**). The standard conditions were also applied to indole, but the reaction time should be prolonged to 12 h to achieve high product yield (**3ca**). The presence of electron donating groups (methyl, methoxy) on the benzene ring of indoles underwent conversion to produce the corresponding 3-sulfenylindoles in good to excellent yields (**3da-3ea**). Steric effects did not play an important role in the isolated yield when a phenyl group was introduced in the C-2 position of indole (**3fa**). However, it appeared that indoles with electron-withdrawing groups became sluggish. For example, the reaction of 5-bromoindole and **2a** gave only 67% yield of the desired product **3ga** even the potential was up to 0.6 V and the reaction time was prolonged to 20 h.

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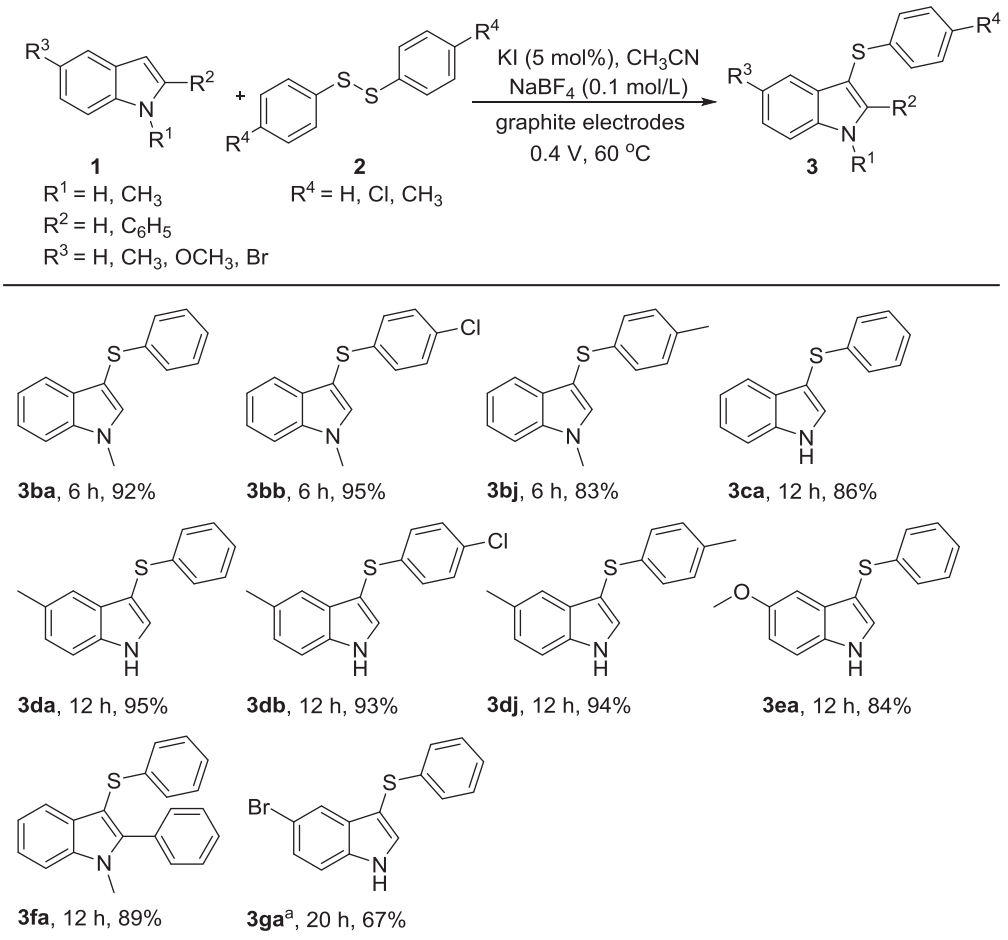
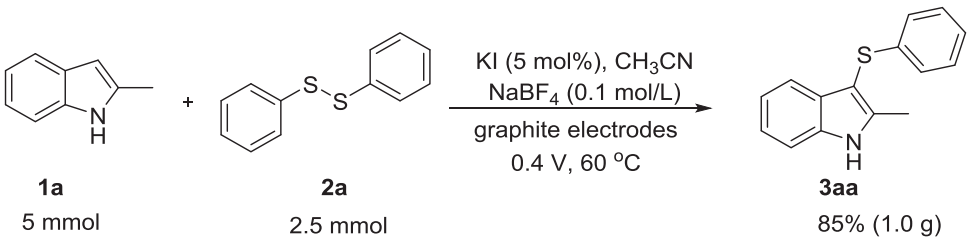


Scheme 2. Scope of indole derivatives. The reactions were carried out with **1** (1 mmol), **2** (0.5 mmol) and KI (0.05 mmol) in 0.1 mol/L $NaBF_4/CH_3CN$ solution (15 mL) at 60°C. Yield of isolated product 67–95%. [a]0.6 V.

To evaluate the scalability of this electrocatalytic system, the sulfenlation reaction of **1a** and **2a** was performed on a gram-scale (Scheme 3). To our delight, the desired product **3aa** was obtained in 85% isolated yield (1.0 g). The result showed the great potential of this electrochemical method in practical synthesis.

Mechanism investigation.—According to the cyclic voltammetry analysis of Fig. 1, an intermediate might be generated from **1a** and iodine. To gain further insight into the reaction mechanism, several control experiments were carried out (Scheme 4). To make **1a** be fully converted at a constant potential of 0.4 V, 2 equiv. of KI was added into 0.1 mol/L $NaBF_4/CH_3CN$ solution (Eq. 3). However, intermediate 3-iodo-2-methyl-indole (**4**) was unstable and its isolated yield was only 15%.[50,51] No desired product **3aa** was observed without electric current (Eq. 4). Then **4** successfully reacted with **2a** in the absence of KI to synthesize **3aa** in 88% isolated yield (Eq. 5). In addition, when 1 equiv. of (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) was added as the radical scavenger[28,30,54] in 0.1 mol/L $NaBF_4/CH_3CN$ solution with **1a** (1.0 mmol), **2a** (0.5 mmol) and KI (0.05 mmol) under the standard conditions, only 37% GC yield of **3aa** was obtained (Eq. 6). In our previous report,[41] when stoichiometric TEMPO was added into the reaction solution of indole and 1,2-diphenyldisulfane in the presence of 5 mol% I_2 with DMSO as the terminal oxidant, the GC yield of sulfenylation product was decreased from 97% to 30%. These results revealed that radical intermediates might be involved in this transformation. In order to investigate the catalytic ability of iodine more clearly, KI was replaced by stoichiometric I_2, and 99% GC yield of **3aa** was obtained (Eq. 7). According to literatures,[55,56] PhSI could be generated in situ from **2a** and I_2. Thus the control experiment of **2a** and I_2 was carried out, and fortunately, PhSI was observed by GC-MS analysis (Eq. 8). Then **1a** (1 mmol) was added into the above solution, and 99% GC yield of **3aa** was



Scheme 3. Gram-scale synthesis.

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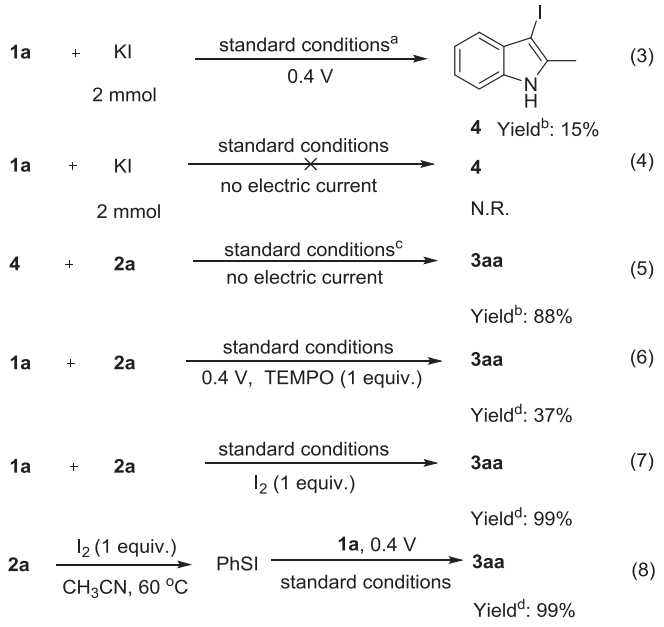
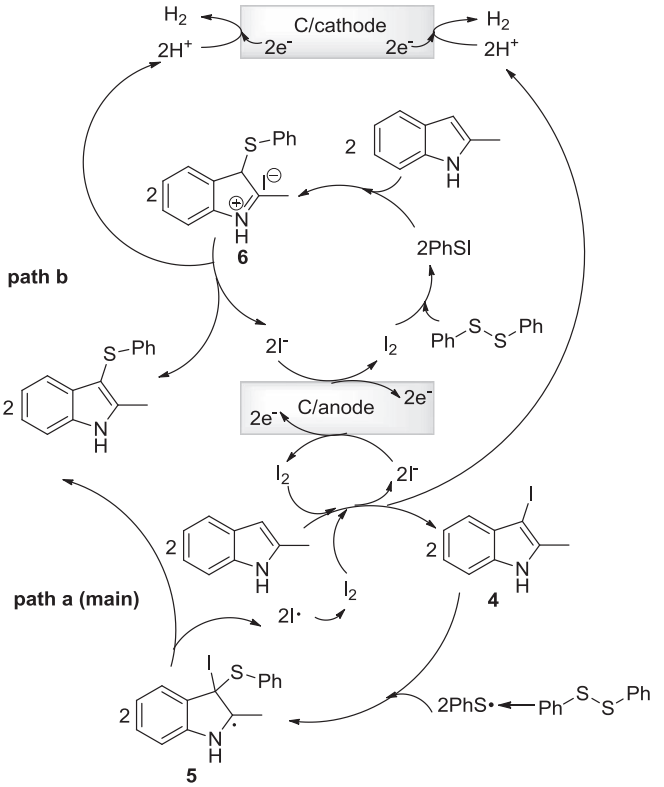


Scheme 4. Control experiments for mechanism.
[a]Standard conditions: 0.1 mol/L $NaBF_4/CH_3CN$ (15 mL), **1a** (1 mmol) or **2a** (0.5 mmol), 60°C, 6 h.
[b]Isolated yield.
[c]Reaction time: 4 h.
[d]Yield was determined by GC with area normalization method.

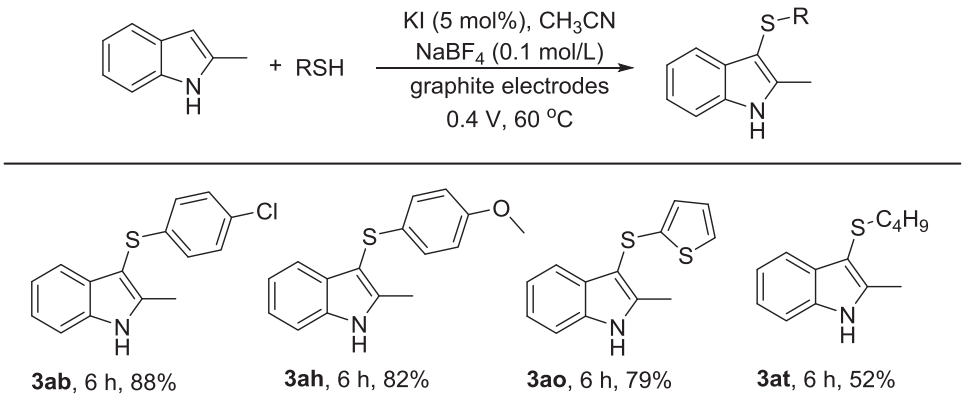


Scheme 5. Proposed reaction mechanism for electrosynthesis of 3-sulfenylindoles.

obtained which suggested that PhSI was the reaction intermediate of **2a** and I_2.

Based on above observations, a plausible mechanism for electrochemical sulfenylation of 2-methylindole with diphenyl disulfide has been proposed is illustrated in Scheme 5. Initially, iodide ion is electrooxidized to the molecular iodine. As soon as it is generated at the anode surface, electrophilic addition of iodine to the C-3 position of 2-methylindole produces intermediate 3-iodo-2-methyl-indole (**4**) and releases iodide ion which can be oxidized in the following redox cycle. Subsequently, thio radical which is formed from diphenyl disulfide reacts with **4** to generate a radical intermediate **5**. Then the desired product 2-methyl-3-(phenylthio)-indole can be produced from the radical intermediate **5**. Meanwhile, iodine radical is released which would be turned to molecular iodine. It is evidenced that the color of the solution turned dark gradually in the reaction of **4** and diphenyl disulfide (Scheme 4, Eq. 5). At the same time, hydrogen ions are reduced to H_2 at the cathode (Scheme 5, path a). However, the radical scavenger TEMPO cannot inhibit the sulfenylation reaction completely (Scheme 4, Eq. 6). It means that multiple pathways may be involved in this transformation. Diphenyl disulfide can react with molecular iodine to produce PhSI, which attacks the C-3 position of 2-methylindole to form intermediate **6**. Then **6** is deprotonated, and the product 2-methyl-3-(phenylthio)-indole is generated (Scheme 5, path b).[19,38–40]

Thiols have also been utilized as the attractive sulfenylating reagents.[16,30,41] Therefore, reactions of **1a** with some thiols to generate 3-sulfenylindoles were carried out under the optimized conditions. As shown in Scheme 6, 4-chlorobenzenethiol, 4-methoxybenzenethiol, thiophene-2-thiol and butane-1-thiol were used as the substrates, and the corresponding products were obtained in good yields (**3ab, 3ah, 3ao, 3at**).



Scheme 6. Reactions of **1a** with thiols. The reactions were carried out with **1a** (1 mmol), thiols (1 mmol) and KI (0.05 mmol) in 0.1 mol/L $NaBF_4/CH_3CN$ solution (15 mL) at 60°C. Yield of isolated product 52–88%.

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Conclusions

In summary, an efficient KI-catalyzed electrosynthesis of 3-sulfenylindoles at a low potential have been developed. The electropolymerization of indoles and over-oxidation of disulfides were effectively inhibited in this electrochemical system. High electrocatalytic activity of iodine for sulfenylation of indoles with disulfides was disclosed by cyclic voltammetry measurements. With this method, various indoles could react with aromatic, heteroaromatic and aliphatic disulfides to generate the corresponding products in good to excellent yields. In addition, several thiols also performed well in the sulfenylation reactions under the optimized condition. According to cyclic voltammetry studies and control experiments, a plausible mechanism was proposed.

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