

# Supercapacitive properties of composite electrodes consisting of activated carbon and 1,4-dihydroxynaphthalene derivatives



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## ABSTRACT

Two 1,4-dihydroxynaphthalene (PhQH<sub>2</sub>)-based derivatives (coded as HBU-551 and HBU-552) are synthesized by reacting with different amines (i.e., tryptamine and phenethylamine, respectively) to use as organic additives of activated carbon supercapacitors. The composite electrodes with HBU-551 and HBU-552 are also prepared by blending with the ratio of 70:25 w/w, and their supercapacitive properties are investigated in terms of redox behaviors and specific capacitance evolutions against scan rate and cycle life. The organic additives and their composites with activated carbon are dominantly characterized by PhQ-PhQH<sub>2</sub> redox transition accompanying a two-electron two-proton process, and weakly affected by reversible redox reaction of nitrogen in the —NH group, which involves an additional one-electron one-proton process. Thus, the composite electrodes show higher specific capacitance over 210 F g<sup>-1</sup> due to the synergistic effect between activated carbon (pseudocapacitance) and organic additives (redox behavior). Cycle performance and high-rate capability can also be enhanced by the adoption of PhQH<sub>2</sub>-based organic additives for their pore-filling morphology to increase the packing density of composite electrodes.

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## 1. Introduction

Quinone and its derivatives are promising organic materials for electrochemical cells because they are cost-effective, environmentally benign, and electrochemically redox-reversible with a moderate specific electrical capacitance. Therefore, quinone-based materials have attracted considerable attention as electrode materials for energy storage devices, such as lithium-ion batteries [1,2], redox flow batteries [3], polymer/air batteries [4], and electrochemical capacitors [5–10]. In particular, the trend of introducing quinone-based organic additives to electrode materials and electrolyte components to enhance supercapacitor performance has been increasing [6–10]. It has been noted that quinone-containing organic species can enhance supercapacitive properties by their redox-active behaviors via quinone-hydroquinone (Q-QH<sub>2</sub>) transition [6–21]. Of these, an activated carbon supercapacitor adopting 2,5-bis((2-(1H-indole-3-yl) ethyl) amino) cyclohexa-2,5-diene-1,4-dione (HBU-272, refer to Fig. 1(e)) as a

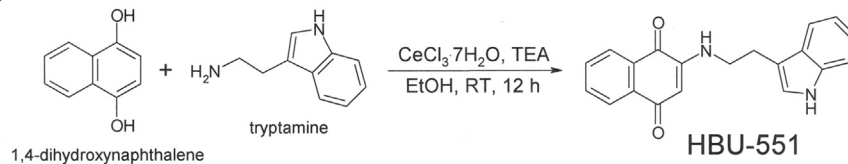
quinone-containing additive achieved higher specific capacitance than 130 F g<sup>-1</sup> at 100–1000 mV s<sup>-1</sup> [10]. The HBU-272 has a quinone structure sandwiched by two tryptamine groups, followed by a single-step four-electron (4e<sup>-</sup>) four-proton (4H<sup>+</sup>) redox process by the Q-QH<sub>2</sub> couple and the —NH groups of indole structures within the HBU-272. Here, the Q-QH<sub>2</sub> transition follows a two-electron (2e<sup>-</sup>) two-proton (2H<sup>+</sup>) transfer mechanism [22,23] (coded by 2e<sup>-</sup>-2H<sup>+</sup>) and the other 2e<sup>-</sup>-2H<sup>+</sup> redox process corresponds to the two —NH groups.

Meanwhile, the couple of 1,4-dihydroxynaphthalene (PhQH<sub>2</sub>) and 1,4-naphthaquinone (PhQ) has a redox chemistry with a slightly different proton transfer mechanism from the Q-QH<sub>2</sub> couple, in which the reactivity depends not only on the electronic properties of the substituents, but also on different structural effects related to the formation of hydrogen bonding [24]. Compared to QH<sub>2</sub>, which was used previously [10], PhQH<sub>2</sub> has an additional aromatic ring, revealing that, as the number of aromatic rings increases, the half-wave potentials are negatively shifted in cyclic voltammetry tested in an aprotic solvent [24]. Moreover, the presence of phenolic (Ph) groups in the PhQH<sub>2</sub> structure does not affect the reversibility of the two-electron

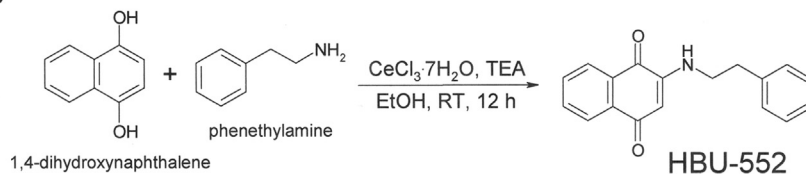
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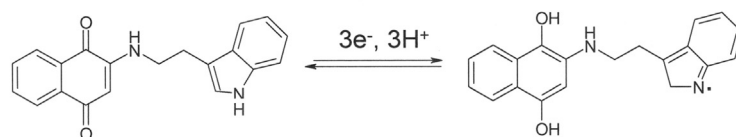
## (a) Synthesis of HBU-551



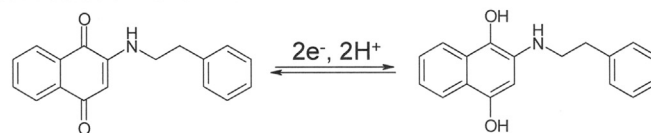
## (b) Synthesis of HBU-552



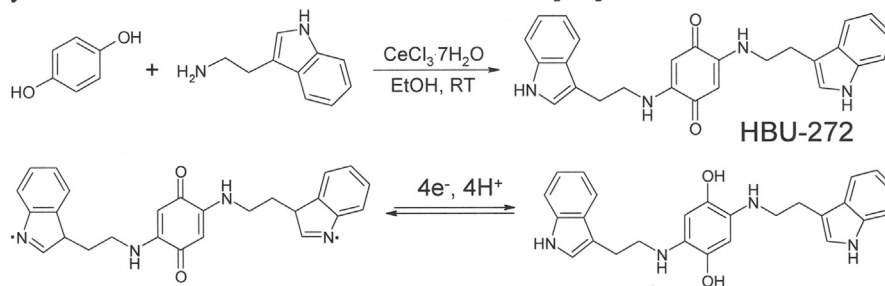
## (c) Redox reaction of HBU-551



## (d) Redox reaction of HBU-552



## (e) Synthesis and redox reaction of HBU-272 [10]



**Fig. 1.** Synthetic routes of (a) HBU-551 and (b) HBU-552. Redox mechanisms of (c) HBU-551 and (d) HBU-552. For comparison, the synthetic route and redox mechanism of HBU-272 are presented in Ref. [10].

reduction process but it modifies the voltammetric parameters, such as peak potential, potential difference between two peaks of Q-QH<sub>2</sub> transition, and diffusion coefficient [25]. In this study, two novel derivatives of PhQH<sub>2</sub> (coded as HBU-551 and HBU-552) are synthesized chemically by reacting PhQH<sub>2</sub> and different amines, and they are used as organic additives in fabricating composite electrode materials of activated carbon supercapacitors. The effects of the newly synthesized organic additives on the electrochemical properties of an activated carbon supercapacitor are also examined in terms of redox behavior, specific capacitance, high-rate capability, and cycle life.

## 2. Experimental

The synthesis procedure of HBU-551 was simple. First, 100 mg (0.62 mM) of PhQH<sub>2</sub> was dissolved in 15 mL of ethanol. Cerium chloride (20 mg, 0.06 mM) and tryptamine (120 mg, 0.75 mM) were added to the solution. Then, triethylamine (0.18 mL, 1.25 mM) was added to the reaction mixture and was stirred at room temperature for 12 h. After reaction was completed, the reaction mixture was poured into 20 mL of crushed ice with constant

stirring. The solid was filtered, washed with H<sub>2</sub>O, dried under vacuum, and finally, 2-(2-(1H-indol-3-yl) ethylamino) naphthalene-1,4-dione (HBU-551) was obtained (160 mg, yield of 85%). The synthesis route of HBU-551 is shown in Fig. 1(a). The synthesized HBU-551 was then collected, and its structure was elucidated by <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectroscopy (Varian Gemini 200 NMR), which was identified as follows: <sup>1</sup>H NMR (400 MHz, DMSO) 3.03 (t, *J* = 7.6 Hz, 2H), 3.48 (q, *J* = 6.8 Hz, 2H), 5.75 (s, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.26 (s, 1H), 7.34 (d, *J* = 8 Hz, 1H), 7.53 (t, *J* = 6 Hz, 1H), 7.57 (d, *J* = 8 Hz, 1H), 7.72 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.83 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.94 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.97 (dd, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), and 10.87 (s, 1H).

Also, 2-(phenethylamino) naphthalene-1,4-dione (HBU-552) (110 mg, yield of 48%) was obtained by the same synthetic procedure as HBU-551 by using phenethylamine (0.11 mL, 0.75 mM) instead of tryptamine. The synthetic route of HBU-552 is shown in Fig. 1(b). The HBU-552 could also be identified as follows: <sup>1</sup>H NMR (400 MHz, DMSO) 2.90 (t, *J* = 7.6 Hz, 2H), 3.43 (q, *J* = 6.4 Hz, 2H), 5.74 (s, 1H), 7.26 (m, 5H), 7.53 (t, *J* = 6 Hz, 1H), 7.72 (td,

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