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# Carbon nanosheets-based supercapacitors: Design of dual redox additives of 1, 4-dihydroxyanthraquinone and hydroquinone for improved performance

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## HIGHLIGHTS

- 2D carbon nanosheets are obtained by carbonizing thiocarbanilide mixed with $Mg(OH)_2$.
- DQ and HQ serve as dual redox additives.
- The consecutive redox processes of DQ and HQ are contributed to the capacitive performance.
- A high energy density of 21.1 Wh $kg^{-1}$ is achieved.

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## ABSTRACT

Using thiocarbanilide and $Mg(OH)_2$ powders as carbon precursor and template, respectively, novel 2D carbon nanosheets with large area have been produced. Next, based on the cooperative effect, 1, 4-dihydroxyanthraquinone (DQ) and hydroquinone (HQ) regarded as efficient dual redox additives have been incorporated into the electrode carbon material and $H_2SO_4$ electrolyte, respectively, to largely elevate the capacitive performance of supercapacitors. More importantly, the cooperative effect results from the redox processes of DQ and HQ consecutively occurring in the electrode carbon material and aqueous $H_2SO_4$ electrolyte, respectively. Besides, the molar ratio of DQ and HQ exerts a crucial role in the determination of the electrochemical behaviors and eventually the optimum condition is the mass ratio of 1:1 concerning the DQ and porous carbon within solid electrode while retaining the HQ concentration as 20 mmol $L^{-1}$ in 1 mol $L^{-1}$ $H_2SO_4$ electrolyte. As a result, the maximum specific capacitance is achieved of 239 F $g^{-1}$ at 3 A $g^{-1}$, and furthermore the maximum energy density up to 21.1 Wh $kg^{-1}$ is almost 3.5 times larger than that of the one without introducing any redox additive.

## 1. Introduction

Supercapacitors have been regarded as one of the mostly promising technologies to figure out our energy storage and environmental challenges [1]. Very recently, a new orientation has evolved in the field of electrolytes by using redox additive/active electrolyte to elevate the performance of supercapacitors. This is because the redox additive/active has markedly achieved extra energy density derived from faradaic pseudo-capacitance, which are simple and effective compared with other method of improvement on supercapacitors' performances [2]. In general, the redox additives can be divided into two categories (organic and inorganic ones). Comparatively, organic redox additives such as hydroquinone [3–5], anthraquinone [6–8], 1,10-phenanthroline [9], indigo carmine [10] and *p*-phenylenediamine [11–13] *etc*, have been widely applied due to their various species and wide voltage windows. Till to now, most of the organics have been employed as redox additives individually and solely. For example, Roldán et al. have reported the addition of hydroquinone to the electrolyte leading to a great increase in the capacitance (901 F $g^{-1}$ at 2.65 mA $cm^{-2}$) and the values was at least two times higher that of the carbon-based supercapacitors without redox additives. However, the cycling behavior shows a conspicuous decrease in the initial capacitance of 65% after 3000 cycles [14]. Interestingly, as Ji

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et al. reported, when the methylene blue was introduced into the electrolyte with HQ, the supercapacitors exhibit higher specific capacitance of 564 F $g^{-1}$, which was 3.7 times more than that of the sample without redox additives, but the cycling behavior retains still the 95.9% of the initial capacitance at the same case [15]. It is thus revealed that incorporating a dual redox system possessing cooperative effect into $H_2SO_4$ solution is a quite versatile strategy, which could largely elevate the capacitive performances for supercapacitors.

On the other side, the quinones with the functional group of phenolic hydroxyl that can release electrons/protons simultaneously have been regarded as simple but efficient redox additives, primarily including anthraquinones (AQ) and hydroquinone (HQ), *etc*. Even so, the anthraquinones regarded as redox additives cannot markedly improve the supercapacitors' capacitance in the aqueous systems ($H_2SO_4$ and KOH), whose solubilities are quite weak at the room temperature. Thereby, how to circumvent the obstacle that has the poor solubility of AQ has become one interesting scientific issue. As a consequence, in particular considering their low solubilities, one alternative approach is to incorporate them into porous carbon materials within solid electrode. For instance, AQ acting as individual redox additive was introduced into carbon matrix by the complicated solvothermal reaction, while keeping the $H_2SO_4$ electrolyte blank without another redox additive [16]. It is thereby discerned that assembling the insoluble redox additives into solid electrode materials and soluble ones into aqueous electrolyte as novel dual redox additive-based cell configuration is quite intriguing and effective for the energy improvement of supercapacitors.

In present work, taking into account the integration of various voltage windows concerning the redox additives of DQ and HQ, we assembled them into a novel dual redox system; noteworthily, the DQ and HQ substances were implemented in solid electrode and aqueous electrolyte, respectively, primarily owing to the discrepancy of solubility between them. What's more, the effect of molar ratio of DQ and HQ upon the capacitive behavior was emphasized by a series of electrochemical tools.

## 2. Experimental section

Herein, 4-dihydroxyanthraquinone (DQ) can serve as redox additive when added in the electrode carbon material for the improvements of supercapacitors' performances. The redox voltage windows of DQ mainly focus on 0.8–1 V in 1 mol $L^{-1}$ $H_2SO_4$ electrolyte, as displayed in the CV curves of 10 mV $s^{-1}$ (Fig. 1a). The former peaks are mainly attributed to two-electron reaction which correlates to the redox of 1, 4-dihydroxyl groups of DQ (Fig. 1d) and the latter peaks correspond to the interaction between the phenolic hydroxyl of DQ and oxygen-containing function groups on the carbon surface [17,18]. However, we can obviously observe the voltage windows (0–0.8 V) without any redox peaks, indicating the lower utilization rate of redox voltage in the **C-DQ-1:1** sample. Thereby, how to improve the utilization rate of redox voltage has become one issue of concern. Consecutively, the HQ is also one of the key redox additive in the aqueous electrolyte because of phenolic hydroxyl gaining/losing two electrons/protons in $H_2SO_4$ electrolyte (Fig. 1d) [3]. More importantly, its redox voltage window is of 0.1–0.6 V in the same case, which is very suitable for above-mentioned requirements, as shown in Fig. 1b. As a result, we have carried out the pre-experiment that a dual system of supercapacitors were assembled by introducing two kinds of redox additives (DQ and HQ) into the electrode materials and aqueous electrolyte, respectively, and the resultants are exhibited in Fig. 1c. Interestingly, two couples of redox peaks at 0.3–0.7 V and 0.7–1 V emerge in the CV curve, respectively, which is ascribed to the cooperative effect between DQ and HQ. Thereby, in order to further explore the mechanism of DQ and HQ, we have been designed relevant experiments and the corresponding resultants will be described in the following sections.

### 2.1. Synthesis procedure of nanoporous carbon materials

In a concise process, thiocarbanilide and $Mg(OH)_2$ powder with a mass ratio of 1: 2 were first evenly milled in a mortar about 30 min and then put on a porcelain boat. After introducing into $N_2$

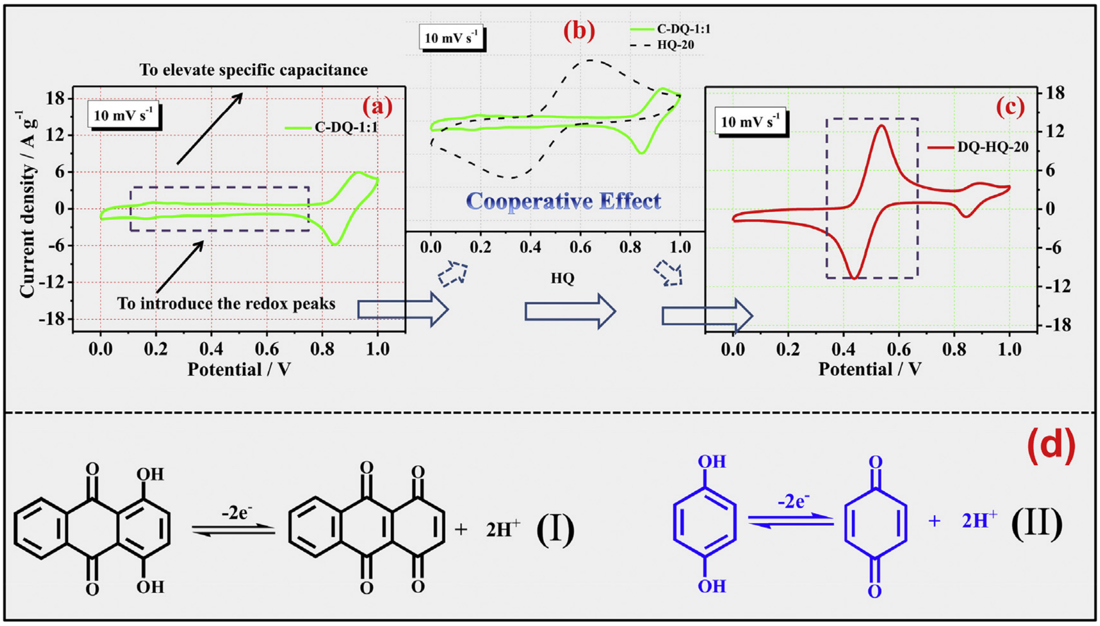

**Fig. 1.** The cooperative effect of DQ and HQ using the CV curves at a scan rate of 10 mV $s^{-1}$: (a) the **C-DQ-1:1** sample; (b) the **C-DQ-1:1** and **HQ-20** samples; (c) the **DQ-HQ-20** sample; (d) the reaction mechanism (I) and (II) of the DQ and HQ in 1 mol/L $H_2SO_4$ solutions, respectively.