



# Study on modification methods to improve Li-Ion storage capacity of carbon black

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To address the problem with regard to greenhouse gas emissions, the unfolding of the electric vehicle installing lithium-ion batteries is widely encouraged in the world by using carbon black (CB) as the conductive agent. In CB materials, modification methods are effective ways to enhance the Li<sup>+</sup> storage capacity of CB. For instance, CB was successfully modified by organic and inorganic compounds for remarkable improvement of storage capacity. Considering the fact that CB possesses remarkable price advantages, the usage of CB is able to remarkably diminish the fabrication cost of lithium-ion batteries, facilitating the electric vehicle to become popular.

## Addresses

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## Introduction

For decades, lithium-ion batteries (LIBs) have gradually become the ideal current source of electrical products and high-energy battery of automobiles. The development of LIB industry is one of the most important subjects around the world; therefore, the popularization of the electric vehicle (EV) can extremely diminish greenhouse gas emissions. In particular, fabrication of high-power electrodes has been developed remarkably in various groups [1–5].

It is acknowledged that carbon black (CB) is widely applied in the fields such as tire, inks, conductive agents, and so on. Nevertheless, with blindly expanding

production, the surplus of carbon production is becoming to be one of the pressing issues in China. Therefore, how to process carbon production to CB as an additional value has become one of the crucial research subjects in China.

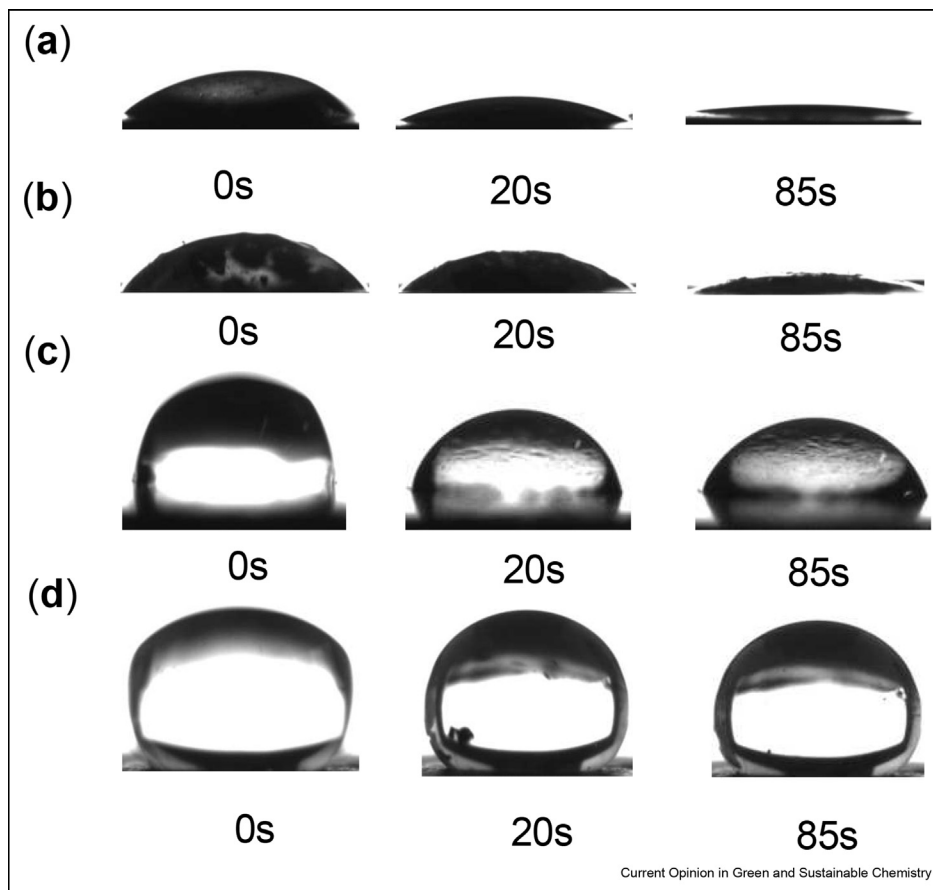
Generally, CB and acetylene black were used as conductive materials in fabrication of carbon anode materials for LIBs in application of green process [6]. However, the reports about CB for charge–discharge of LIBs are limited. After some methods to attempt to explore the mobility of lithium ion for charge–discharge capacity of CB had been developed, research expanded was applicable [7]. Herein, the present review mainly introduces improvement of Li<sup>+</sup>-ion storage capacity of CB [7,10].

## Organosilicon modification of CB

The functional organic groups were successfully introduced on the surface of CB via the organic modification method, based on the excellent reactive properties to –OH and –COOH groups. The surface of CB was modified by tert-butylchlorodimethylsilane (TBDMCl), with alkyl groups enhancing steric hindrance effect of TBDMCl. On the modification the chemical, it was able to increase the hydrophobicity, and the formed –C–OSiR groups on the surface of CB gave rise to the increase in electrochemical performances of LIBs.

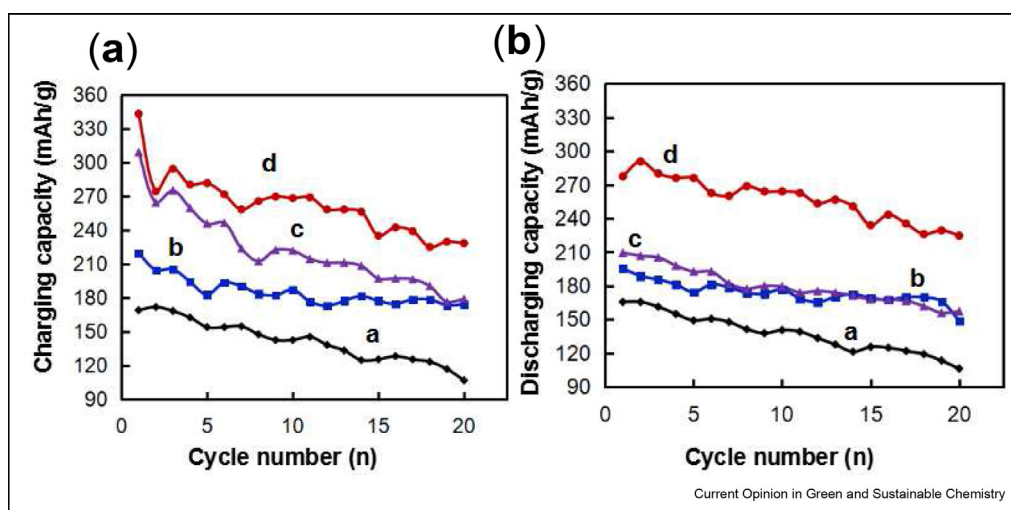
The relevant evidence was also observed in water contact angle results, as shown in [Figure 1](#). Therefore, in the contact angle measurements (a) were the results of the sourced CB, and (b), (c) and (d) were the water droplet pictures on the CB modified with TBDMCl, when the amount of TBDMCl was 1.5, 3.0, and 5.0 times against the molar sum of –COOH and –OH on the CB surface, respectively. Compared with water retention, water could easily penetrate into the unmodified CB (a). But the penetrating capacity of the MCB remarkably decreased with increase in the reaction degree of the surface modification of TBDMCl. Particularly, the value of contact angle of MCB (d) was 117° and larger than those with MCB (c) (106°), MCB (b) (51°), and CB (a) (41°). This indicated that water could not penetrate into MCB (d) approximately, causing the result that the –OH and –COOH groups were largely modified by the –C–OSiR and –C–OOSiR structures. The remarkable improvement of the hydrophobic performance of the MCB (d) indicated that high applicability was possible

Figure 1



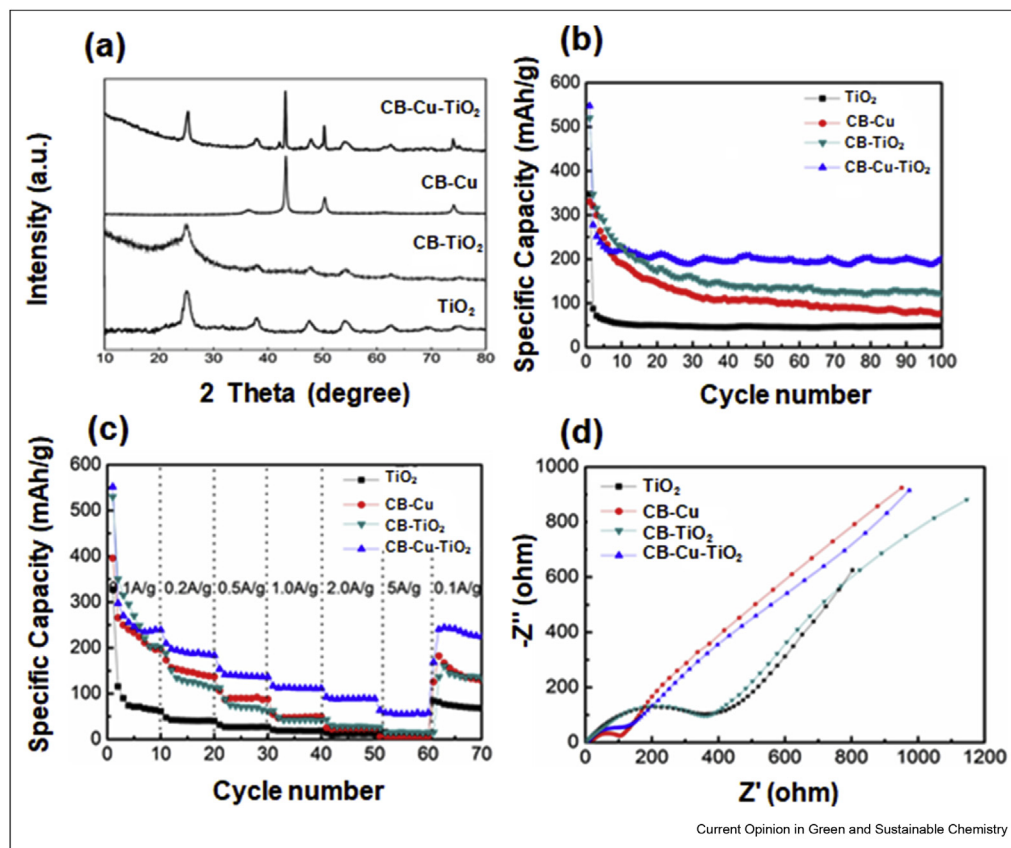
Pictures of water contact angle results: **(a)** CB and **(b–d)** MCB [7]. Therefore, (b), (c), and (d) were for the CB (a) modified with the different amounts of TBDMCI in 1.5, 3.0, and 5.0 times against the molar sum of  $-\text{COOH}$  and  $-\text{OH}$  on the CB surface, respectively. CB, carbon black; MCB, modified carbon black; TBDMCI, tert-butylchlorodimethylsilane.

Figure 2



Charge-discharge capacity of CB (a) and MCB (b–d). **(a)** Lithium-ion charging curves of CB (a) and MCB (b–d). **(b)** Lithium-ion discharging curves of CB (a) and MCB (b–d) [6]. CB, carbon black; MCB, modified carbon black.

Figure 3



XRD results and electrochemical performances of CB and MCB (b–d). (a) Illustrations of XRD results of CB and CB-based composite materials (a). (b) are the Cycling performance results of TiO<sub>2</sub>, CB–Cu, CB–TiO<sub>2</sub>, and CB–Cu–TiO<sub>2</sub>. (c) Rate performance results of TiO<sub>2</sub>, CB–Cu, CB–TiO<sub>2</sub>, and CB–Cu–TiO<sub>2</sub>. (d) Nyquist plot results of TiO<sub>2</sub>, CB–Cu, CB–TiO<sub>2</sub> and CB–Cu–TiO<sub>2</sub> in the frequency range of 100 kHz–0.01 Hz [10]. CB, carbon black; XRD, X-ray diffraction.

in fabrication of carbon anode materials [7]. FTIR results supported the structures of modified organosilicon CB (modified carbon black [MCB]). Compared with the CB (a), the new characteristic peaks of alkyl group around 2923 cm<sup>-1</sup> and -COOSiR<sub>3</sub> group at 1087–1093 cm<sup>-1</sup> were observed in MCB (b–d) [7].

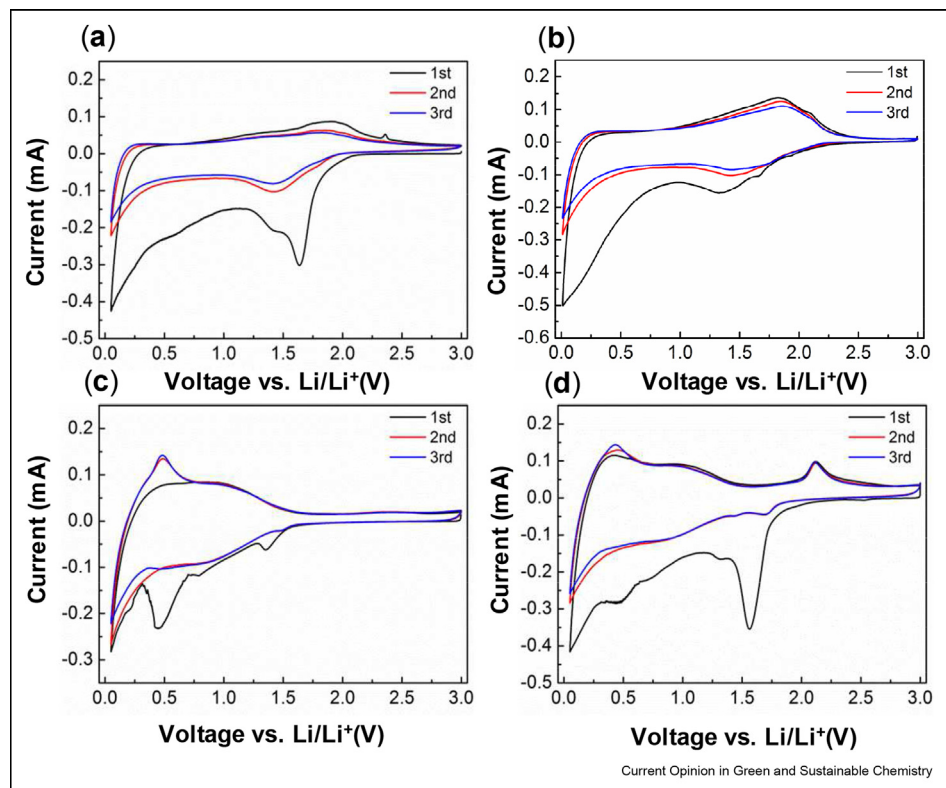
The Li<sup>+</sup>-ion storage capacity of the unmodified CB and MCB was determined by charge–discharge measurements. As a result, the Li<sup>+</sup>-ion storage capacity of MCB was 343 mAh/g in the first cycle and was slightly lower than the theoretical capacity of black lead at 372 mAh/g, indicating slightly higher capacity than the general mesocarbon microbeads [8]. On the other hand, the values of Li<sup>+</sup> ion storage capacity were at 169 mAh/g, 220 mAh/g and 309 mAh/g for CB (a), MCB (b), and MCB (c), respectively. Thus, compared with the CB (a), MCB (b), and MCB (c), the MCB (d) had a high possibility in usage for fabrication of carbon anode materials. In storage mechanism, we consider that the organometallic structures of -C-OSiR and -C-OOSiR on the MCB surface improved the ion storage capacity [7].

The conductivities of CB (a) and MCB (b–d) were measured *via* the two-terminal method. In the MCBs, MCB(b), MCB(c) and MCB(d) had conductivities around 127.5 Sm<sup>-1</sup>, 132.8 Sm<sup>-1</sup>, and 148.1 Sm<sup>-1</sup>, respectively. The increase in conductivity was improved by silicone-modified effect. Especially, the conductivity of the MCB (d) was similar to the CB (a), 155.2 Sm<sup>-1</sup>. Compared with the CB (a), the decrease in the conductivity of MCB was possibly attributed to the silicon modification of -OH and -COOH groups because of decrease in the ion conduction. But the introduction of the -SiR<sub>3</sub> group possibly increased the electronic conductivity of the MCB owing to the -SiR<sub>3</sub> groups attending the electrochemical reactions. The surface treatment of TBDMCl influenced the charge (Figure 2a) and discharge (Figure 2b) behavior (Figure 2). In comparison of b, c, and d, the MCB (d) exhibited more excellent charge–discharge property.

### Cu- and TiO<sub>2</sub>-modified CB electrode

On the other hand, TiO<sub>2</sub> high operating voltage and excellent cycling stability was used attractively and widely

Figure 4



The CV measurement results: (a)  $\text{TiO}_2$ , (b) CB-Cu, (c) CB- $\text{TiO}_2$ , and (d) CB-Cu- $\text{TiO}_2$  [10]. CB, carbon black; CV, cyclic voltammetry.

in the fabrication of electrodes of LIBs [9]. However, some defects in such low conductivity and low theoretical capacity restricted the application of  $\text{TiO}_2$  (168 mAh/g) in fabrication of LIBs. However, CB-Cu improved the electrochemical performances of  $\text{TiO}_2$  successfully [10].

The structure of CB-Cu- $\text{TiO}_2$  was verified by X-ray diffraction (Figure 3a). The characteristic peaks of CB-Cu, CB- $\text{TiO}_2$ , and  $\text{TiO}_2$  were observed as supported for the structure of CB-Cu- $\text{TiO}_2$  formed definitely. The cycling performances of the CB-based composite  $\text{TiO}_2$  had a current density of 0.1 A/g and a potential range of 0.05–3.00 V. As a result, as the charge–discharge was cycled with 100 times, the CB-Cu- $\text{TiO}_2$  had the high and stable  $\text{Li}^+$ -ion storage capacity with 201 mAh/g, which was higher than 48 mAh/g, 123 mAh/g, and 77 mAh/g for the  $\text{TiO}_2$ , CB- $\text{TiO}_2$ , and CB-Cu, respectively, as shown in Figure 2b.

The rate performances of  $\text{TiO}_2$ , CB-Cu, CB- $\text{TiO}_2$ , and CB-Cu- $\text{TiO}_2$  (Figure 3c) indicated that the  $\text{Li}^+$ -ion storage capacity of CB-Cu- $\text{TiO}_2$  still remained at 225 mAh/g, when the adjusted current density was 0.1 A/g again after the cycled operations of 60 times, namely, the charge–discharge was cycled at each 10 times with

different current densities of 0.1 A/g, 0.2 A/g, 0.5 A/g, 1.0 A/g, 2.0 A/g, and 5.0 A/g, respectively (Figure 3c). In contrast, after the analogous operations with CB-Cu- $\text{TiO}_2$ , the  $\text{TiO}_2$ , CB-Cu, and CB- $\text{TiO}_2$  electrodes only showed storage capacities of 68 mAh/g, 129 mAh/g, and 133 mAh/g, which were remarkably smaller than that of CB-Cu- $\text{TiO}_2$  (225 mAh/g). Consequently, we considered CB-Cu- $\text{TiO}_2$  showed noticeable improvement capability against the polarization and excellent electrochemical stability, comparing with  $\text{TiO}_2$ , CB-Cu, and CB- $\text{TiO}_2$ .

In Figure 3d, for the electrochemical impedance results of  $\text{TiO}_2$ , CB-Cu, CB- $\text{TiO}_2$ , and CB-Cu- $\text{TiO}_2$ , the diameter of the semicircle of anode electrodes using CB-Cu- $\text{TiO}_2$  was much smaller than that of anode electrodes fabricated by  $\text{TiO}_2$  and CB- $\text{TiO}_2$ . It was considerable that the CB-Cu- $\text{TiO}_2$  electrode possessed the improvement charge-transfer impedances and the CB-Cu- $\text{TiO}_2$  electrode also showed lower  $\text{Li}^+$ -ion transformation impedance than that of the  $\text{TiO}_2$  and CB- $\text{TiO}_2$  electrode. As per Warburg impedance results, this was due to introduction of Cu and  $\text{TiO}_2$  on the CB surface, which remarkably improved the electrochemical performances of CB with

the aid of Cu possessing significantly excellent conductivity.

Figure 4 shows cyclic voltammetry profiles for CB–Cu–TiO<sub>2</sub>. It was observed that peaks of current density were decreased in the 2nd or 3rd cycle remarkably from the first one, attributing to the formation of solid electrolyte interface layers in the first cycle. It is observed in Figure 4d that the cyclic voltammetry behaviors of CB–Cu–TiO<sub>2</sub> (d) contained the characteristic peaks of TiO<sub>2</sub> (a), CB–Cu (b), and CB–TiO<sub>2</sub> (c). Meanwhile, after the first cycle, no change of intensities about the current reductive peak (1.7 V) and oxidative peak (2.1 V) of CB–Cu–TiO<sub>2</sub> revealed that CB–Cu–TiO<sub>2</sub> possessed tremendous electrochemical stability. As a consequence, CB–Cu enhanced the electrochemical performances of CB–Cu–TiO<sub>2</sub>, causing that CB–Cu–TiO<sub>2</sub> possessed the high applicability in the field to fabricate LIBs as anode electrode materials [10].

## Conclusions

With the development of the population of automobiles in China, the government vigorously boosts the population of the EV installing LIBs. Nevertheless, the high production cost of LIBs extremely restricts the population of EVs without using CB, which is a very cheap industrial product in China. If CB can be applied as Li-ion storage materials, the cost seems to be diminished.

This review highlighted that the modification of CB became the effective route to improve electrochemical performances. Especially, introducing the organic groups on the surface of CB could improve Li<sup>+</sup>-ion storage capacity of general carbon materials such as graphite and graphite oxide. In addition, doping Cu metal and TiO<sub>2</sub> compounds on CB also improved storage capacity. Finally, these results attributed that the methods were useful to widen application of CB as anode materials for LIBs.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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- \* of special interest
- \*\* of outstanding interest

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Article introduces the new way to improve the Li<sup>+</sup> storage capacity by adding the Cu and TiO<sub>2</sub> into carbon black.