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# Catalysis of a carbon material from *Botryococcus braunii* residues for reduction of nitroarenes

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**ABSTRACT**

A novel catalyst was prepared by carbonization of *Botryococcus braunii (B. braunii)* residue. In this study, reductive reaction of nitrobenzene was carried out with a catalyst based on biomass residues. The carbons from *B. braunii* residues allow production of aniline from nitrobenzene. This is the first research of development of a catalyst from carbon containing magnetic components, which was produced from a flocculant contained biomass residues. Mass production of oil from *B. braunii* has been paid much attention in view point of development of new energy source. However, the oil extracted *B. braunii* residues are still intractable issue. Here we propose a possibility of the material from the algae after discharge of oils having large amount of $Fe_3O_4$ and carbon with industrial treatment as a catalyst for reduction of nitroarene.

**Keywords:** *Botryococcus braunii*, iron-carbon catalyst, microalgae, carbonization, magnetic property

## Introduction

*B. braunii*, a microalgae, produces high content of oil and is now receiving many attentions. However, the large amount of oil-extracted *B. braunii* residues leaves us a problem. Solutions to practically utilize the residues are desired.

Aromatic amines are widely used in industry such as dye, pesticide and pharmaceutical industry. Aromatic amines are usually obtained by reduction of aromatic nitro-compounds. Careful reaction is required to avoid oxidation during the reduction. Moreover hydrogen gas is needed for the reaction, which is explosive and dangerous. Catalysts for reductive reaction have been developed in various forms from metal component and metal-free carbon [1-11]. Recently $Fe_3O_4$ with graphene or graphite have received many attentions due to the high catalytic activity. Large surface of the micro or nano-sized $Fe_3O_4$/carbons particles contributes increase of catalytic activity [12-14].

In our previous report, we revealed that carbonized *B. braunii* residues treated with polysilicato iron industrially as flocculants composes of large amount of carbon, and $Fe_3O_4$ or $\alpha$-Fe [15]. This indicates a possibility that carbonization of *B. braunii* residues can create a very low-cost and efficient catalyst. In this research, we demonstrate that carbonized *B. braunii* residues can function as a catalyst for the synthesis of aromatic amines.

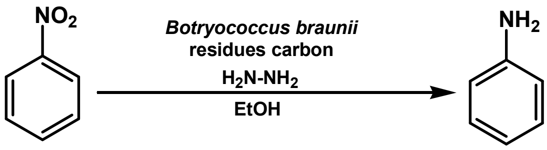
## Experimental Section

### *Sonification*

A 0.4 g of *B. braunii* residues carbonized at 900 °C was crushed into powder in a mortar in prior to use. Then the black powder was immersed in ethanol (15 mL) and treated with sonification (≥ 2h). Ethanol was evaporated followed by drying in vacuum to obtain fine particles for use of catalyst.

### *Reduction of nitrobenzene*

A 0.102 g of the fine carbon as a catalyst from industrial treated *B. braunii* residue was placed in a Schlenk flask with nitrogen flow. Note that the powder has magnetism, and are partially attracted by the magnetic stirring bar. As shown below, a 1.4 mL ethanol was then added as reaction solvent following by addition of nitrobenzene (0.264 g, 2.14 mmol) and hydrazine monohydrate (0.388 g, 7.76 mmol). The mixture was stirred for 24 h at 70 °C to perform reduction from nitrobenzene to aniline. Progress of the reaction was monitored by thin-layer chromatography. The catalytic powder was removed by centrifugation after the reaction. The reaction mixture was analyzed with gas chromatograph (GC).

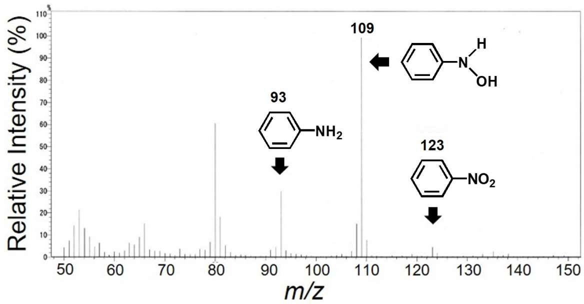



## Results and discussion

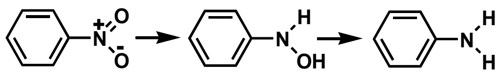
### *Gas Chromatography Analysis*

Molecular weights of the resultant in this reaction were detected by a gas chromatography-mass (GC-MS) spectrometer. As shown in Figure 1, both nitrobenzene (starting material, $M_w$ = 123 g/mol) and aniline (product, $M_w$ = 93 g/mol) were detected from the reaction solution. The mass analysis results of target compound is 96% similar to that of pure aniline, indicating this reduction produces aniline from nitrobenzene. Thus, we achieved reductive reaction of nitrobenzene with an aid of carbonized *B. braunii* residues powder as a catalyst.

As shown in Figure 1, phenylhydroxylamine (intermediate, $M_w$ = 109 g/mol) was also detected. This indicates nitrobenzene was firstly reduced to phenylhydroxylamine, then stepwisely to aniline, as shown in Scheme 1.




of reductive reaction using carbonized *B. braunii* residues as a catalyst



**Scheme 1.** Plausible reduction steps for aniline.

### *X-ray photoelectron spectroscopy (XPS)*

XPS measurement was carried out for catalyst collected before and after reaction. The carbonized *B.braunii* residues contain large amount of carbon, oxygen, and iron, as reported in our previous research [15]. The fine carbon after reaction was recovered. As shown in Figure 2, two new peaks (605 eV and 692 eV) appear for the catalyst after reductive reaction. These two peaks are due to $Fe_{LMM}$, indicating that iron atoms contained in the fine carbon may contribute to the reductive reaction (Figure 2).

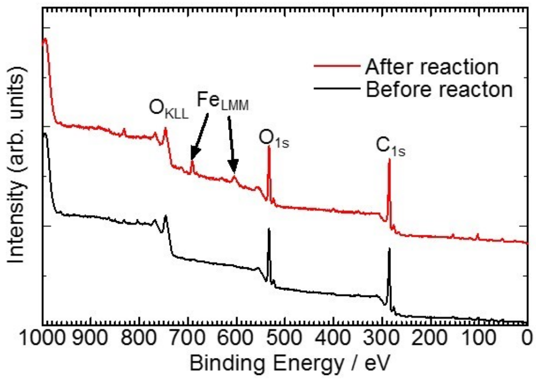



**Figure 2.** X-ray photoelectron spectroscopy (XPS) results of *B. braunii* residues derived catalyst before and after reductive reaction.

### *Scanning electron microscopy*

Figure 3 shows a scanning electron microscopy image of the catalyst after reaction. We have revealed that carbonization of *B. braunii* could generate crystals of $Fe_3O_4$ with octahedral shape in microscale [15]. However, in Figure 3, no octahedral crystal could be obviously observed under scanning electron microscope. Instead, some small particles in micro order could be observed. This also indicates that iron atoms participate in the reductive reaction.

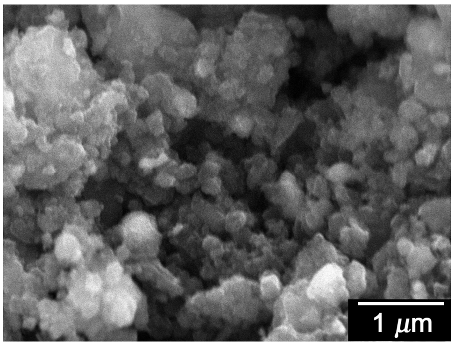



**Figure 3.** Scanning electron microscopy image of the *B. braunii* residues derived catalyst after reductive reaction.

## Conclusions

In this paper we demonstrate that carbonized *B, braunii* residues can be used as a catalyst. This research provides a simple way to prepare iron-carbon catalytic system. Microalgae are considered to be an energy source in next generation. Application of industrial waste after discharge of oils from algae is next issue in future. To the best of our knowledge, this is a first report on application of *B. braunii* residues for catalyst. This result suggests great potential for application of biomass residues in industry.

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