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作品名稱 **Reducibility of Silver ions by the Charcoal: Regarding Mechanisms, Art, and Liquid Waste Management**

得獎獎項 **四等獎**

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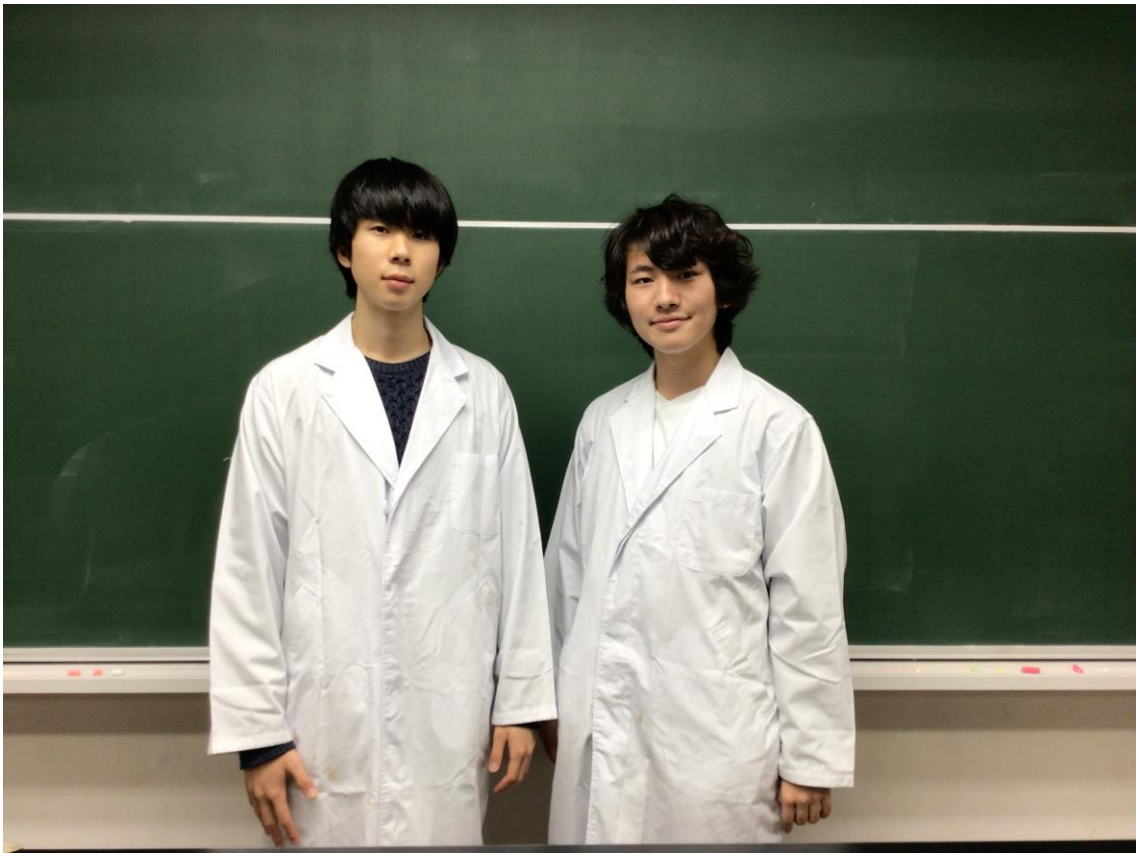


Abstract

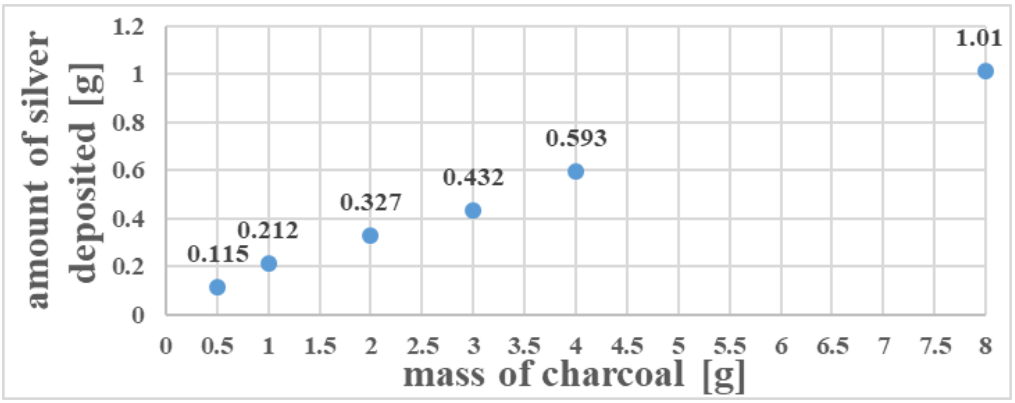
We elucidated the cause of the phenomenon, in which silver deposits on a bamboo charcoal when the bamboo charcoal is soaked in an $AgNO_3$ water solution. From the experimental results, we considered that the hydrogen which is generated while the bamboo wood is carbonized is chemisorbed as C-H bonds on the surface edge of charcoal (the end of the carbon), and that these hydrogen atoms become hydrogen ions, which then reduce the silver ions and deposit silver. In addition, we created a graph of the mass of deposited silver versus the mass of charcoal, and the graph showed that the mass of deposited silver was strongly correlated with the surface area calculated from the mass of the charcoal. Besides, we showed that charcoal can be used in applications for the treatment of inorganic liquid waste, depositing metals from inorganic liquid waste by bamboo charcoals. Also, the charcoal is used for interior decoration because of its deodorizing effect and beauty. In our study, we create a work of art used silver-deposited charcoal with a motif of Karesansui (Traditional Japanese rock garden).

1. Background and Objectives

It has been reported that silver deposits on a bamboo charcoal when bamboo charcoal is soaked in an $AgNO_3$ water solution for 20 days[1]. But the cause of this phenomenon was never clarified. In order to elucidate the cause, we conducted experiments with cedar charcoal, bincho charcoal, and activated charcoal in addition to bamboo charcoal, and found that (1) the deposition of silver was observed in all of the charcoals. In addition, we created **Table 1**, which shows the relationship between the mass of charcoal and the mass of silver deposited by using the Mohr method. Although the mass of charcoal and the mass of silver deposited did not have a proportional relationship, (2) a positive correlation between the mass of charcoal and the mass of deposited silver was ascertained. Besides, we confirmed that (3) silver crystals on the charcoal were shaped like a metallic tree (**Fig. 1**). From the results of (1) to (3), we considered that the substances which react with silver ion are common to "charcoal" and that the silver ions are reduced by a substance that exists inside the charcoal. While thinking about what is common to "charcoal," We came up with that "carbonization" is common to all charcoals. So, we researched carbonization and found the reference which states that a large amount of hydrogen is produced when charcoal is created[2), 3)].

Fig. 1 Deposition of silver on the charcoal

Table. 1 The mass of charcoal and the mass of deposition of silver



Based on the above, we hypothesized that the hydrogen which is generated while the charcoal is made from bamboo or wood remains inside the charcoal and reduces silver ions. In this research, we verified this hypothesis.

2. Method

2.1 Deposition of silver when using carbon rods

Carbon rods are made under high temperature and contain almost no hydrogen. So, we soaked a carbon rod in 30 mL of a 0.10 mol/L $AgNO_3$ water solution and kept it at 30 ℃ in a thermostatic chamber for 30 days. As a result, silver deposition was not observed.

2.2 Silver deposition on carbon rods when hydrogen is adsorbed on them

We thought that silver could be deposited by adsorbing hydrogen on the carbon rod. Therefore, we electrolyzed a $NaNO_3$ water solution using the carbon rod and made the

carbon rod which adsorbed hydrogen. Next, we put this carbon rod under the same conditions as in 2.1. As a result, silver deposition was observed on the surface of the carbon rod.

Fig. 2 The carbon rod soaked in $AgNO_3$ water solution

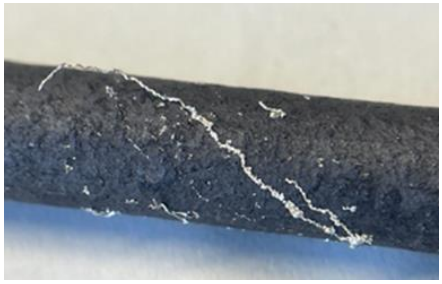
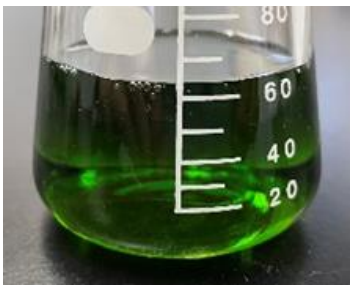
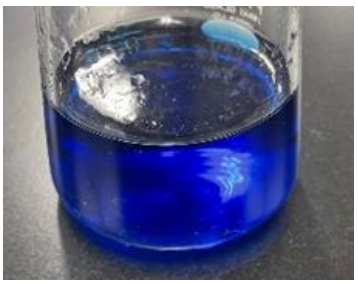


Fig. 3 The deposited silver on the carbon rod with adsorbed hydrogen

2.3 Production of hydrogen ions during the reaction.

If the hypothesis is correct, the $AgNO_3$ water solution after the reaction should be acidic due to the generation of hydrogen ions. In order to test whether hydrogen ions generate during the reaction or not, we added a BTB solution to an $AgNO_3$ water solution only, Bincho charcoal only, and an $AgNO_3$ water solution with Bincho charcoal respectively. As a result, the $AgNO_3$ water solution only showed neutral pH and Bincho charcoal only showed basic pH. The $AgNO_3$ water solution with charcoal showed acidic pH (**Fig. 3**). We confirmed the generation of hydrogen ions because of this result.





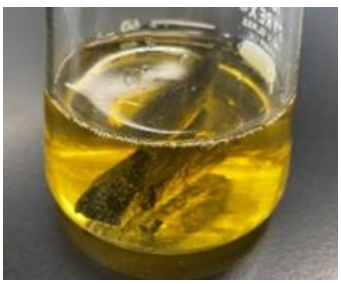


Fig. 3 Only $AgNO_3$ aq | Only bincho charcoal | $AgNO_3$ aq with a bincho charcoal

3. Result

From the results of the experiments, it is suggested that the cause of this phenomenon is the reducing silver ions by the hydrogen which generates during the charcoal making process from bamboo or wood and remains inside the charcoal.

4. Consideration

From the reference about the adsorption of hydrogen inside the graphite, we understood that hydrogen forms C-H bonds[4] with the end of graphite (surface edge). Therefore, we considered that hydrogen forms a C-H bond with the surface edge of charcoal. So, we did a temperature-programmed desorption measurement (TPD: We raise temperature to 1,800 ℃ at 10 ℃/min under an atmospheric pressure of 10^{-5} Pa, and we detected the expected desorption by a mass spectrometer) at the Nishihara Laboratory of the Advanced Institute for Materials Research (AIMR) / Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University. **Fig. 4** was its result, and a large amount of hydrogen desorption was confirmed. This result indicates that there is a large amount of C-H bonds on the surface edge of the charcoal and that hydrogen is chemisorbed atomically.

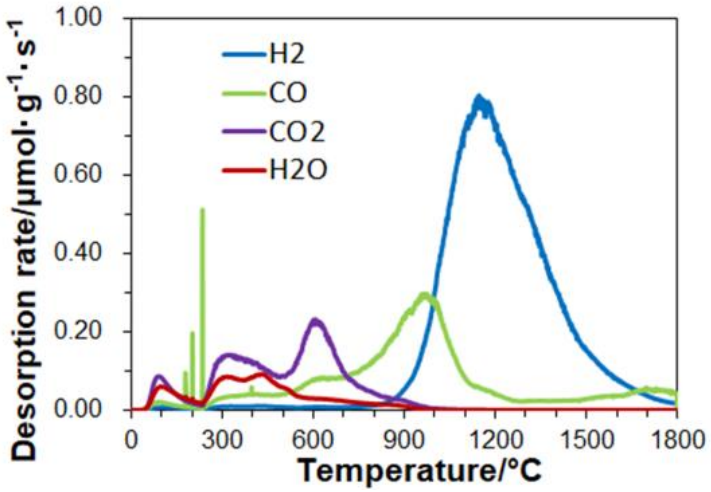
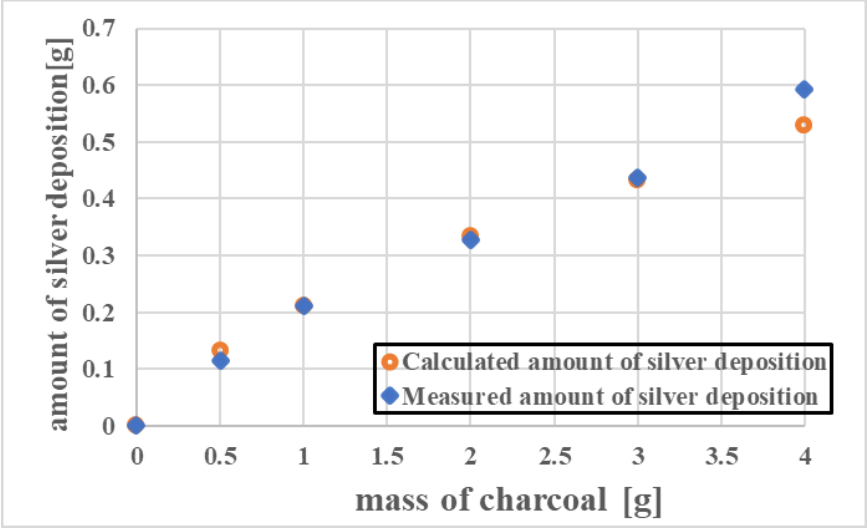


Fig. 4 The result of TPD

Table. 2 The theoretical value and the measured value of deposited silver



At first, **Table. 1** did not form a straight line, and we could not figure out what it depended on. However, we figured out that hydrogen is chemisorbed on the surface of the charcoal. So we hypothesize that the mass of silver deposited could be approximated by the surface area calculated from the mass of the charcoal, and we created **Table. 2**. In the **Table. 2**, the theoretical value (= the mass of deposited silver calculated from the surface area of the charcoal) and the mass of silver actually deposited showed similar result. Then, we calculated the theoretical value by using **Equation. 1**. The mass of silver deposited when 1.0 g of bincho charcoal was used was 0.212 g, which we used as a constant.

$$y = 0.212\ x^{2/3}$$

y : mass of silver deposited, x : mass of charcoal used (**Equation. 1**)

5. Reaction mechanism

The state of the silver deposited from the charcoal indicates crystallization, so we can consider electrons are supplied to the silver ions through the charcoal and silver, and the silver grows like a silver tree. As evidence that electrons are supplied through the charcoal, the shape of the deposited silver changes depending on the resistance value of charcoal. The cedar charcoal used in this study has a higher resistance value than bincho charcoal, which was also used in our study[5)], The cedar charcoal with low electrical conductivity has a clean crystalline shape as shown in **Fig. 5** due to a slow electron supply, while the Bincho charcoal with high electrical conductivity has dendritic (dendrite) crystals as shown in **Fig. 7**. Since the crystalline state of silver differs depending on the electrical conductivity, it can be said that the transfer of electrons through charcoal is occurring in silver deposition. Also, if the hydrogen atoms of the C-H bonds on the surface edge are reacting directly, silver should be deposited on the entire surface of the charcoal.

Fig. 6 Silver (planar crystals) deposited from cedar charcoal

Fig. 7 Silver (dendritic crystals) deposited from bincho charcoal

Therefore, we determined the reaction process below.

1. The hydrogen of the C-H bonds become hydrogen ions and send the electrons to the silver ions through the charcoal and the silver.
2. The silver ions receive the electrons from the silver and deposited the silver on the silver.

Note that in this reaction, the substance which reacts with the silver ion at first and becomes the foothold for silver deposition can be the oxygen functional groups on the surface of the charcoal or carbon radicals that are mainly present on the carbon surface edge [6]. However, since there are no reductive oxygen functional groups on the carbon surface edge [4], carbon radicals may react with a silver ion at the beginning of the reaction.

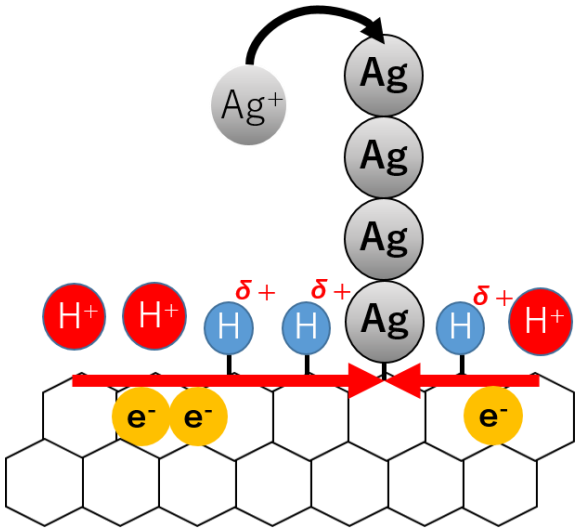


Fig. 8 The diagram of electron supply during the reaction of silver deposition

6. Application of the phenomenon

We applied the reducibility of charcoal to the treatment of inorganic liquid waste. When bamboo charcoal was soaked in inorganic liquid waste, metal precipitation was observed (Fig. 10).

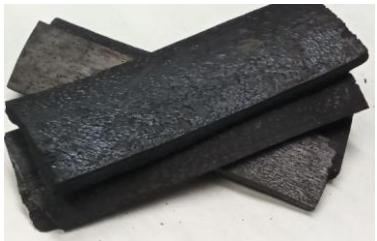


Fig. 9 Bamboo charcoal

Fig.10 Bamboo charcoal reacted with inorganic liquid waste

In addition, the charcoal is also used in various places as interior decoration. The silver deposited on surface of charcoal is highly reflective, and the contrast between the shine and the black of the charcoal gives it an artistic quality. Therefore, we created a work of art with the motif of Karesansui (Traditional Japanese rock garden).

Fig. 11 The work of art with the motif of Karesansui

7. Acknowledgements

In conducting this study, we would like to express gratitude to teachers and seniors for their constructive suggestions. We are grateful to the Nishihara Laboratory, Advanced Institute for Materials Research (AIMR) / Institute of Multidisciplinary Research for Advanced Materials (IMRAM) Science, Professor Hirotomo Nishihara, Assistant Professor Takeharu Yoshii and Mr. Ginga Nishikawa for their thoughtful guidance, including lending us TPD equipment.

8. References

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This research explored the mechanism of silver reduction with charcoals. The idea is interesting and the results and the enthusiasm of the students are encouraging. However, it is recommended to go deeper into the mechanistic investigations.