

Carbon Monolith Surface Chemistry Influence on the Silver Deposit Amount and Crystallite Size

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The surface of carbon monolith (CM) was chemically treated in order to obtain antibacterial filters with silver deposit for water treatment. The chemical treatment involved submerging the as-received CM in HNO₃, KOH and H₂O₂ solution. The specific surface area was examined by N₂ adsorption. Silver deposition at the surface of CM samples was performed using cheap and simple procedure of immersing CM samples in aqueous solution of AgNO₃. Temperature programmed desorption method has been used in order to investigate the nature and thermal stability of surface oxygen groups before and after silver deposition. The composition and crystallinity of silver deposits have been examined by X-ray diffraction. Chemical treatment does not cause any drastic changes of CM specific surface area, but increases a total amount of surface oxides. Amount of deposited silver is several times higher for all chemically treated samples. The results show that increasing the amount of CO yielding groups on CM surface leads to increased amount of Ag deposit and decreases its crystallite sizes

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1. Introduction

The last few years have been marked with a growing interest in carbon monolith (CM) as an alternative for conventional carbon materials. Compared to the conventional activated carbons, carbon monolith, which has a self supporting structure, had the lowest pressure drop, highest permeability, high surface to volume ratio and lowest cost [1]. Depending on the application, CM can be produced with desirable shape and morphology, controlled composition, structure and porosity [1–4] CMs are potentially useful in a wide variety of applications such as: residential water filtration, volatile organic compound emission control [3–6], indoor air purification, chemical separation [7], catalysis, biocatalysts [8], adsorption, porous electrodes under continuous flow condition and chromatography columns.

In our previous work we have used the cylindrical CM impregnated with silver for disinfection of drinking water. Silver coated CM, which combines good properties of silver as a biocide with adsorption properties of carbon materials, acted as an efficient filter for the removal of bacteria from polluted water [9]. Application of CM in water disinfection is influenced by its surface chemistry. Antibacterial activity of silver coated CM depends on the amount of silver deposited as well as silver attrition from CM surface. It was shown that finer silver particles had higher resistance to attrition in comparison to the larger

ones [10]. Therefore, antibacterial activity deteriorates with larger silver particles, which have higher attrition probability [11].

The amount of silver deposited depends on the surface area and the quantity of surface oxides that can act as initial active sites for silver deposition [12]. To obtain good filter characteristics it is necessary to deposit optimal amount of silver on the CM inner capillary walls, and provide low silver attrition. The main objective of this work is to modify the CM surface to increase the yield of silver deposited and decrease its crystallite sizes. CM surface was modified by using HNO₃, KOH and H₂O₂. Silver was deposited at the surface of CM by cheap and simple procedure of immersing CM samples in aqueous solution of AgNO₃ [9, 13, 14]. The influence of the chemical treatment on the specific surface area, surface functional groups and the amount of silver spontaneously deposited at the CM surface were studied. In addition, by comparing the amount of silver deposit with the amount of the surface oxides before and after silver deposition we have revealed the possible mechanism of silver deposition.

2. Experimental

CMs in the shape of cylinder (length 3.0 cm, diameter 1.8 cm) with 8600 parallel capillary channels (80 μm in diameter each) inside the cylinder were purchased from Fractal Carbon (London, UK). Design and structure of the CM used is shown in Fig. 1. This is a composite material, consisting of glassy carbon bed and activated carbon on the inner capillary walls.

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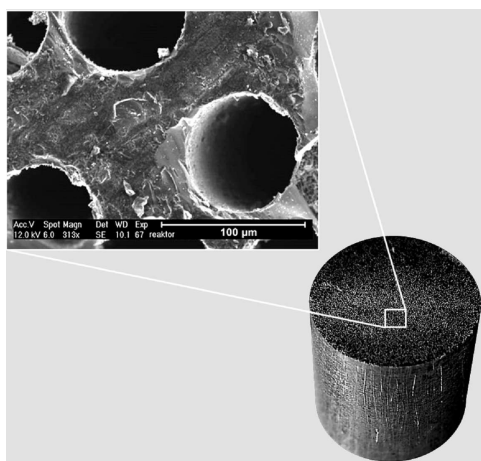


Fig. 1. Carbon monolith optical photograph and the micrograph of the perpendicular cross-section.

A. 2.1. Chemical surface treatment

The chemical treatments involved submerging the as-received CM in HNO_3 , KOH and H_2O_2 solution. Chemically treated samples are designated CM/ HNO_3 , CM/ KOH and CM/ H_2O_2 , respectively. Samples CM/ HNO_3 and CM/ KOH were obtained by heating the CM in 4 M HNO_3 and 4 M KOH , respectively, for two hours, while the CM/ H_2O_2 was obtained by submerging the CM in 4 M H_2O_2 at room temperature until complete degradation of H_2O_2 (when there was no further gas evolution). After chemical treatment the CM samples were thoroughly washed with distilled water to neutral pH, and dried at 110°C for 24 h. All samples were stored in the dessicator until use.

B. 2.2. Silver deposition

Silver deposition at the surface of CM samples was performed by immersing CM samples in aqueous solution of AgNO_3 . 0.1 g of CM was immersed in 100 ml of AgNO_3 solution ($100 \text{ mg}/\text{dm}^3$) at 25°C for 48 h in the dark. After deposition samples were dried at 110°C for 24 h. Silver deposition at the CM surface has been observed by measuring a reduction of silver concentration in the solution using the PYE UNICAM SP9 atomic absorption spectrometer (Pye Unicam Ltd., UK).

C. 2.3. Surface characterization

Specific surface area of CM samples was determined by nitrogen adsorption at the temperature of liquid nitrogen using Automatic Surface Area Analyzer, model 4200 (Leeds & Northrup Instruments, USA).

The pH of the aqueous slurries of the CMs samples was measured. The slurries were prepared with boiled

distilled water in the ratio of 10 ml/g, this suspension was stirred and the pH was measured several times until the constant value was reached.

X-ray diffractometer Siemens D5000 Kristalloflex was used to verify the composition of the silver deposit. Diffraction lines were measured using Ni-filtered $\text{CuK}\alpha_{1,2}$ radiation.

Temperature programmed desorption (TPD) method in combination with mass spectrometry has been used in order to investigate the nature and thermal stability of CM samples surface oxygen groups before and after silver deposition. The TPD profiles were obtained with a custom built set-up, consisting of a quartz tube placed inside an electrical furnace. TPD system were calibrated as it was explained in the literature [15]. CM samples were outgassed in the quartz tube and subjected to TPD at a linear heating rate of 10 K/min to 1173 K under high vacuum. The amounts of CO and CO_2 released from carbon samples (0.1 g) were monitored with Extorr 3000 (Extorr Inc., USA) quadrupole mass spectrometer.

3. Results and discussion

The values of pH slurry and specific surface area of the various CM samples are shown in Table I. Prior to treatment CM shows basic properties [9]. Upon treatment with KOH the pH remains basic whereas HNO_3 and H_2O_2 treatments resulted in acidic pH values. As expected, sample CM/ HNO_3 has the highest acidity, because HNO_3 oxidation produces a large amount of acidic surface groups [16]. H_2O_2 oxidation generates less acidic surface than HNO_3 treatments [16, 17]. It is generally reported that liquid phase oxidations do not change significantly the texture of activated carbons [18, 19], although under more drastic condition (concentrated acid, heating until complete evaporation) a decrease in surface area and pore volume has been observed [20, 21]. Our results for specific surface area (Table I) show that chemical treatment does not cause any drastic changes of CM specific surface area.

TABLE I

Surface characteristics of CM samples.

| Sample | Specific surface area [m^2/g] | pH slurry | CO/CO_2 [mmol/g] | $\text{CO}+\text{CO}_2$ |
|----------------------------|---|-----------|----------------------------------|-------------------------|
| CM | 445 | 9.1 | 1.7 | 0.722 |
| CM/ HNO_3 | 430 | 4.3 | 0.8 | 1.057 |
| CM/ H_2O_2 | 404 | 5.0 | 1.4 | 0.926 |
| CM/ KOH | 443 | 9.3 | 5.7 | 0.840 |

The emission of CO_2 and CO during TPD experiment result from surface oxygen groups which decompose at specific temperature range [22–26]. Fig. 2a presents the amounts of evolved CO and CO_2 before silver deposition for the four CMs tested, obtained by integration under TPD curves. All treated samples show an increase in

the amount of surface oxygen complexes, evident from the increase of the amount of the CO and CO₂ release. Fig. 2a shows that KOH treatment appears to enhance the formation of CO yielding groups much more than HNO₃ or H₂O₂ treatments. Samples CM/HNO₃, CM/H₂O₂ and CM have the comparable amounts of CO evolving groups. Treatments with HNO₃ and H₂O₂ increased surface oxidation, which resulted in the evolution of the large amounts of CO₂. KOH treatment removed a considerable amount of acidic surface oxygen groups, so the amount of CO₂ evolved from CM/KOH is lower than in as-received CM. These results are consistent with pH slurry results and indicate that acidic groups such as carboxyl and lactone are additionally formed by HNO₃ and H₂O₂ treatments, but are decreased or eliminated by KOH treatment. Thus, the abundance of CO₂-yielding groups shows the following sequence: CM/HNO₃ > CM/H₂O₂ > CM > CM/KOH. The chemical treatments also affects CO/CO₂ ratio of CM samples (Table I). For CM/HNO₃ and CM/H₂O₂ increase of CO₂ evolving groups decreased CO/CO₂ ratio. Accordingly, drastic increase of CO evolving groups from CM/KOH tripled the CO/CO₂ ratio of CM.

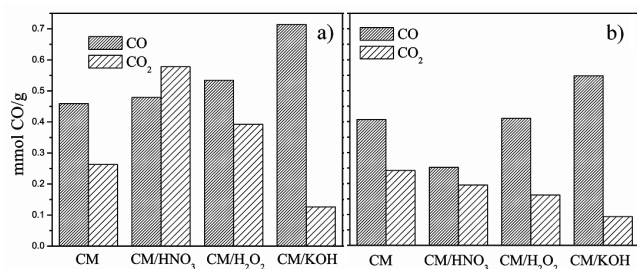


Fig. 2. Amounts of CO and CO₂ evolved from the CM samples surface a) before and b) after silver deposition.

Possible mechanism of silver deposition is through ion exchange reaction between silver ions and carboxylic groups [12]. In our previous work [9] we have shown that silver deposition on CM sample is redox adsorption [12]. The amount of deposited silver on CM samples is given in Table II. The results showed that the treatment with H₂O₂ increased the amount of silver deposit approximately three times. The larger deposits were obtained by HNO₃ and KOH treatment. In addition, for all chemically treated samples the amount of deposited Ag is higher than the total amount of surface oxides.

Table II Amounts of deposited Ag and crystallite sizes (L) of deposited metallic silver on CM.

The composition and crystallinity of silver deposits examined by X-ray diffraction is given in Fig. 3. X-ray diffraction pattern display two peaks of metallic silver on the surface of CM samples. Diffraction patterns around 2 θ values of 38 °C, 44 °C, corresponding to (111), (200) planes of metal silver respectively, deposited as the face centered cubic (FCC) Ag structure [14]. Sharp peaks, corresponding to the diffraction profiles of Ag metal lat-

TABLE II

Amounts of deposited Ag and crystallite sizes (L) of deposited metallic silver on CM

| Ag (mmol/g) | L (nm) |
|----------------------------------|--------|
| CM | 0.406 |
| CM/HNO ₃ | 2.523 |
| CM/H ₂ O ₂ | 1.290 |
| CM/KOH | 1.828 |

tice are superimposed on the broader profiles typical for carbon disordered structure [27]. Crystallite sizes of deposited metallic silver on CM samples are given in Table II.

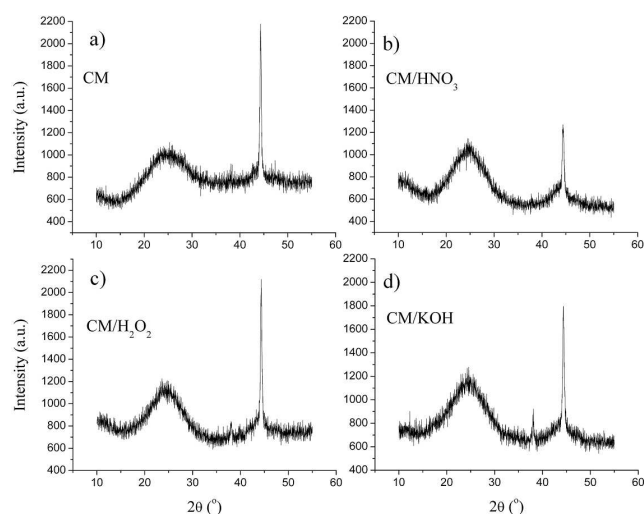


Fig. 3. X-ray diffraction patterns of a) CM, b) CM/HNO₃, c) CM/H₂O₂ and d) CM/KOH.

Fig. 2b shows the amount of evolved CO and CO₂ after silver deposition. For all samples the amounts of CO and CO₂ decrease after silver deposition. During Ag deposition consumption of both CO₂ and CO yielding groups occurs. The CO/CO₂ ratios after silver deposition and the difference between amounts of CO and CO₂ (Δ CO and Δ CO₂) before and after silver deposition are given in Table III. For CM and CM/KOH samples practically no changes of CO/CO₂ ratio occurred after silver deposition. According to values of Δ CO and Δ CO₂ it can be concluded that higher consumption of CO yielding groups during Ag deposition was compensated by lower consumption of CO₂ yielding groups. For CM/HNO₃ and CM/H₂O₂ CO/CO₂ ratio was raised after Ag deposition as a consequence of higher consumption of CO₂ yielding groups. Also, decrease of desorbed CO₂ amount for those two samples was the most pronounced. In contrast, decrease of CO₂ amount for CM and CM/KOH was similar. Additionally, in comparison to CM all chemically treated samples show drastic decrease in the amount of evolved

CO.

TABLE III

Changes in the amount of surface oxygen complexes after silver deposition.

| Sample | CO/CO ₂ | ΔCO | ΔCO_2 | $\Delta\text{CO}+\Delta\text{CO}_2$ |
|----------------------------------|--------------------|-------------------|---------------------|-------------------------------------|
| | | | | [mmol/g] |
| CM | 1.7 | 0.052 | 0.021 | 0.073 |
| CM/HNO ₃ | 1.3 | 0.227 | 0.383 | 0.610 |
| CM/H ₂ O ₂ | 2.5 | 0.123 | 0.229 | 0.352 |
| CM/KOH | 5.9 | 0.166 | 0.033 | 0.199 |

Comparing the obtained results (Table II and Table III), it is clear that there is no direct relationship between the amounts of deposited Ag and $\Delta\text{CO}+\Delta\text{CO}_2$. For CM/KOH sample the amount of deposited Ag is higher comparing to CM/H₂O₂, although the value of $\Delta\text{CO}+\Delta\text{CO}_2$ is lower. It is likely that the metal silver formed in redox reaction is an electrical conductor, thus some portion of Ag⁺ ions can be reduced at a silver crystallite surface without reaction with surface oxide. Also, during Ag⁰ precipitation Ag⁺ solution can oxidize surface sites on carbon materials and such oxidations can create surface oxides [12]. Thus, some of the surface oxides act as initial sites for silver reduction and after that first step Ag⁺ react with silver crystallite surface and build bulky Ag forms which are confirmed by X-ray diffraction (Fig. 3).

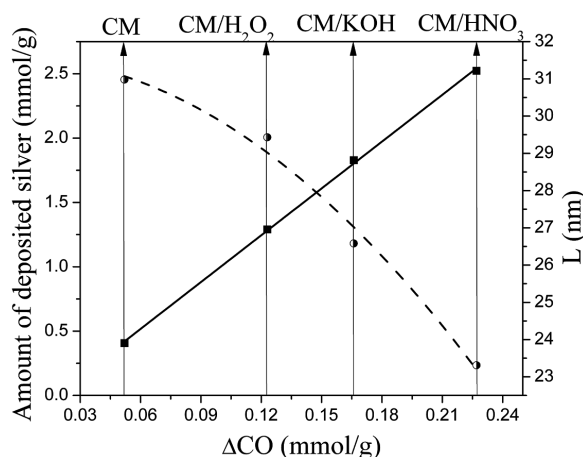


Fig. 4. The amount of deposited Ag (solid line) and crystallite size (dashed line) as a function of ΔCO .

Figure 4 shows the amount of deposited Ag and crystallite size as a function of ΔCO . Regardless to the reagent used in the liquid phase treatment of CM, there is a linear relationship between the amount of deposited Ag and ΔCO , even if there is a difference in consumption of surface oxides during Ag deposition. Therefore, based on the ΔCO_2 values, it is clear that CO₂ yielding groups (especially carboxylic groups) are not crucial

for Ag deposition although those groups participate in the process. The relationship between Ag crystallite size and ΔCO (Fig. 4) shows that higher consumption of CO yielding groups causes decrease of Ag crystallite size.

4. Conclusions

Carbon monolith is sensitive toward chemical treatments by nitric acid, hydrogen-peroxide and potassium-hydroxide, which increase the total amount of surface oxides. Treatments with HNO₃ and H₂O₂ increased the amount of CO₂ evolving groups, which resulted in decreased pH slurry. In contrast, KOH treatment increased of CO evolving groups. The amount of deposited silver, obtained by immersion into AgNO₃ solution, is several times higher for all chemically treated samples comparing to the untreated CM. This is in line with increased amount of surface oxides after chemical treatments. Silver deposition causes decrease of the amounts of both CO and CO₂ evolving groups. The results show linear relationship between the amount of deposited silver and consumed CO evolving groups, although there is no such relationship with total amount of consumed surface oxides ($\Delta\text{CO}+\Delta\text{CO}_2$). Based on the relationship between Ag crystallite size and ΔCO (Fig. 4) it could be concluded that by modifying CM surface to enlarge the amount of CO yielding groups, the amount of Ag deposit formed as fine crystals with small crystallite sizes can be significantly increased.

Acknowledgments

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