# Mechanisms of Diffusion–Reduction Interaction of Microcrystalline Cellulose and Silver Ions

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**Abstract** — The preparation of microcrystalline cellulose samples containing intercalated silver(0) particles includes two main stages: diffusion of silver ions from aqueous  $AgNO_3$  into the microcrystalline cellulose matrix, followed by reduction of the silver ions bound to cellulose macromolecules to Ag(0) and growth of Ag(0) particles inside the cellulose matrix and on its surface. Mechanisms of interaction of silver ions with cellulose as reducer and with other reducers and ligands are considered.

The problem of intercalation of transition and main group metal ions into a natural polymer, cellulose, attracts enduring researcher's interest. However, there are few papers dealing with cellulose interaction with silver ions [1-3]. At the same time, research in this field may be useful for development of methods for cellulose modification and design of new polymeric materials exhibiting bactericidal properties and new conducting materials. Silver metal deposition on a cellulose substrate has been utilized as one of the test methods for hydroxycellulose. Thus, Moon et al. have accomplished silver metal deposition from aqueous solutions of silver salts on filter paper oxidized under UV irradiation [4]. The referees indicated that reduction of silver ions from their salt solutions involve both end aldehyde groups and hydroxy groups of polysaccharides. We previously found [5] that microcrystalline cellulose (MCC) is a suitable matrix for Ag(0) reduction from silver salt solutions. This is due to specific properties of MCC, i.e. its powder morphology, high sorption capacity, and ability to develop active surface during reactions [6].

The present paper is a continuation of our previous studies [5, 7] and deals with the analysis of complexation processes, mechanisms of chemical binding and reduction of silver ions to silver metal, and growth of silver(0) particles in a cellulose matrix.

Interaction of aqueous solutions of silver salts with a cellulose matrix (Cell) is a complex multistage process. In the first stage, coordination of the hydrated silver ions  $[Ag(H_2O)_2]^+$  with alcohol groups of cellulose macromolecules takes place, leading to formation of outer- and inner-sphere complexes **I** and **II**.



Then the silver ions are reduced by cellulose end aldehyde and alcohol groups. As a result, two oxidized forms of cellulose arise (Scheme 1):

### Scheme 1.

$$Cell-C_{H}^{\mu} + H_{2}O \xrightarrow{-2\bar{e}} Cell-C_{O}^{\mu} + 3H^{+},$$

$$Cell-CH_{2}OH \xrightarrow{-2\bar{e}} Cell-C_{H}^{\mu} + 2H^{+},$$

$$Ag^{+} + \bar{e} = Ag(0).$$

The presence of silver(0) in cellulose samples has been confirmed by X-ray phase analysis and X-ray photoelectron spectroscopy [7]. The appearance of  $COO^-$  groups as a result of oxidation of cellulose aldehyde groups by silver ions, has been confirmed by Raman spectroscopy [7]. In the case of interaction of the ammonium silver complex  $[Ag(NH_3)_2]^+$  with cellulose, a similar redox process occurs (Scheme 2).

Sample no.	Sample	Reducer, additional treatment	Sample color, particle	Silver content, wt%	
			size $[n \text{ in } Ag(0)_n]$	in bulk <sup>a</sup>	on the surface <sup>b</sup>
1	Cell <sup>c</sup>	_	White	_	_
2	Cell–Ag(0)	Cell	Yellow, small; $n = 3-11$	0.6	<1.0
3	Cell–Ag(0)	Cell, $NH_3 \cdot H_2O$	Red-brown, small, large;	0.6	1.5
	_	5 2	n 3–11, 1000		
4	Cell–Ag(0)	Cell, 250°C	Yellow, small; $n = 3-11$	1.3	1.2
5	Cell-Ag	Glyc, $NH_3 \cdot H_2O$	Red-brown, small, large;	6.1	12.6
	_	- 5 2	n 3–11, 1000		
6	Cell-Ag	1,10-Phen, Glyc, NaHCO <sub>3</sub>	Grayish green, gigantic; $n > 5000$	3.0	4.1
7	Cell-Ag	NaBH <sub>4</sub>	Yellow, small; $n = 3-11$	5.3	2.2
8	Cell–Ag	$NaBH_{4}^{T}$ (repeated treatment)	Graish brown, gigantic; $n > 1000$	6.2	2.6
9	Cell–Ag	$KH_2PO_2, H_3PO_4$	Gray, gigantic; $n > 10000$	7.6	16.5
10	Ag(0)		Gray, gigantic	_	_
	1				1

Table 1. Characteristics of cellulose samples containing silver(0) particles

<sup>a</sup> X-ray fluorescent analysis. <sup>b</sup> X-ray photoelectron spectroscopy. <sup>c</sup> Initial cellulose.

#### Scheme 2.

$$Cell-C \bigvee_{H}^{0} + 2NH_{3} + H_{2}O \xrightarrow{2\overline{e}} Cell-C \bigvee_{OH}^{0} + 2NH_{4}^{+},$$

$$Cell-CH_{2}OH + 2NH_{3} \xrightarrow{-2\overline{e}} Cell-C \bigvee_{H}^{0} + 2NH_{4}^{+},$$

$$[Ag(NH_{3})_{2}] + \overline{e} \longrightarrow Ag(0) + 2NH_{3}.$$

Initial cellulose acts as a two-electron reducer in both cases, whereas  $Ag^+$  ions are one-electron oxidants. Oxidation of one aldehyde or alcohol cellulose group forms two Ag(0) atoms that combine into an  $Ag(0)_2$  particle [8]. These particles and free silver ions are involved into formation of  $Ag(0)_n$  particles.

**Diffusion–reduction processes involving cellulose matrix as reducer.** When heated, a mixture of MCC with aqueous AgNO<sub>3</sub> changes color from white to rose (Table 1, sample no. 1). This fact can be explained by appearance of primary reduced  $Ag(0)_n$  centers (n = 4-10) in the MCC matrix as a result of electron transfer from the cellulose macromolecule to Ag<sup>+</sup> ions, which follows cellulose coordination with the latter (see Schemes 1 and 2). This transfer is induced by visible light. The silver(0) content in this sample (sample no. 2) is low (0.6 wt% in bulk).



When the process was performed in aqueous ammonia, a sample was obtained with a silver(0) content in bulk lower that 0.6 wt %. Silver(0) (1.5 wt%) appears on the surface of cellulose fibers (sample no. 3).

Cellulose subjected to thermal treatment at  $250^{\circ}$ C reduces Ag<sup>+</sup> ions in a neutral medium relatively rapidly during their diffusion into the matrix. This is probably due to the fact that the content of end aldehyde groups is increased by heating. Moreover, the formation of C=C bonds in the MCC structure under thermal treatment can facilitate binding Ag<sup>+</sup> ions via coordination of type **A**.



Evidence for the appearance of double bonds and additional aldehyde groups in the cellulose was obtained by studying the effect of the temperature on the MCC structure by solid-state high-resolution <sup>13</sup>C NMR spectroscopy [10]. Figure 1a shows the <sup>13</sup>C NMR spectrum of MCC, containing 8 typical signals. Under chemical and temperature effects in various media natural cellulose undergoes chemical or structural modifications. The latter are accompanied by transformation of the cellulose I crystallographic cell. This transformation can occur by the following paths (Fig. 1b): (1) rotation of the anhydroglucose rings about the C<sup>4</sup>–O bond, which can occur at 100°C and higher temperatures, or abound the O–C1 bond (the latter is sterically hindered); and (2) rotation about the

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 $C^5-C^6$  bond (rotational isomerism of the hydroxymethyl group). The result is dislocation of all H bonds in the cellulose system typical of the cellulose modification I and probable partial formation of an H-bond system typical to other cellulose structural modifications, as evidenced by data in Table 2 and in [9].

Heating of cellulose at 150–380°C leads to noticeable changes in its <sup>13</sup>C NMR spectra (Fig. 2, Table 2). Analysis of the spectra and data in Table 2 indicates changes in X-ray crystallinity and weight loss. Thus, the weight loss at 250°C is rather large (21.4 wt%) [9]. Therewith, scission of cellulose chains, formation of shorter fragments and, correspondingly, formation of additional aldehyde groups take place. Consequently, Ag<sup>+</sup> reduction in the cellulose matrix proceeds faster and to a greater extent. The silver(0) content in the sample (sample no. 4) is 1.3 wt% in bulk and 1.2 wt% on the surface. Because of the low contents, the aldehyde groups and double bonds are impossible to detect by spectral methods.

Considerable changes are observed in the  ${}^{13}$ C NMR spectra of cellulose samples heated above 250°C. All carbon signals shift and change shape, implying changed chain arrangement and steric environment of carbon atoms in the reaction products compared with those in the initial cellulose. The C<sup>6</sup> signal shifts from 66.5 to 62.5 ppm, which suggests transformation of cellulose I to cellulose II and/or amorphization. In addition, a strong and broad signal appears at 120–135 ppm, associated with the C=C bond formation in cellulose chains, induced by heating. These results are consistent with the scheme of thermal degradation of cellulose, described in [10].

In the presence of a solvent (glycerol), the diffusion–reduction process probably occurs in two stages. In the first stage, in the process of  $Ag^+$  diffusion into the MCC matrix, several complex forms of silver ions, i.e. the aqua complexes  $[Ag(H_2O)_2]^+$ , the solvates  $Ag(Glyc)^+$ , and polynuclear complexes, exist in the system  $Ag^+$ –Glyc–H<sub>2</sub>O–Cell. It is known that  $Ag^+$  ions form with alcohols unstable solvates [11]. However, 1,2-ethanediol solvates  $Ag^+$  ions stronger than water [12]. According to [13], the polyatomic alcohol mannite [(CH<sub>2</sub>OH–(CHOH)<sub>4</sub>CH<sub>2</sub>OH)] forms the complex  $AgBO_2 \cdot C_6H_{14}O_6$ . One can suppose that  $Ag^+$  ions can form with glycerol fairly strong chelates and polynuclear coordination compounds, as well as solvates.

Diffusion of silver ions into the MCC matrix proceeds at high temperatures. Silver ions are probably transferred from the aqua complex  $[Ag(H_2O)_2]^+$  to the  $Ag^+(Glyc)_n$  and then  $Ag^+$ -Cell forms. Obviously, glycerol promotes transfer of silver ions from

 Table 2. Characteristics of microcrystalline cellulose

 subjected to thermal treatment

Heating temperature, °C	I <sub>1</sub> <sup>a</sup>	I2 <sup>a</sup>	Weight loss, wt%
Initial cellulose	0.25	0.20	_
150	0.20	0.30	3.5
200	0.30	0.20	4.7
250	0.50	0.50	21.4
280	0.80	0.80	66.0
300	_	-	70.0

<sup>a</sup> Data obtained by <sup>13</sup>C NMR spectroscopy.  $I_1$  is the intensity ratio of the down- and upfield components of the C<sup>6</sup> signal at 62.5 and 66.5 ppm, determined by the rotameric composition of the hydroxymethyl groups; and  $I_2$  is the intensity ratio of the amorphous and crystalline components of the C<sup>4</sup> signal at 84 and 88 ppm, determined rotation of the glucoside units about the C<sup>4</sup>–O<sup>1</sup> bond.

the aqueous to MCC phase, i.e. acts as a specific phase-transfer catalyst.

$$\underset{cellulose}{\operatorname{aqueous phase}} Ag^{+}Glyc + 2H_{2}O \xrightarrow{\longrightarrow} Ag(H_{2}O)_{2}^{+} + Glyc$$

$$\underset{Ag^{+}Glyc + Cell \longrightarrow}{\operatorname{Ag^{+}(Cell)}} Ag^{+}(Cell) + Glyc$$



**Fig. 1.** (a) Solid-state high-resolution  ${}^{13}C$  NMR spectrum of microcrystalline cellulose and (b) proposed transformation paths of anhydroglucose cellulose units.

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**Fig. 2.** Solid-state high-resolution <sup>13</sup>C NMR spectra of microcrystalline cellulose heated at (1) 150, (2) 200, (3) 250, (4) 280, (5) 300, and (6) 380 °C.

High-temperature treatment of MCC in the glycerol medium contributed into structural changes in the cellulose matrix. It is known that heating at 50–200°C in glycerol leads to destruction of MCC [14]. Here, like on heating in air, additional aldehyde groups are formed. This enhances the reductive power of the cellulose and favors increased production of silver(0) in the matrix.

The role of glycerol as reaction medium is enhanced by its partial oxidation to give a mixture of glycerol aldehyde, 1,3-dihydroxyacetone, and some acids (for instance, glyceric acid) [15, 16]. The first component is able to reduce silver ions. Hence, the assistance of glycerol and specific temperature conditions make for greater amounts of silver(0) in the cellulose matrix compared with those obtained by other methods. The silver (0) contents in sample no. 5 are 6.1 wt% in bulk and 12.6 wt% on the surface.

It is known that one of the general methods of synthesis of noble metal clusters is reduction of their salts by various reducers in the presence of ligands stabilizing low oxidation states of the metals [17]. 1,10-Phenanthroline (Phen), a  $\pi$ -electron-deficient ligand, is a widely used ligand of the above type [17].

In the first stage,  $Ag^+$  complexes with 1,10-phenanthroline (**B**) are formed. The composition of these complexes corresponds to the formula  $[Ag(Phen)_2]^+$ [18–20].



The complex participates in the redox process (Scheme 3).

As seen from this scheme, 1,10-phenanthroline inserts into the cellulose matrix, being coordinated

#### Scheme 3.



with  $Ag(0)_2$ . This is indirectly confirmed by the XPS data: The samples contain both silver(0) and nitrogen on the surface of cellulose fibers.

The reaction proceeds in aqueuos-glycerol medium, and, therefore, the role of glycerol as a polyatomic alcohol is analogous to that described above. The process of formation of metal particles is rather complicated [22] and can be shown by Scheme 4.



Since the  $[Ag(Phen)_2]^+$  complexes are large-sized, their reduction to gigantic particles like  $[Ag_m(Phen)_y]^$ in the MCC matrix may be hindered by steric reasons or provide smaller silver(0) particles. As found by transmission electron microscopy [22], the size distribution of silver(0) particles in the cellulose samples prepared in 1,10-phenanthroline medium is bimodal: Both small ( $\geq 10$  nm) and large ( $\geq 60$  nm) particles are present. The silver(0) contents in sample no. 6 are 3.0 wt% in bulk and 4.1 wt% on the surface.

**Diffusion–reduction process involving sodium boron hydride as reducer.** Sodium boron hydride is a strong reducer. The redox reaction involves several concurrent processes. One of them is reduction of the  $Ag^+$  ions intercalated into the MCC matrix; the other one is reduction of the  $Ag^+$  ions fixed on the microfibril surface. It was also established that reduction of  $Ag^+$  ions also takes place in bulk solvent. The reduction process can be represented by Scheme 5.

#### Scheme 5.

$$(H_2O)Ag^+(O \xrightarrow{H^{-1}H^1}_{H}) \xrightarrow{H^{-1}}_{H} \xrightarrow{BH_4^{-}}_{-2H_2O} Ag^{0} \text{ and } Cell-OH$$

The reaction mainly occurs on the Ag(0) active centres formed by the redox process induced by

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visible light during  $Ag^+$  diffusion into the MCC matrix. Once primary Ag(0) centers have appeared, growth of silver(0) particles commences. The silver(0) contents in sample no. 7 are 5.3 wt% in bulk and 2.2 wt% on the surface. After repeated treatment by the reducer, the silver(0) content in sample no. 8 is 6.2 wt% in bulk and 2.6 wt% on the surface.

**Diffusion–reduction process involving potassium hypophosphite as reducer.** Potassium hypophosphite most commonly used for reductions in alkaline media. The hypophosphite anion is a two-electron reducer.

$$\stackrel{\text{H}}{\overset{|(+)}{\to}}_{H}O + 3OH^{-} \longrightarrow \stackrel{O}{\overset{-}{\to}} \stackrel{N}{\overset{|(3+)}{\to}}_{O}O + 2H_{2}O + 2\bar{e}$$

Nevertheless, its reductive properties can also be manifested in acidic media, where the reaction rate is lower. To activate cellulose in this reaction, after completion of  $Ag^+$  diffusion into the MCC matrix we added to the reaction mixture first phosphoric acid and then the reducer. In this case, the reduction takes place mainly in solution. However, reduction in the MCC matrix is also possible due to its activation, namely, loosening of its morphological structure as a result of acid treatment.

Orthophosphoric acid protonates donor cellulose oxygen atoms. As a result, they lose the ability to coordinate with silver ions to form outer- and innersphere complexes. Thus, acid medium precludes participation of MCC in the redox process as reducer, and reduction of silver ions starts even when  $KH_2PO_4$  is added. The reduction process and subsequent growth of silver(0) particles occur both on the cellulose surface and in its pores. As shown by XPS [7] and raster electron microscopy [22], most silver(0) particles reside on the cellulose fiber surface. Therefore, the silver(0) content on the surface of this sample (sample no. 9) is very high : 16.5 wt% against 7.6 wt% in bulk.

The redox process can be represented by Scheme 6.

Hence, the preparation of cellulose samples with intercalated silver(0) particles consists of two main stages. The first one involves diffucion of  $Ag^+$  ions

## Scheme 6

$$\begin{array}{rcl} 3\mathrm{Ag^{+}} &+& \mathrm{H_{3}PO_{4}} \longrightarrow & \mathrm{Ag_{3}PO_{4}} \downarrow &+& \mathrm{3H^{+}},\\ &&& 2\mathrm{Ag_{3}PO_{4}} \downarrow &+& \mathrm{3H_{3}PO_{2}} &+& \mathrm{3H_{2}O}\\ &\longrightarrow&& 3\mathrm{Ag(0)_{2}} &+& \mathrm{3H_{3}PO_{3}} &+& \mathrm{2H_{3}PO_{4}}. \end{array}$$

from aqueous  $AgNO_3$  solutions into the MCC matrix and complexation with it. The second stage involves reduction of the  $Ag^+$  ions bound to MCC molecules to silver(0) with subsequent formation of silver(0) particles. At the beginning of the process, in the course of  $Ag^+$  diffusion into the MCC matrix, silver ions are partially photochemically reduced and form small  $Ag(0)_n$  particles (n = 4-10) which act as catalytic centers in the subsequent reduction process. The reduction is accomplished by the cellulose itself via oxidation of its end aldehyde and alcohol and groups or by specific reducers. The subsequent conversion of primary reduced Ag(0) centers into small silver(0) particles and their growth to gigantic particles also proceed just in the cellulose matrix.

Hence, mechanisms of diffusion-reduction interaction of silver ions with cellulose in the presence of solvents and ligands, as well as mechanisms of reduction of the ions in the cellulose matrix and on the surface of cellulose fibers are suggested. It was shown that the silver(0) content and silver(0) particle size depend on the reducer type, solvent, reaction medium, and ligand type.

It was established that in the systems MCC–  $[Ag(H_2O)_2]^+$ , MCC– $[Ag(NH_3)_2]^+$ , MCC– $[Ag(NH_3)_2]^+$ , MCC– $[Ag(NH_3)_2]^+$ –glycerol, MCC– $[Ag(H_2O)_2]^+$ – $[BH_4]^-$ , and MCC– $[Ag(H_2O)_2]^+$ – $H_2PO_2^-$ , reduction of silver ions to silver(0) takes place with subsequent formation of  $Ag(0)_n$  particles. In the absence of specific reducers, silver ions are reduced to silver(0) due to reductive properties of cellulose. With strong chemical reducers, such as sodium boron hydride and potassium hypophosphite, more silver(0) is formed in the cellulose matrix and growth of silver(0) particles is stimulated.

# EXPERIMENTAL

Characteristics of the samples of microcrystalline cellulose and cellulose–silver(0) intercalates are given in Table 1 and in [5, 7]. The bulk and surface concentrations of silver(0) were determined by X-ray fluorescence analysis and X-ray photoelectron spectroscopy, respectively. The presence of silver(0) was confirmed by X-ray phase analysis and X-ray photoelectron spectroscopy [7, 22]. Relationship between the sample color and the number of silver(0) atoms in

the silver(0) particles is given in Table 2 according to [17, 23, 24]. From these data it follows that the silver(0) particles intercalated into the cellulose matrix contain both small and gigantic numbers of atoms.

High-temperature treatment of microcrystalline cellulose was performed in a vacuum at 150 and  $250^{\circ}$ C for 2 h.

**Diffusion–reduction process involving cellulose matrix as reducer** (Table 1). Diffusion of the  $Ag(H_2O)_2^+$  aqua complexes into the cellulose matrix was performed by heating cellulose in 0.1 M or 0.2 M aqueous AgNO<sub>3</sub> solutions at 90–100°C under continuous stirring for 1 h. The Cell:Ag<sup>+</sup> molar ratios were 5 or 10. The liquid modulus  $\gamma$ , i.e. solution-tosample weight ratio was 10. In the course of heating the color of the reaction mixture was changing from white to pink. After washing and drying, a light yellow powder was obtained (sample no. 2).

To accelerate the redox process, concentrated aqueous  $NH_3$  was added to the reaction mixture ( $\gamma$  changed from 10 to 15), and it was heated at 70°C for 40 min. A brown color developed. After thorough washing with hot water, the solid material was filtered off and dried at 90°C to obtain a reddish brown powder for both molar ratios (sample no. 3).

To elucidate the effect of high-temperature treatment on the reductive power of cellulose, the latter was heated at 150°C or 250°C for 2 h. Therewith, the sample got light yellow. It was then treated with 0.2 M aqueous AgNO<sub>3</sub>. The Cell: Ag<sup>+</sup> molar ratio was 10, and  $\gamma$  was 10. The mixture was heated at 90°C for 1 h. A reddish brown color developed. After washing and drying, the residue changed color from reddish brown to yellow (sample no. 4).

To elucidate the effect of the solvent (glycerol) on the reductive power of cellulose, the latter was kept in a 0.2 M aqueous-glycerol AgNO<sub>3</sub> solution with vigorous stirring at 180°C for 10 min. The Cell:Ag<sup>+</sup> molar ratio 10, and  $\gamma$  was 10. The reaction mixture got dark gray. After cooling to room temperature, concentrated aqueous NH<sub>3</sub> was added ( $\gamma$  changed to 12), and heating was continued for 40 min. A brown color developed. After washing and drying, a reddish brown powder was obtained (sample no. 5).

To elucidate the effect of the solvent (glycerol) and additional complexation of silver ions with 1,10phenanthroline [Ag(0) and Ag(0)<sub>n</sub> stabilizer] on the reductive power of cellulose, the latter was heated in 0.2 M aqueous AgNO<sub>3</sub> at 90°C with stirring for 1.0 h. The Cell:Ag<sup>+</sup> molar ratio was 10, and  $\gamma$  was 10. After cooling, aqueous 1,10-phenanthroline hydrate was added (Ag<sup>+</sup>: 1,10-phenanthroline hydrate molar ratio 0.3;  $\gamma$  changed to 15). The mixture was heated again at 90°C for 10 min. A light yellow color developed because of the formation of a poorly soluble complex [Ag(Phen)<sub>2</sub>]NO<sub>3</sub>. A concentrated glycerol solution was added ( $\gamma$  changed to 35), and the reaction mixture was heated at 150°C for 5 min; therewith, it changed color to light brown. After addition of 1.2 mmol of NaHCO<sub>3</sub> and the reaction mixture was heated again at 150°C for 5 min, as a result of which it got greenish-gray. After thorough washing with hot water, filtration, and drying at 90°C, a greenish gray powder was obtained (sample no. 6).

**Diffusion–reduction process involving sodium boron hydride as reducer.** Microcrystalline cellulose was heated at 90°C and stirred in 0.2 M aqueous AgNO<sub>3</sub> for 1 h. The Cell: Ag<sup>+</sup> molar ratio was 10, and  $\gamma$  was 10. The reaction mixture was cooled, and 0.13 M aqueous NaBH<sub>4</sub> was added at room temperature with vigorous stirring. The g value changed to 15. A grayish-brown color immediately developed. After washing and drying, a grayish brown powder was obtained (sample no. 7; after repeated treatment with the reducer, sample no. 8).

**Diffusion–reduction process involving potassium hypophosphite as reducer.** Microcrystalline cellulose was heated in 0.2 M aqueous AgNO<sub>3</sub> at 90°C with vigorous stirring for 40 min. The Cell: Ag<sup>+</sup> molar ratio was 10, and g was 10. After addition of 5 M aqueous H<sub>3</sub>PO<sub>4</sub> ( $\gamma$  changed to 15), heating was continued for 40 min, aqueous KH<sub>2</sub>PO<sub>2</sub> was added (Ag<sup>+</sup>: KH<sub>2</sub>PO<sub>2</sub> molar ratio 0.4,  $\gamma$  changed to 50), and the mixture was additionally heated at 90°C with stirring for 15 min. A grayish-brown color immediately developed. After thorough washing, decantation, and drying at 90°C, a gray powder was obtained (sample no. 9).

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