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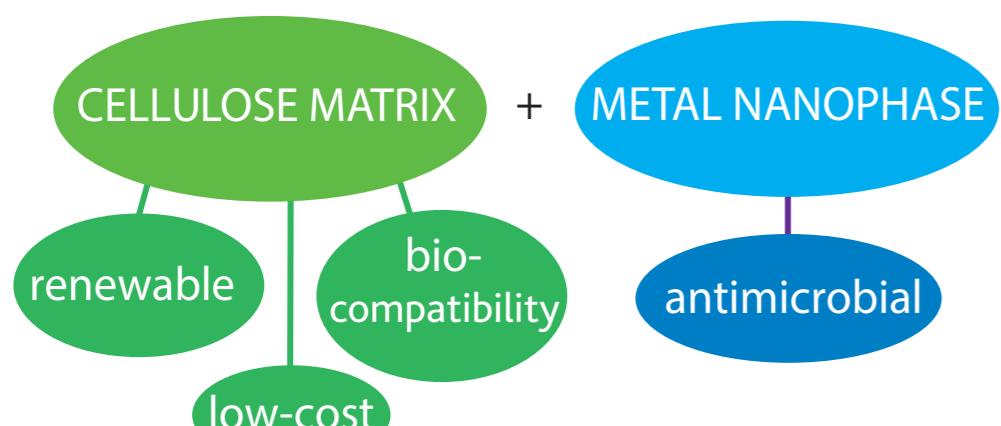
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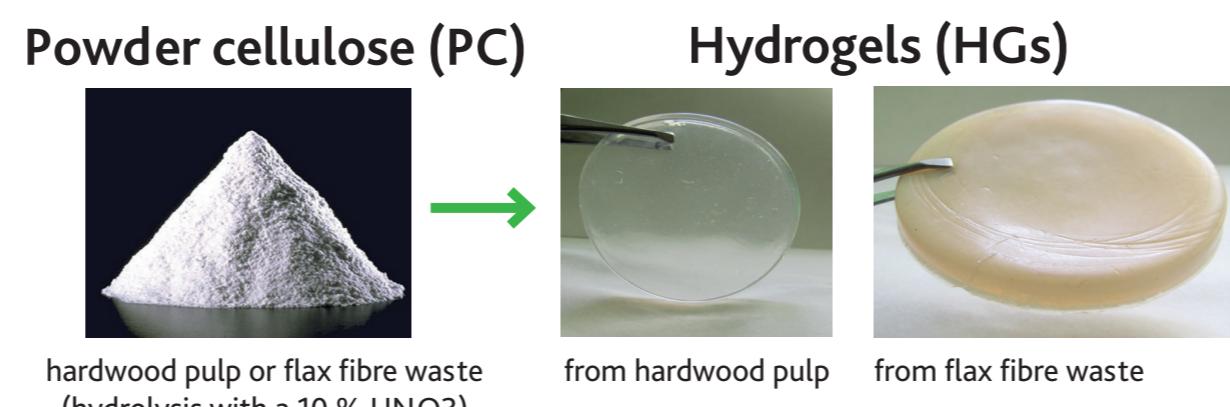
BACKGROUND and OBJECTIVE

Composite materials based on natural polymers contained metal nanophase have remarkable capability to various applications. Cellulose is rarely used for the direct synthesis of hydrogels (HG), commonly they are manufactured from cellulose derivatives, nanocellulose or bacterial cellulose.

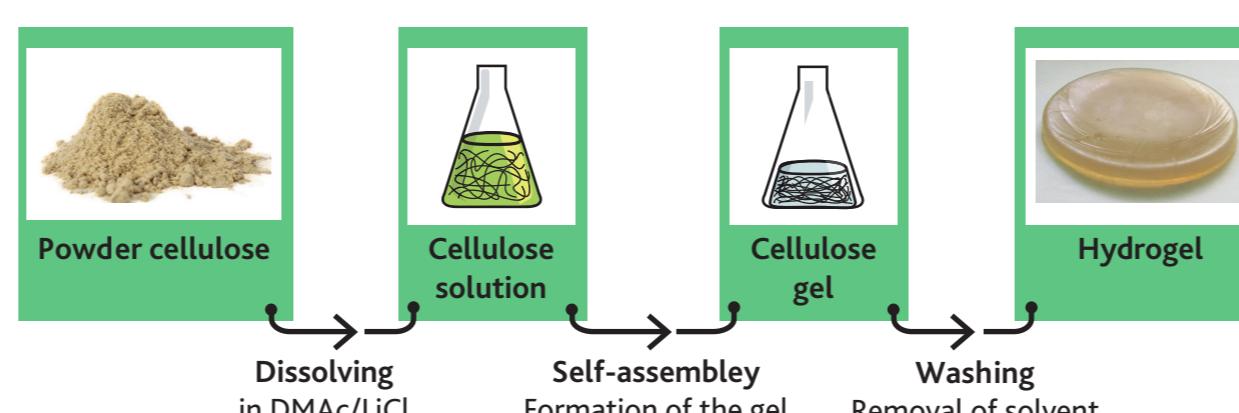
In this study, HGs obtained from the cellulose solutions in N,N-dimethylacetamide/LiCl (DMAc/LiCl) were used as matrices for embedding metal nanoparticles (NPs). The results on the properties of HG/Me hybrid composites as well as chemical aspects of modification of cellulose by chemical reduction of the noble metals, namely silver and gold, will be presented.



EXPERIMENTAL TRIALS



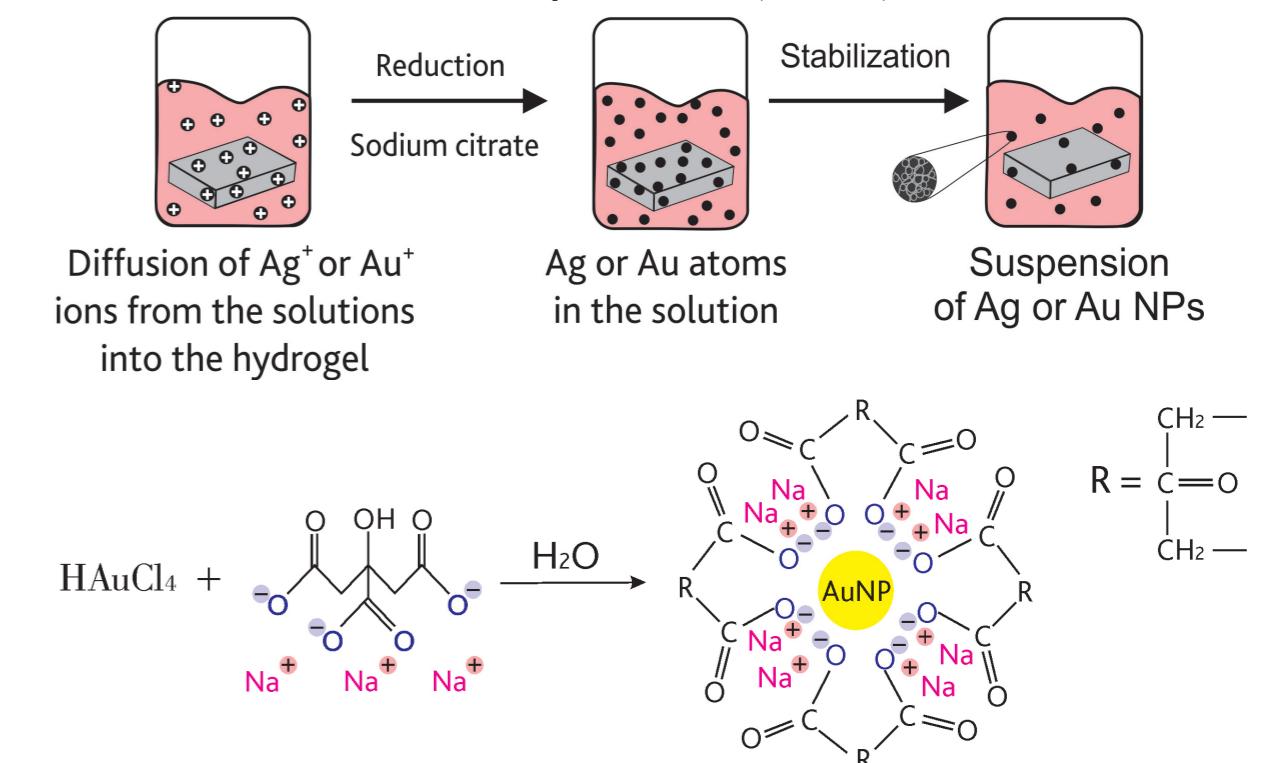
The HGs were prepared via spontaneous self-assembly and aggregation of cellulose chains from DMAc/LiCl solutions (Pic. 1). In the HGs which contained 3 wt.% or less of cellulose, up to 2500 wt.% of water was trapped. The material demonstrated high porosity and specific surface areas.



Pic. 1. Formation of HG

DIFFUSION-REDUCTION METHOD

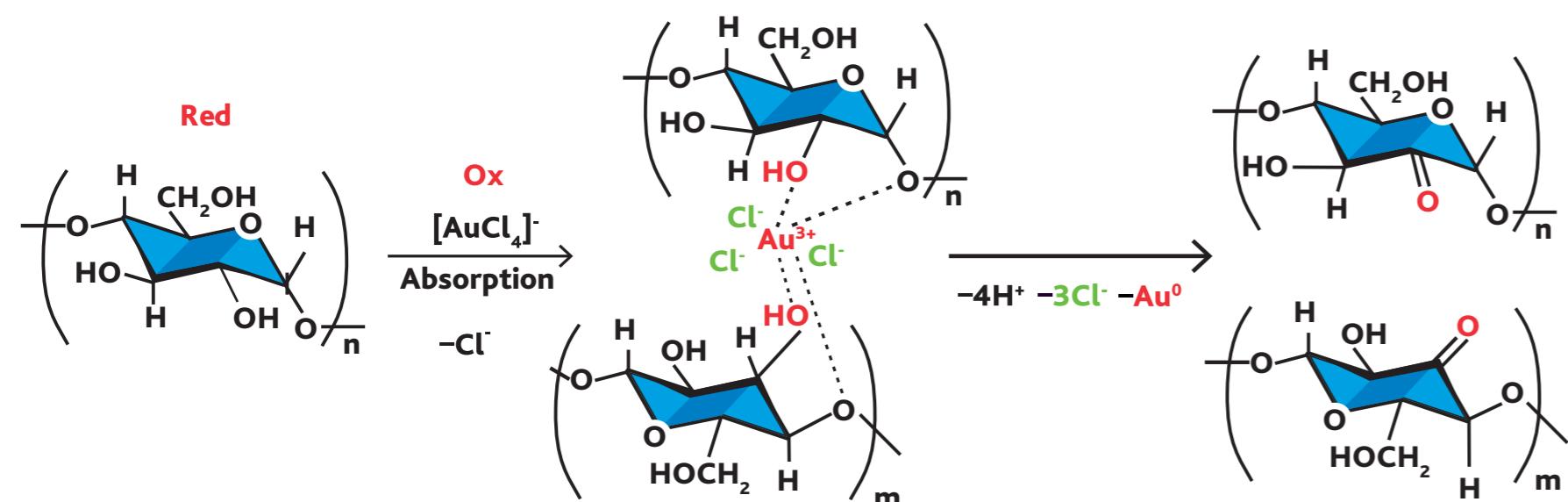
Synthesis of Ag and Au nanoparticles was carried out directly in the matrices of HGs. We applied Turkevich method (Zhao et al, 2013) of reduction gold ions from $\text{Na}[\text{AuCl}_4]$ solution and silver ions from AgNO_3 solution with trisodium citrate (TSC) as a reducer. TSC was used as both reducing and stabilizing agent, dicarboxy acetone resulting from the oxidation of citrate also contributed to the stabilization of the particles (Pic. 2).



Pic. 2. Synthesis of Au or Ag NPs by Turkevich method

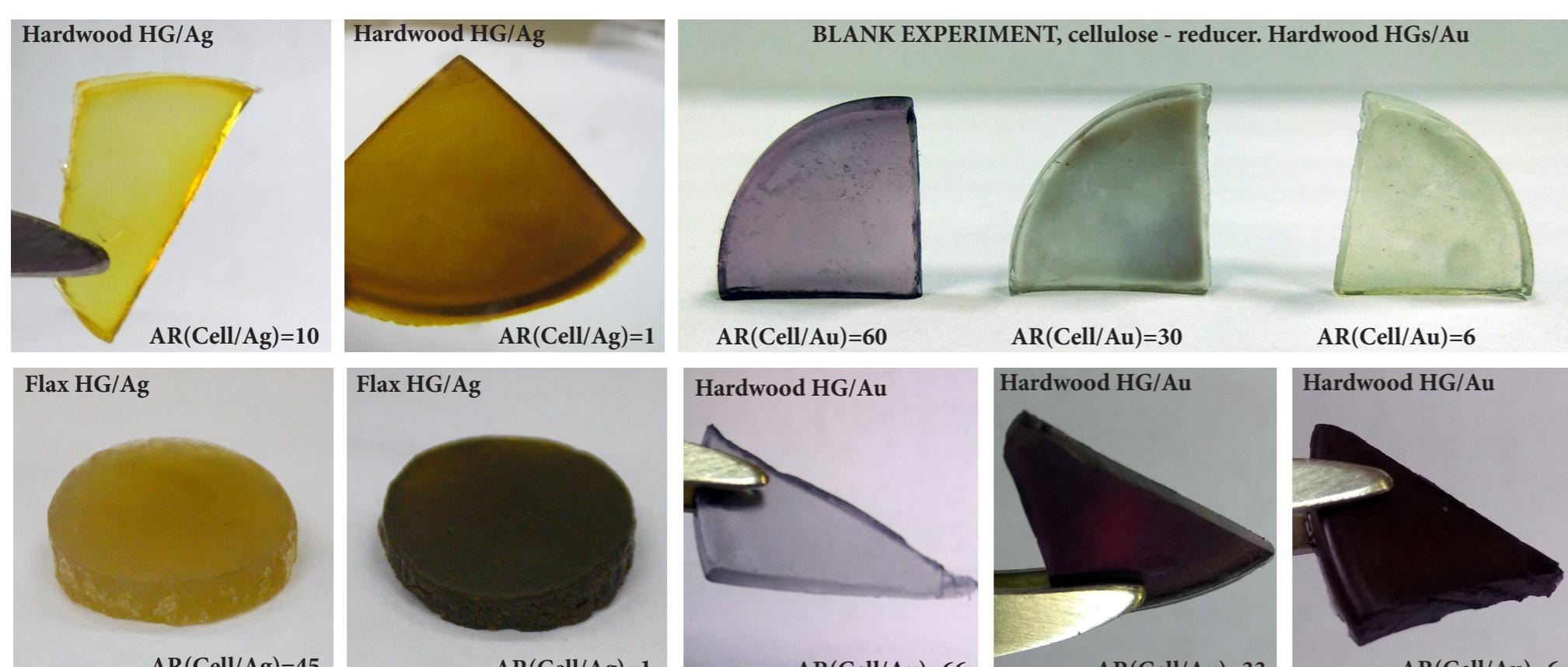
RESULTS

The mechanism of metal reduction consisted of the coordination of metal ions with hydroxyl groups in the cellulose chain. During absorption-diffusion processes, some OH groups were oxidized to carboxyl groups, which led to further binding of metal ions and their reduction to zero-valent metals with the help of a reducing agent.



Pic. 3. The mechanism of $[\text{AuCl}_4]$ reduction in the cellulose matrix

A blank experiment was carried out to demonstrate that the end (reducing) aldehyde groups in cellulose chains allowed the reduction without a reducing agent. It was the same procedure of diffusion of metal ions from their salts to the matrix but without adding TSC. The more Au-ions were introduced in the solution, the lighter was the color of the composite. That might be explained by the fact that cellulose has not enough end reducing groups capable to interact with all Au ions.



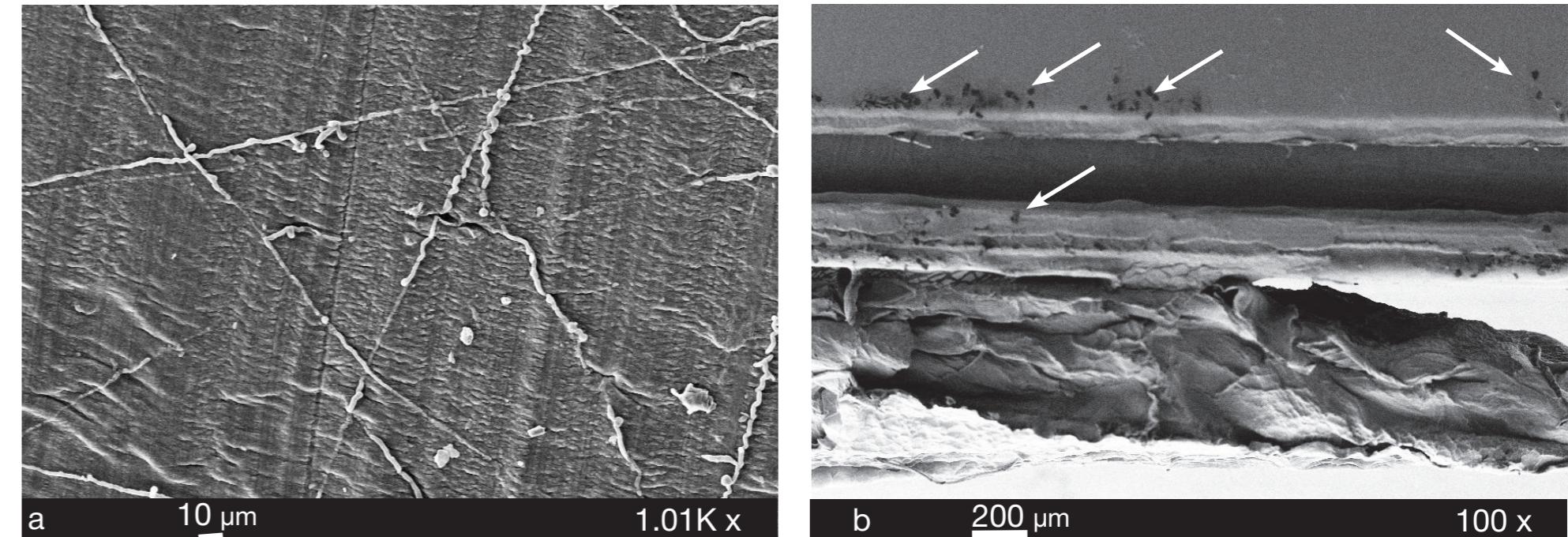
The composites HG/Au obtained with TSC were colored in purple and the color became darker when aspect ratio cellulose/Au was lower, which means that the amount of Au-ions in the solution was the biggest in the row. HG/Ag were colored from light-yellow to dark brown. Obviously, the color of samples depended directly on the aspect ratio of cellulose to metal. The composites HG/Ag and HG/Au contained the low amount of metals(0): up to 0.9 wt. % of Ag and up to 1.5 wt.% of Au.

The composites containing Ag and Au exhibited the antibacterial properties against gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*) bacteria (Table 1).

Table 1. Antibacterial properties of the composites HG/Ag

C_{Ag}^{\prime} wt %	The diameter of the growth inhibition zone	
	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>
0.3	12.0 \pm 0.7	11.0 \pm 0.6
0.4	13.0 \pm 0.8	11.0 \pm 0.7

RESULTS



Pic. 4. SEM images of HG/Au, AR Cell/Au = 6

The NPs of both metals intercalated to cellulose samples had various shapes (spherical or rectangular) and different sizes (pic. 4). The gold NPs mostly ranged 40-120 nm, some of them formed huge agglomerates with sizes of dozen μm . A high concentration of TSC more rapidly stabilized AuNPs of smaller sizes, whereas a low concentration of TSC led to large-size AuNPs and even to the aggregation of them. Since we used rather low concentrations, the sizes of particles were comparatively big. The size of the silver NPs varied between 20-260 nm. The size distribution of the gold NPs was more uniform than that one of the silver NPs.

X-ray diffraction analysis of PC and HG revealed the structure of cellulose modification I and II, respectively. In the case of the embedding of Ag NPs to the HG matrix, the structure of cellulose II did not change. However, it slightly changed due to intercalation of Au NPs. The presence of silver moderately affected the crystallinity of the composites (Table 2). With the increase in the content of silver in the HG, the crystallinity of the composite also slightly increased and there was no noticeable change in the crystallite size.

Table 2. X-ray parameters of the composites

Sample	Maximum content of Ag, wt. %	Crystallinity (Amorphous fitting method), %	Transverse sizes of cellulose crystallites, nm
1	0	-	-
2	0.25	30.6	1.13
3	0.37	33.8	1.21

CONCLUSIONS

Cellulose was used as the depot for metal nanorarticles. The hybrid nanocomposites of cellulose hydrogels contained gold or silver nanoparticles were obtained via diffusion-reduction method. Composites HG/Au and HG/Ag contained low amount of metals and demonstrated antimicrobial properties.

References

Zhao P. et al / Coord. Chem. Rev. 2013, 257, 638-665