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Novel Approaches to Metallization of Cellulose by Reduction of Cellulose-Incorporated Copper and Nickel Ions

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Summary: Copper and nickel nanoparticles were synthesized in the insoluble microcrystalline cellulose support by reduction of metal ions with several reducers in various media resulting in cellulose-metal nanocomposites. Wide-angle X-ray scattering results showed that supramolecular structure of cellulose did not change. Crystalline Cu_2O and Cu^o nanoparticles were prepared with reducers $NaBH_4$ and $N_2H_4 \cdot H_2SO_4$, CuO nanoparticles – with cellulose itself as a reducer. Crystalline Ni^o nanoparticles were synthesized with $N_2H_4 \cdot 2HCl$ and $NaBH_4$; Ni^o nanoparticles in amorphous form were prepared with $KH_2PO_2 \cdot H_2O$. SEM revealed large agglomerates of metal particles on the fibre surface. ASAXS and TEM have shown the nanoparticles to be in the range 5–55 nm.

Keywords: cellulose; copper; nanoparticles; nickel; reducers

Introduction

Polymer nanocomposites which consist of metal nanophase dispersed in a polymer support are one of the major application areas for nanoscale technology in the last decades. This is due to their novel material properties, which differ from both the isolated atoms and the bulk phase. Interest to the properties of the above objects has required the need for the control of the particle dispersity, their size, the shape and organization on the surface and in the bulk of the polymeric template.

A huge number of physical and chemical methods for the preparation of nanomaterials has been developed. In recent years chemical reduction of metals in a polymer matrix has been widely used. In our previous studies the synthesis of silver, platinum, palladium, copper and nickel nanoparticles has been performed in the presence of a support matrix of native cellulose which played a role of a nanoreactor.[1–4] The synthesis to prepare cellulose-metal nanocomposites has been carried out by different routes via interaction of metal ions with several reducers and in various media in the insoluble cellulose template. The preparation of metal nanoparticles, control of their size, shape and oxidation state has been performed in order to study how the formation of metal or metal oxide nanoparticles, the crystallization and their average size are affected by a reducer and by experimental parameters.

In this paper the main results on the chemical aspects of a metallization of cellulose by chemical reduction of copper and nickel ions taken as examples are considered. To show specific features of the metal nanoparticle incorporation into cellulose support and to study the structure of cellulose-metal nanocomposites WAXS, ASAXS, XANES, XPS, SEM and TEM were applied.

Experimental Part

Microcrystalline cellulose (MCC) was used as a porous template for copper and nickel particles. The properties of MCC have been described elsewhere.[1] The DP_v of MCC

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was 170. The pore volume, the pore radius and the specific area were 2.16 cm^3/g, 20 μm, and 230 m^2/g, respectively.

Synthetic procedure included diffusion of Cu^{2+} and Ni^{2+} ions (from solutions of their salts $CuSO_4$ or $Cu(CH_3COO)_2$ and $NiSO_4 \cdot 7H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$) into the cellulose matrix and their reduction with reducers sodium boron hydride ($NaBH_4$), hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$) or hydrazine dihydrochloride ($N_2H_4 \cdot 2HCl$) and potassium hypophosphite ($KH_2PO_2 \cdot H_2O$) in various media. The media included H_2O or ammonium hydrate ($NH_3 \cdot H_2O$); sometimes glycerol was added.[1,2]

A synthetic route to prepare MCC-metal composites depended on the reducer and on the media. Cellulose itself can reduce Cu^{2+} to Cu^{1+} in $NH_3 \cdot H_2O$ medium due to the end aldehyde groups in cellulose chains:

$$\begin{aligned} &R - C = O + [C(NH_3)_4](OH)_2 \rightarrow \\ &\qquad R - COOH + Cu_2O + NH_3 + H_2O, \end{aligned}$$

where R is cellulose.

When $NaBH_4$ and $N_2H_4 \cdot H_2SO_4$ were used Cu^{2+} ions can be reduced to Cu^{1+} or to metallic copper Cu^0:

$$\begin{aligned} &Cu^{2+} + BH_4^- + H_2O \rightarrow Cu^0 \\ &\qquad \text{and/or } Cu_2O + B_2O_3 + H_2 \end{aligned}$$

$$\begin{aligned} &Cu^{2+} + N_2H_4 + OH^- \rightarrow Cu^0 \\ &\qquad \text{and/or } Cu_2O + NH_3 + N_2 \uparrow + H_2O \end{aligned}$$

When $NaBH_4$, $KH_2PO_2 \cdot H_2O$ and $N_2H_4 \cdot 2HCl$ were used Ni^{2+} ions can be reduced to metallic nickel Ni^0. In both cases copper oxide(II) CuO and nickel oxide NiO can also be obtained due to the high capacity of Cu^{1+} and Ni^0 to oxidation:

$$\begin{aligned} &Ni^{2+} + BH_4^- + H_2O \rightarrow Ni^0 \text{ and/or} \\ &\qquad NiO + B(OH)_4 + H_2O \end{aligned}$$

$$\begin{aligned} &Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni^0 \text{ and/or} \\ &\qquad NiO + H_2PO_3^- + H_2 \uparrow + 2H^+ \end{aligned}$$

$$\begin{aligned} &Ni^{2+} + H_2PO_2^- + OH^- \rightarrow Ni^0 \text{ and/or} \\ &\qquad\qquad NiO + H_2PO_3^- + H_2 \uparrow \end{aligned}$$

$$\begin{aligned} &Ni^{2+} + N_2H_4 + OH^- \rightarrow Ni^0 \text{ and/or} \\ &\qquad NiO + N_2 \uparrow + H_2O \end{aligned}$$

As a result MCC-metal composites with various metal contents were prepared (below MCC-Cu and MCC-Ni samples).

Elemental analysis of the resulting compounds was carried with a Hewlett-Packard C,H,N-analyser.

Wide-angle X-ray scattering (WAXS) measurements were applied to determine the degree of order in the matrix, the crystal structure of the metal particles, and the size of crystallites in the matrix and in the particles. The average size of the crystallites was determined using the Scherrer formula.[5]

Anomalous small-angle X-ray scattering (ASAXS) and X-ray absorption spectroscopy near edge structure (XANES) measurements were applied to make structural studies for 1–100 nm length scale and to characterize the shape and size of homogeneous metal particles and the particle size distribution. These measurements have been carried out at the experimental station JUSIFA B1 at Hamburg Synchrotron Radiation Laboratory (HASYLAB) in Germany.[4]

X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5400 spectrometer to make the surface analysis and to evaluate the degree of metal oxidation on the surface of cellulose fibres. The spectra were calibrated by the C 1s line of hydrocarbon components with $E_{bond} = 285.0$ eV.[1,2]

Scanning (SEM) and transmission (TEM) electron microscopy methods were used to study the surface morphology, the shape and the particle size distribution in the micrometer range on the surface (SEM) and in a nanoscale in the bulk (TEM) of the MCC fibrils. SEM study was performed with a Jeol JCM-35 CF instrument.[1,2] TEM study was made with a ZEISS EM 10C electron microscope.[1]

Results and Discussion

Experimental conditions, namely the type and the concentration of the reducer, the reaction medium as well as the temperature of ions diffusion into the matrix and that of

Table 1.
Metal content in the bulk of MCC-metal nanocomposites (elemental analysis), on the surface (XPS) and crystallite sizes of metal nanoparticles.

Reducer or medium	Metal content in the bulk (max.), w.%		Metal content on the surface (max), w.%		XANES and WAXS results			
					crystalline metal forms		crystallite size, nm	
	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
$NH_3 \cdot H_2O$	13.0	–	23.1	–	CuO	–	5.6—19.8	–
$NaBH_4$	4.2	11.1	17.9	23.4	Cu_2O	Ni^0 NiO	7.4—55	5–35
$N_2H_4 \cdot H_2SO_4$	8.0	—	26.1	—	Cu^0&Cu_2O	–	12.3—53.5 4.7 to 53	–
$N_2H_4 \cdot 2HCl$	–	10.0	–	31.5	–	Ni^0	–	10.8–13.5
$KH_2PO_2 \cdot H_2O$	–	12.8	–	5.8	–	$Ni^{0*)}$	–	5–40

$^{*)}$$Ni^0$ in amorphous form.

their reduction strongly affect the metal content in the MCC-metal composites. The maximum copper content in the MCC-Cu samples was 13.0 w.% ($NH_3 \cdot H_2O$ medium, reducer cellulose itself) and the maximum nickel content in the MCC-Ni samples was 12.8 w.% ($NH_3 \cdot H_2O$ medium, reducer $KH_2PO_2 \cdot H_2O$) (Table 1).

WAXS, ASAXS, XANES and XPS Results

According to WAXS results the chemical processing of nanoparticle formation in the MCC template did not decrease crystallinity of MCC and did not affect the crystalline arrangement of the matrix. Thus, the size of cellulose I crystallites (the thickness of MCC crystallites at the 200 direction) was estimated to be 7.2 ± 0.1 nm and was the same in MCC-metal samples as in the pristine MCC sample (Figure 1(a)).

The formation of copper nanoparticles is extremely sensitive to reaction conditions. X-ray intensity curves of MCC-Cu samples prepared with various reducers contain reflections of crystalline Cu^0, Cu_2O or CuO (Figure 1(a)).[3] Synthesis in $NH_3 \cdot H_2O$ medium (with cellulose itself as a reducer) yielded crystalline CuO. The average size of crystallites depended on the reducer and on the experimental procedure was determined from the reflections 111 of Cu^0, Cu_2O or CuO (Table 1). The CuO nanoparticle size differed from 5.6 nm to 19.8 nm. Reduction with $NaBH_4$ yielded mainly crystalline Cu_2O, the nanoparticle size of which differed from 7.4 to 55 nm. Reduction with $N_2H_4 \cdot H_2SO_4$ yielded both crystalline Cu_2O and Cu^0. The size of Cu_2O nanoparticles ranged from 4.7 to 53 nm and that of Cu^0 nanoparticles ranged from 12.3 to 53.5 nm.

The formation of nickel crystalline phases and the size of nickel crystallites in MCC-Ni samples also strongly depended on the reducer and on the reducer concentration. Intensive reflections of Ni^0 (Figure 1(b)) and NiO appeared in X-ray diffraction patterns of the samples prepared with the reducer $N_2H_4 \cdot 2HCl$. The ratio of those crystalline phases mostly depended on the reducer concentration. The higher the concentration of $N_2H_4 \cdot 2HCl$, the higher the amount of Ni^0 in the samples. The average size of Ni^0 crystallites determined from the reflection 111 of Ni^0 was 10.8–13.5 nm.

The diffraction patterns of the MCC-Ni samples prepared with reducers $KH_2PO_2 \cdot H_2O$ and $NaBH_4$ showed reflections from cellulose as well as a broad and weak diffraction maximum at $q = 3.09$ Å^{-1} (Figure 1(c)). The maximum could be either the reflection 111 of face-centred cubic Ni^0, the reflection 011 of hexagonal closed-packed Ni^0 or of amorphous Ni^0. The positions of those reflections were the same and it was not possible to conclude which crystalline phase dominated in the nanoparticles.[4]

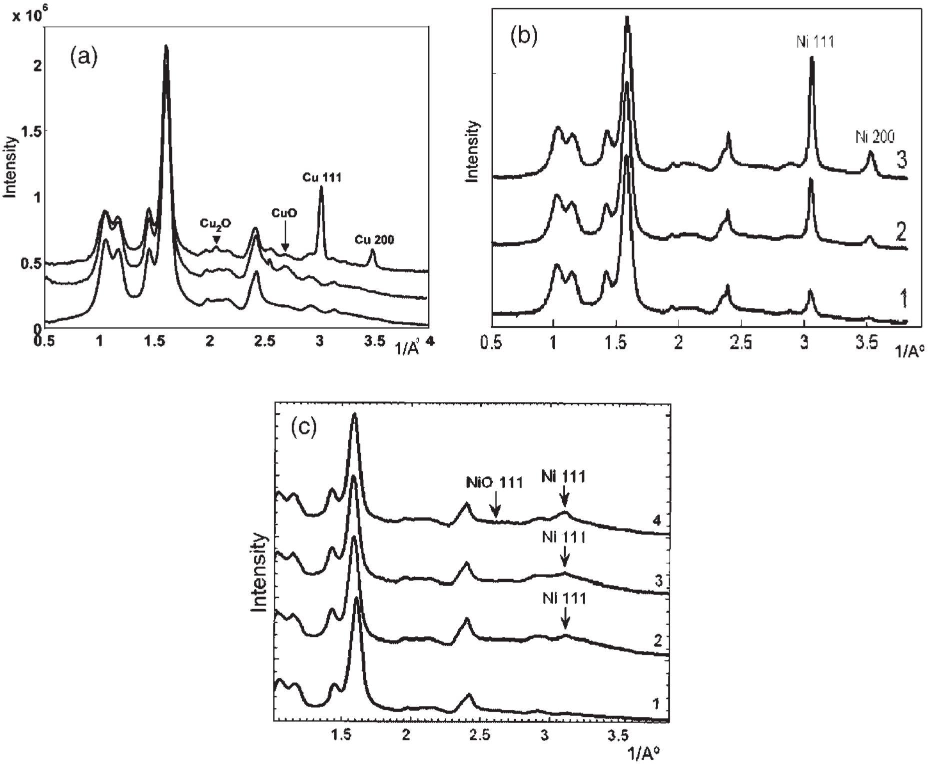

Figure 1.

(a–c). X-ray intensity curves of MCC-Cu (a) and MCC-Ni (b and c) samples: a) initial MCC sample (1) and MCC-Cu samples [reducers MCC (2) and $N_2H_4 \cdot H_2SO_4$ (3)]; b) MCC-Ni samples with Ni content 6.9 w. % (1), 7.4 w.% (2) and 10.0 w.% (3) (reducer $N_2H_4 \cdot 2HCl$); c) MCC-Ni samples with Ni content 8.8 w. % (1) (reducer $NaBH_4$) and 8.8 w. % (2), 10.2 w. % (3), 12.8 w.% (4) (reducer $KH_2PO_2 \cdot H_2O$).

The oxidation state of Ni^0 was determined from XANES results. The X-ray absorption measurements showed that the Ni K_{edge} was at the same position for the samples MCC-Ni as for the Ni-foil (Figure 2). XANES spectrum of the samples prepared with $NaBH_4$ exhibited features indicating that nickel was as in the form of Ni^0 and in the form of NiO.[6] The spectrum of the sample prepared with $K_2HPO_2 \cdot H_2O$ had smoother features indicating that Ni^0 was in weakly ordered nanoparticles. The size of Ni^0 nanoparticles determined by ASAXS ranged from 5 to 40 nm.

Thus, the results obtained with WAXS indicated that the crystalline arrangement of the MCC template did not change during the formation of nanoparticles, i.e. the nanoparticles were anchored on the surface or in the amorphous parts of the cellulose microfibrils. The same phenomenon was already observed on cellulose–

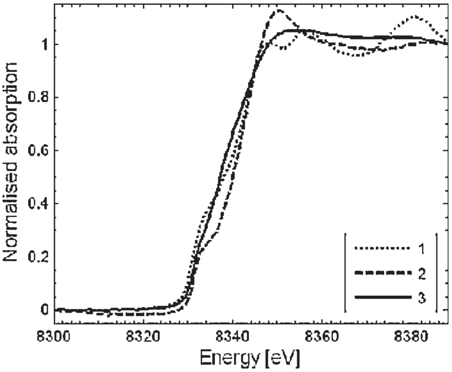

Figure 2.

The normalized XANES spectra of a Ni foil (1) and of the samples MCC-Ni prepared with $NaBH_4$ (2) and with $KH_2PO_2 \cdot H_2O$ (3).

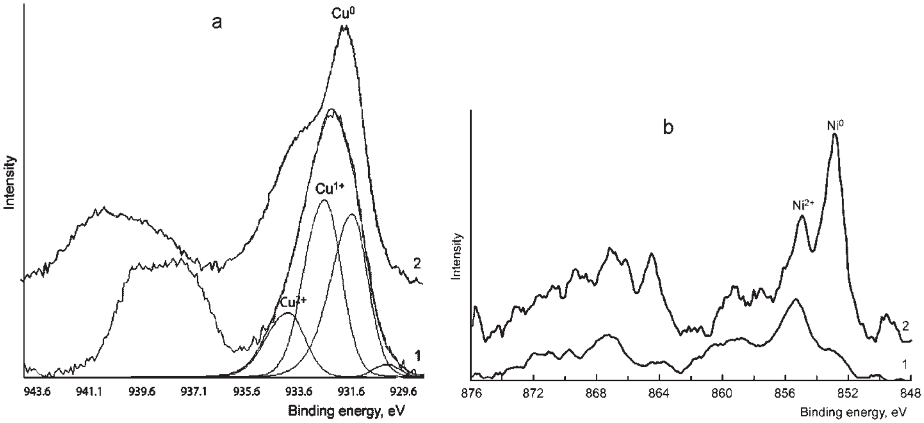

Figure 3.
XPS spectra of the Cu $2p_{3/2}$ (a) and Ni $2p_{3/2}$ (b) lines. a) MCC-Cu samples [reducers $NaBH_4$ (1) and $N_2H_4 \cdot H_2SO_4$ (2)]; b) MCC-Ni samples [reducers $NaBH_4$ (1) and $KH_2PO_2 \cdot H_2O$ (2)].

metal nanocomposites in our previous studies.[2–4] This means that cellulose played a role as a nanoreactor for the nanoparticles of copper and nickel.

X-ray Photoelectron Spectroscopy

XPS results showed that the metal content on the fibre surface in the MCC-metal samples was much higher than that in the bulk (Table 1). The only exception showed MCC-Ni samples prepared with $KH_2PO_2 \cdot H_2O$. In the XPS spectra of MCC-Cu and MCC-Ni samples prepared with $NaBH_4$ Cu^{1+} (in Cu_2O) and Ni^{2+} (in NiO) prevailed, respectively. In the samples prepared with $N_2H_4 \cdot H_2SO_4$ Cu^0 and Ni^0 were mainly distributed on the surface (Figure 3). A good coincidence of those results with the determination of crystalline phase of metals in the bulk made with WAXS and XANES could be seen from the data listed in Table 1. These data also showed that metals on the surface are only slightly subjected to an additional oxidation. Thus, MCC matrix protected metal nanoparticles from oxidation not only in the bulk but also on the fibre surface.

Scanning and Transmission Electron Microscopy

SEM micrographs of MCC-Cu and MCC-Ni samples showed their μm-scale structure. The globular spheres mainly aggregated into larger agglomerates on the fibre surface of the samples (Figure 4(a) and (b)). TEM micrographs visualized a shape and a particle size distribution in the bulk (Figure 4(c)). The size of nanoparticles in the bulk was much smaller than that on the surface. Thus, the average size of Cu0 particles on the surface was 500–600 nm (Figure 4(a) and (d)), Ni0 particles ranged 120–380 nm (Figure 4(b) and (e)). However, the average size of Cu0 nanoparticles in the bulk was 5–25 nm as followed from the histogram (Figure 4(f)) and that of Ni0 nanoparticles[4] was 5–40 nm. In the bulk and on the surface smaller particles clustered together to form larger particles. The pores in the fibrous cellulose assisted separate growth of particles inside the fibres so that the particles were not as aggregated as on the surface of the fibres as could be seen by SEM.

Conclusion

Synthetic procedures have been successfully developed to include copper and nickel nanoparticles of different size and shape into the MCC template. As a result, MCC-metal nanocomposites have been prepared. The content of copper and nickel

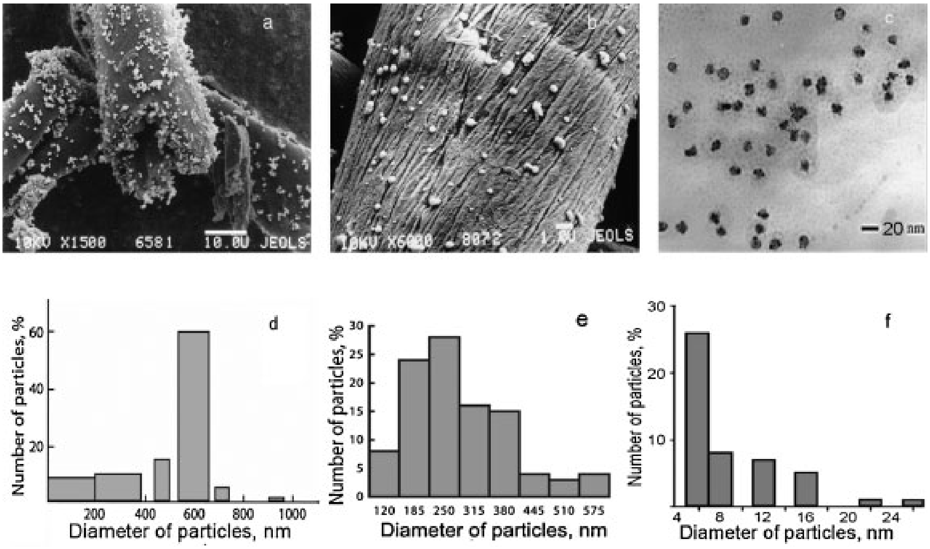

Figure 4.
(a–f). SEM images of Cu and Ni particles on the fibre surface of MCC-Cu samples (reducer $N_2H_4 \cdot H_2SO_4$) (a) and MCC-Ni (reducer KH_2PO_2) (b) and their histograms (d and e correspondingly). TEM image (c) and histogram (f) of Cu nanoparticles in the bulk of the sample MCC-Cu.

in the nanocomposites strongly depended on the experimental procedure, especially, on the reaction medium and the reducer type.

According to WAXS results MCC did not exhibit any changes in the supramolecular structure, i.e. played the role as a nanoreactor. Crystalline CuO, Cu_2O and Cu^0 nanoparticles were prepared with reducers cellulose itself, $NaBH_4$ and $N_2H_4 \cdot H_2SO_4$, correspondingly. Crystalline Ni^0 and NiO nanoparticles were synthesized with $N_2H_4 \cdot 2HCl$ and $NaBH_4$, Ni^0 nanoparticles in amorphous form were prepared with $KH_2PO_2 \cdot H_2O$.

SEM revealed the agglomerates of the metal particles on the fibre surface. ASAXS and TEM have shown the nanoparticles to be in the range 5–55 nm. MCC matrix protected metal nanoparticles from oxidation not only in the bulk but also on the fibre surface as could be seen by XPS. Nanoparticles were found to be relatively stable.

The variations in experimental conditions provided the opportunity to prepare metal nanoparticles with the wide range of oxidation degree, of size and shape and to control their surface properties, stability, and reactivity. This allowed adjusting the properties of the resulting nanocomposites.

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