

IMPLICATION OF NANOMETALS FORMATION IN POTATO STARCH GEL ON STRUCTURE OF POLYSACCHARIDE CHAINS

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Introduction

Research on polymer-metal nanoparticle composites received much attention in recent years owing to their application in opto-electronics, nonlinear optical devices and colour filters. Metal nanoparticles are usually prepared by reduction of metal ions in solution. Meanwhile, because of the troublesome aggregation of nanoparticles induced by their high surface energy, surface passivating reagents and capping reagents are usually involved in the reaction system. From the view of green chemistry, all the reagents including reducing reagent, reaction medium and capping reagent should be environmental benign [2], [3].

In this work, we report an environmentally benign „green,, method for the preparation of Au and Ag nanoparticles in starch matrix. Synthesis of nanopowders of selected metals in potato starch gel matrix was performed using mild reducing conditions. Gels were dried on flat surface to obtain foils containing nanometal structures.

Starch biocomposites containing metal nanocrystals were characterized by means of IR and UV spectra together with TEM/SEM photographs. Energy-Dispersive X-Ray Spectroscopy (EDS) and thermal properties of biocomposites also were measured. The absolute molecular weights, radii of gyration, R_g , and thermodynamic properties of the obtained foils were measured by size exclusion chromatography with dual detection (SEC-MALLS-RI). Size of Ag and Au nanocrystals was in the range 10 nm – 20 nm and was dependent on reaction conditions.

Experimental

Materials Potato starch (5g, National Starch, Kalisz Poland) was added to 95cm³ of distilled water. Resulted suspension was heated at 90 °C degree for 2h with constant stirring. Silver (PS/Ag) and gold (PS/Au) nanocrystals were produced by adding to starch gel either 1cm³ of AgNO₃ solution (0.05 M/dm³) or 0.4cm³ of HAuCl₄ solution (0.03 M/dm³). Reaction mixtures were stirred for 0.5h, then NaBH₄ aqueous solution (1 cm³, 0.05 M/dm³) was slowly added. Mixtures were kept stirring for additional 1 hr, then cooled and applied to a clean, smooth either Teflon or glass surface and left to evaporate in the air. The dry foil was collected and stored in closed container.

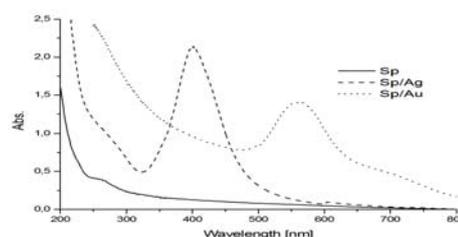
Apparatus and Procedures
The UV-VIS absorption spectra of PS, PS/Ag and

PS/Au nanocomposites were recorded using a Shimadzu 2101 scanning spectrophotometer in the range 200 - 700 nm. Analyses of sizes and morphologies of the as-prepared nanoparticles were studied using a high resolution JEOL 7550 scanning electron microscope equipped with EDS analyzer for local chemical analysis. The differential scanning calorimetry (DSC) experiments were performed in Mettler-Toledo 821e calorimeter equipped with an intracooler Haake in 40μl aluminum crucibles under constant flow of argon (80 ml/min) within temperature range 25-400°C. X-ray powder diffractometry was performed according using X'pert type Phillips diffractometer with a cobalt lamp of $\lambda=1.78896 \text{ \AA}$ (30 mA and 40 kV) and in the scanning region of 2θ from 5 to 60° in 0.02° intervals. Molecular weight M_w and radii of gyration R_g of polysaccharide chains from PS and PS/Ag and PS/Au samples were measured by system consisting of a pump (Shimadzu 10AC, Tokyo, Japan), an injection valve (model 7021, Rheodyne, Palo Alto, CA, USA), two connected size exclusion columns TSKgel GMPWXL (300 × 7.8 mm, Tosoh Corporation, Tokyo, Japan) and TSKgel 2500 PWXL (300 × 7.8 mm, Tosoh Corporation, Tokyo, Japan). A multiangle laser light scattering detector (MALLS) (Dawn-DSP-F, Wyatt Technology, Santa Barbara, CA, USA) and a differential refractive index detector (L-7490, Merck, Darmstadt, Germany) were connected to the columns.

Results and Discussions

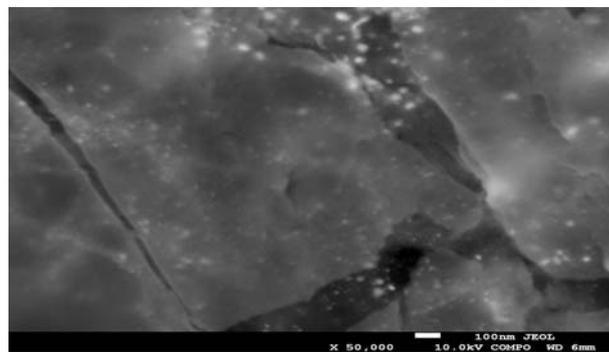
The UV-vis absorption spectra of potato starch and Sp/Ag and Sp/Au nanocomposites are presented Fig.1. Formation of strong absorption band centered at 410nm in the case of Sp/Ag foil and at 580 nm, in the case of Sp/Au foil clearly suggest formation of Ag and Au nanoparticles embedded in starch matrix..

Fig1. UV- Vis absorption spectra of potato starch

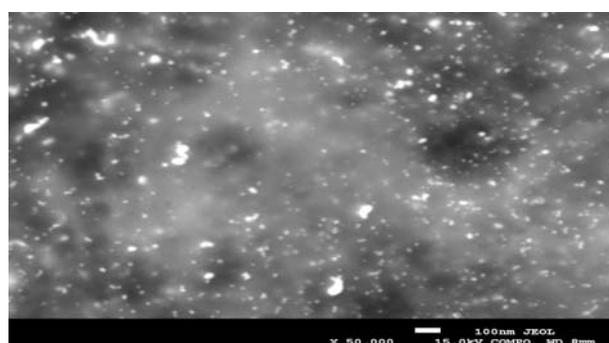


(Sp), silver (Sp/Ag) gold (Sp/Au) nanocomposites.

Typical TEM images of silver (A) and gold (B) nanoparticles embedded in the starch matrix are displayed on Fig.2. Spherical Ag and Au nanocrystals are well separated in starch matrix and particle size distribution ranges between 10 and 20 nm for both silver and gold nanostructures.



A



B

Fig.2 Representative TEM images of Sp/Ag (A) and Sp/Au nanocomposites.

DSC thermograms registered for and Sp/Ag and Sp/Au nanocomposites together with thermogram of Sp are displayed on Fig.3. The shapes of thermograms taken for starch and Sp/Au composite consisting roughly of one endothermic and one exothermic peak are similar to some extent. In both cases exothermic peak centered

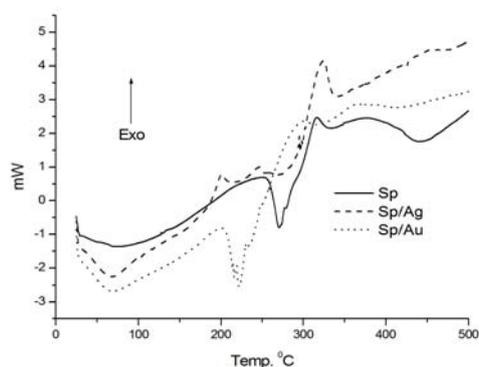


Fig.3. DSC thermograms of potato starch (Sp), starch silver nanocomposite (Sp/Ag) and starch gold nanocomposite (Sp/Au).

at 310 °C for Sp and 320 °C for Sp/Au could be attributed to decomposition of the polymer.

Temperature of endothermic transition for Sp/Au nanocomposite (220 °C) is much lower than temperature of such transition recorded for starch indicating disintegration of polysaccharide matrix during nano gold formation. DSC thermogram patterns observed for Sp/Ag differs greatly from thermograms of starch and starch silver nanocomposite. Two exothermic peaks one at 200 °C and second at 330 °C could be observed indicating that silver nanocrystals formation leads to the more ordered orientation of polysaccharide chains as compared with starch and Sp/Au composite. Thermal properties of starch and starch silver (Sp/Ag) and gold (Sp/Au) nanocomposites are in good agreement with results of molecular weight measurements of polysaccharide chains constituting starch nanometals composites (Table 1). It is clear that formation of nano gold crystals leads to significant fragmentation of polysaccharide chains, whereas crosslinking between chains, mainly from amylopectin fraction, is observed during nano silver structures.

Table 1. Absolute molecular weight of the original starch fractions and their changes after generation of nano Ag (Sp/Ag) and nano Au crystals inside starch gel. (Rg, radius of gyration).

	$M_w \times 10^7$	$M_w \times 10^7$	Rg	Rg
Sample	Fraction I	Fraction II	Fraction I (nm)	Fraction II (nm)
Starch	3.87	3.64	105.8	122
Sp/Ag	4.20	3.18	89.0	101.3
Sp/Au	-	0,48	-	51.9

Conclusions

In our work we have developed a green method to synthesize silver and gold nanoparticles. We shown that starch constitute excellent matrix for gold and silver nanoparticles allowing obtaining nanocrystals uniform in size and shape.

References

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3. Sun C., Qu R., Chen H., Ji C., Wang C., Sun Y., and Wang B., Degradation behavior of chitosan chains in the ‘green’ synthesis of gold nanoparticles. *Carbohydrate Polymers* **343** (2008) 2595 – 2599.