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Synthesis of gold nanoparticles in organogels

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The preparation of nanocomposites based on natural polysaccharides and gold nanoparticles in the thin films of water is described.

Nanocomposites based on natural polysaccharides and metal nanoparticles are successfully used as optical markers,[1–4] antimicrobial preparations[5–7] and magnetic materials[8] in biomedicine, for the removal of heavy metal ions from water[9] and as catalysts in fine organic synthesis.[10] Polysaccharides serve as a matrix for the reliable stabilization of nanoparticles in both liquid and solid phases. In this work, we attempted to enlarge the functional possibilities of polysaccharides using their ability to stabilize organogels containing 98–99% organic phase at the very low concentrations of polysaccharides. We found that the organic phase of the resulting organogels consisted of microspheres several micrometers in size, which were surrounded by thin films of an aqueous phase of sizes from tens to hundreds of nanometers. This causes a significant change in the physicochemical and thermodynamic properties of water as a solvent.[11,12] In our opinion, the presence of thin water films with a structure of this kind can hamper the uncontrollable growth of metal nanoparticles in aqueous solutions due to steric and other factors.

For obtaining thin water films, which possess an extremely high specific surface area, we prepared organogels as continuous three-dimensional structures formed by an aqueous phase and a dispersion medium based on a hydrocarbon (*n*-heptane) (Figure 1). The organogels of different compositions (the volume ratio between aqueous and hydrocarbon phases was varied from 1:1 to 1:10, Figure 2) were prepared by mixing of aqueous solutions containing 1 wt% xanthan polysaccharide, 0.1% Tween-20 and 0.01% of an aqueous 0.01 M solution of $HAuCl_4 \cdot 3H_2O$. After the formation of stable organogel, a calculated amount of an aqueous solution of ascorbic acid as a reducing agent was added to it.

The analysis of the structure of organogel showed that the sizes of water films between the spherical particles of a hydrocarbon phase can be as small as 1 mm in spite of heterogeneity. The structural ordering of water molecules in capillaries and thin films can be responsible for the anomalous behavior of reagents that interact in these media. First of all, the rate of diffusion of reactants can be considerably decreased; this is usually observed under the conditions of heterogeneous catalytic reactions occurring in narrow pores.

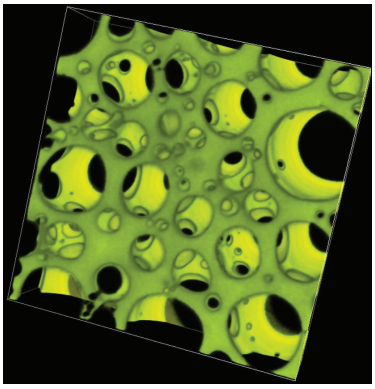

Figure 1 Three-dimensional structure of an aqueous phase obtained by confocal microscopy.

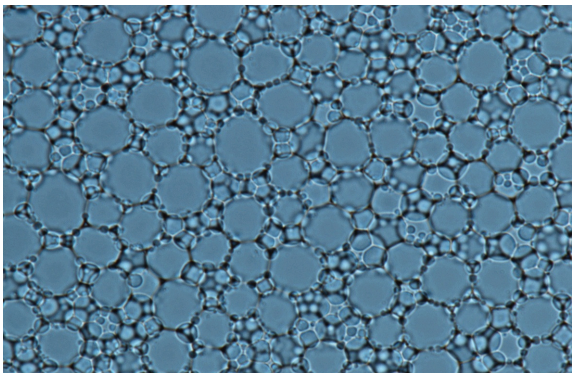

Figure 2 Micrograph of water–heptane organogel (1:10), magnification ×100.

To determine the effect of water film thickness on the rate of chemical reactions, we studied the growth of gold nanoparticles obtained in the organogels with different water–heptane ratios from 1:1 to 1:10.

Table 1 summarizes the results of the synthesis of gold nanoparticles in the organogels with xanthan at different water–heptane ratios. The reaction occurred rapidly at ratios from 1:1 to 1:2, and the reaction times were comparable with synthesis times in a usual aqueous solution. A further increase in this ratio led to an increase in the synthesis duration to 24 h (1:10). In this case, the formation of colloidal solutions colored from dark blue to light pink was observed. This fact suggests the presence of gold nanoparticles of different sizes and shapes in the reaction products.

Figure 3 shows the electron micrographs of gold nanoparticles obtained in the organogels with different aqueous phase–heptane

Table 1 Effect of gel composition on reaction time.

Water–heptane ratio	Reaction time/h	Gel color
1:1	1.1	Dark blue
1:2	1.25	Blue
1:3	1.5	Violet
1:5	15	Pink
1:10	24	Light pink

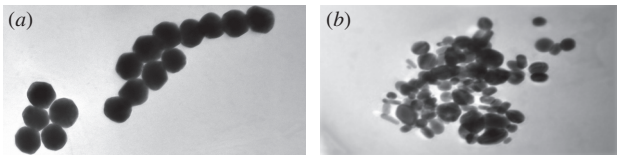

Figure 3 Electron micrographs (magnification factor, ×80 000) of gold nanoparticles obtained in an organogel at water to heptane ratios of (*a*) 1:10 and (*b*) 1:3.

ratios. The gold nanoparticles obtained at high ratios (1:10) were spheres of very similar sizes within the limits of 20–25 nm. At lower ratios (1:5 or lower), the appearance of spheroids with different aspect ratios and a significant spread of particle sizes (from 5 to 40 nm) were observed.

Thus, we found that, in principle, gold nanoparticles with a narrow particle size distribution can be prepared in the organogels based on the aqueous solutions of the natural polysaccharide xanthan, a surfactant and *n*-heptane at water–heptane volume ratios from 1:1 to 1:10. The structure of the obtained gels was studied by confocal laser microscopy. The established dependence of the shape and size of nanoparticles on the film thickness of an aqueous phase and the stability of the complexes of polysaccharides with gold nanoparticles make it possible to consider the process of the synthesis of gold nanoparticles in organogels as a promising trend in the synthesis of nanoprobes.

The results obtained allow one to consider bionanocomposites obtained in the organogels as promising nanomarkers for biomedical purposes.

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