PATTERNS OF THE *IN SITU* FORMATION OF NANOCOMPOSITES FROM POLYMER/INORGANIC HYBRIDS AND NICKEL NANOPARTICLES: THE ROLE OF THE MATRIX STRUCTURE AND THE CONCENTRATION OF COMPONENTS

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Polymer/inorganic hybrids consisting of a silica sol and polyacrylamide (SiO_2-*g*-PAAm) with different numbers and lengths of grafted chains have been synthesized and characterized. Their main molecular and structural parameters were determined using elemental analysis, DTGA, static light scattering, viscometry, potentiometric titration, and TEM. The functional properties of hybrids as hydrophilic matrices in the *in situ* synthesis of nickel nanoparticles (NiNPs) were controlled by UV-Vis spectroscopy and the original approach developed [1]. The kinetic features and efficiency of the formation of NiNPs in hybrid solutions have been established depending on the structure and concentration of the hybrid matrices and the concentration of Ni-salt.

Parameters of silica/polyacrylamide hybrids

Hybrid	r_{avSiO2} [1] nm	M_{vPAAm} [2] kDa	N [3]	d_{avHyb} [4] nm	h_{avPAAm} [5] nm	σ_{lim} [6] mol/kg	$[\eta]$ [7] m^3/kg	k [8]
SiO_2-*g*-PAAm1	7.7	822	72	21.0±4.7	2.8	1.10	0.39	0.11
SiO_2-*g*-PAAm2		1513	8	21.6±2.8	3.1	1.86	-	-
SiO_2-*g*-PAAm3		5084	5	30.1±9.0	7.3	2.29	0.89	0.25

[1] Average radius of silica sol nanoparticles (static light scattering).
[2] Average viscosity molecular weight of grafted chains (viscometry).
[3] Average number of PAAm grafts per SiO_2 particle.
[4] Average diameter of individual hybrid nanoparticles (TEM and ImageJ).
[5] Average thickness (height) of the "corona" of PAAm: $h_{avPAAm} = d_{avHyb}/2 - r_{avSiO2}$.
[6] The limit value of the amount of absorption of hydroxyl ions (potentiometric titration).
[7] Intrinsic viscosity of solutions (viscometry).
[8] Viscometric Huggins constant.

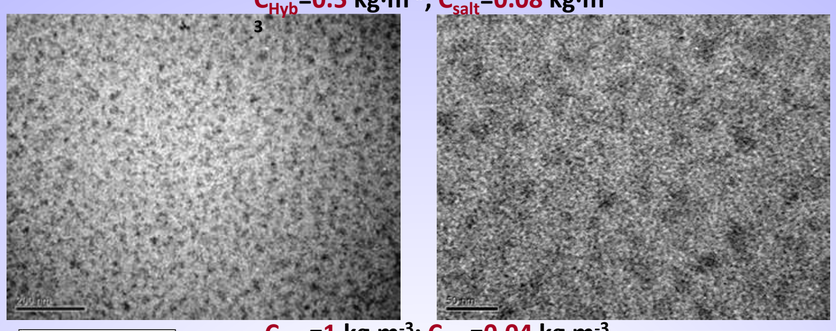
Determination of the kinetics and yield of NiNPs

The method is based on the phenomenon of light scattering on the resulting metal nanoparticles < 30 nm in size, which is determined by the turbidity (τ) of the reaction mixture at λ=500 nm (at which there are no absorption bands). Under these conditions, τ depends on the size (a) and the number (N) of the resulting nanoparticles [1]:

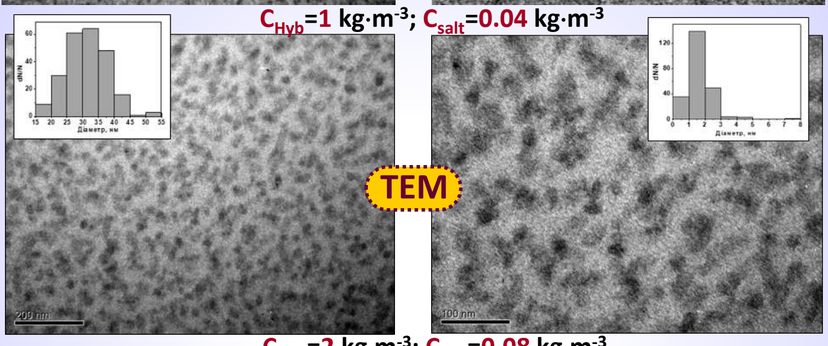
$$\tau = -\frac{1}{l}\ln\left(\frac{I_\tau}{I_0}\right) = 2.303\frac{D}{l} = \left(\frac{N}{V}\right)\frac{128\cdot\pi^5\cdot a^6}{3\cdot\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)$$

Morphology and size of nanocomposites

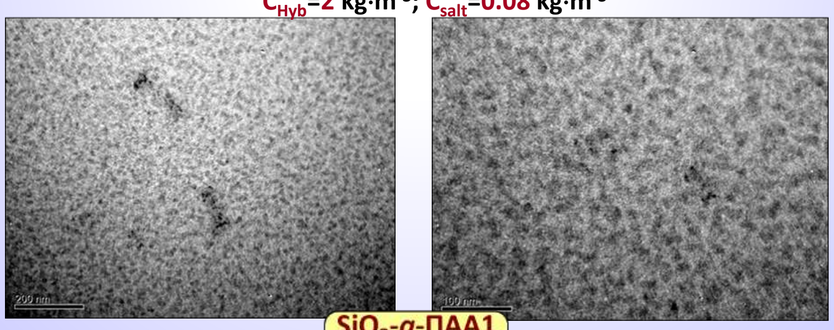
C_{Hyb}=0.5 kg·m^{-3}; C_{salt}=0.08 kg·m^{-}



C_{Hyb}=1 kg·m^{-3}; C_{salt}=0.04 kg·m^{-3}



C_{Hyb}=2 kg·m^{-3}; C_{salt}=0.08 kg·m^{-3}

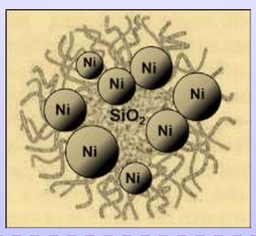


SiO_2-*g*-ПАА1

$d_{av(NiNPs/Hyb)}$=31±6 nm

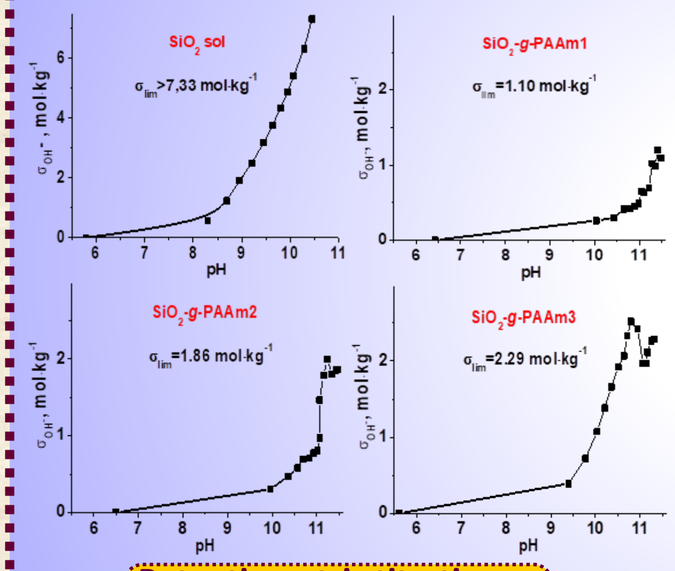
$d_{avNiNPs}$=1.7±0.8 nm

Schematic structure of nanocomposite



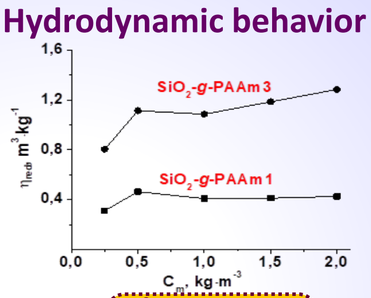
Properties of SiO_2-*g*-PAAm with different number amd length of grafts

Surface charge of SiO_2 nanoparticles



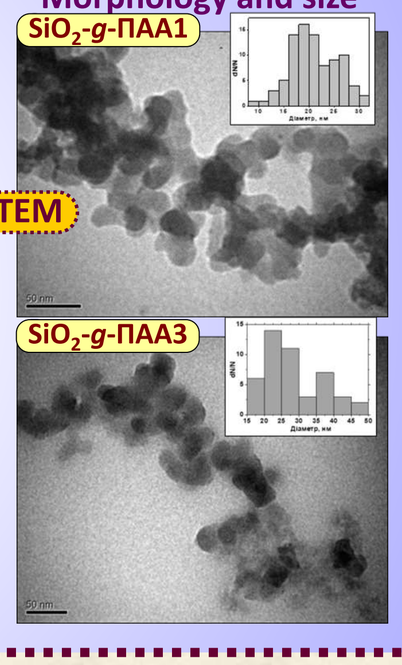
Potentiometric titration

Hydrodynamic behavior



Viscometry

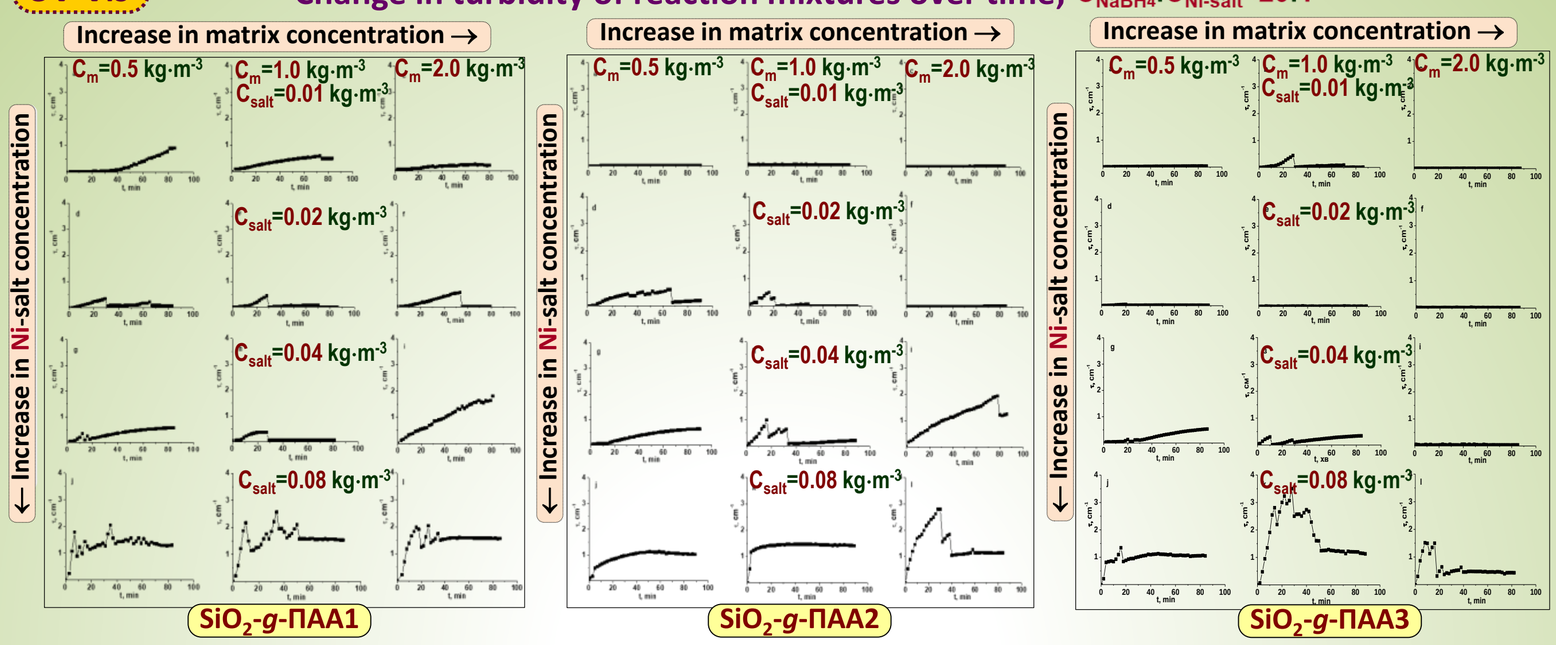
Morphology and size



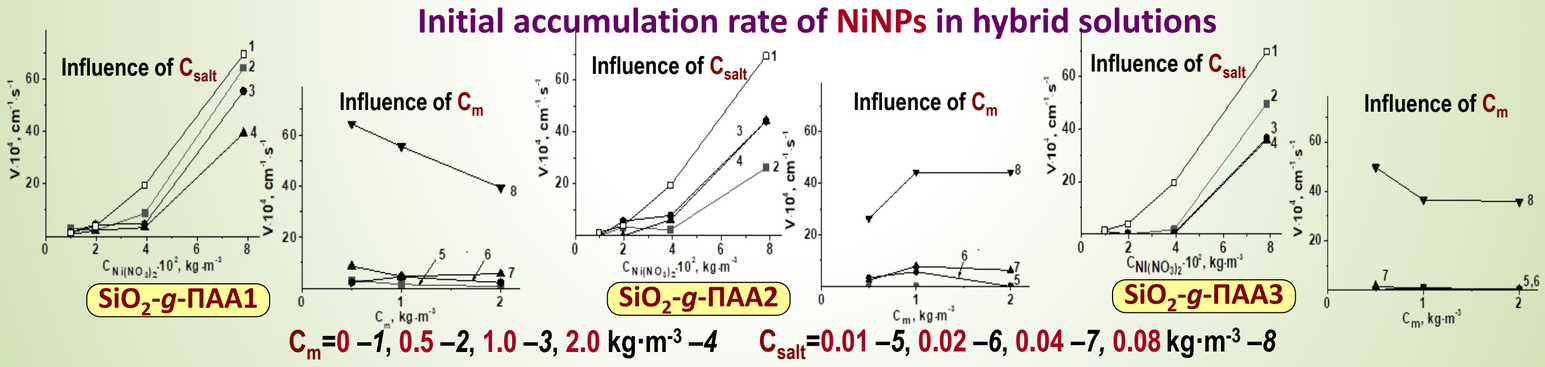
Kinetics and efficiency of NiNP formation in hybrid solutions

UV-Vis

Change in turbidity of reaction mixtures over time; C_{NaBH4}:$C_{Ni\text{-}salt}$=20:1



Initial accumulation rate of NiNPs in hybrid solutions



C_m=0 –*1*, 0.5 –*2*, 1.0 –*3*, 2.0 kg·m^{-3} –*4* C_{salt}=0.01 –*5*, 0.02 –*6*, 0.04 –*7*, 0.08 kg·m^{-3} –*8*

"Yield" of NiNPs in hybrid solutions

Hybrid	$C_{Ni(NO3)2}$ kg·m^{-3}	τ_{80}, cm^{-1} [1] at C_m, kg·m^{-3} 0.5	1.0	2.0
SiO_2-*g*-ПАА1	0.04	0.57	—	1.64
	0.08	1.30	1.57	1.57
SiO_2-*g*-ПАА2	0.04	0.62	—	1.57
	0.08	1.05	1.43	1.13
SiO_2-*g*-ПАА3	0.04	0.51	0.33	0.04
	0.08	1.05	1.20	0.43

[1] Turbidity of reaction mixture in 80 min after $NaBH_4$ addition

Conclusions:

A series of polymer/inorganic hybrids based on silica sol and polyacrylamide (SiO_2-*g*-PAAm) with different number and length of PAAm chains was obtained by radical graft polymerization of AAm from the surface of SiO_2. The main molecular and structural parameters of the hybrids, such as the chemical composition, average radius and charge of SiO_2 particles, the number of grafts per one particle and their molecular weight, the average diameter and hydrodynamic volume of hybrid particles, and the thickness of the PAAm layer, were determined. For this, elemental analysis, DTGA, static light scattering, viscometry, potentiometric titration, and TEM were used.

The functional properties of hybrids as hydrophilic matrices in the *in situ* synthesis of NiNPs by borohydride reduction of metal ions from the *$Ni(NO_3)_2 \cdot 6H_20$* salt in an aqueous medium have been studied. Using the method of UV-Vis spectroscopy and the developed original approach, the kinetics and the yield of NiNPs in hybrid solutions were characterized, depending on the structure and concentration of hybrid matrices and the concentration of the metal salt.

An increase in the rate of accumulation and yield of NiNPs in solutions of all hybrids was found with an increase in salt concentration in the range of 0.010-0.078 kg·m^{-3}, as well as a predominant decrease in the reaction rate with an increase in the concentration of hybrid matrices from 0.5 to 2.0 kg·m^{-3}. It was shown that the structure of the hybrid matrices, determined by the number and length of PAAm chains, as well as the permeability of the grafted polymer layer, was one of the key factors affecting the formation rate and yield of NiNPs. It provided greater or lesser accessibility of the active groups of the "corona" and the inorganic "core" for metal ions and reducing agent molecules.

Morphological studies of purified reduction products were carried out by TEM. Based on them, the main structural elements of highly dispersed NiNPs / SiO_2-*g*-PAAm nanocomposites were established – swollen "hairy" particles of hybrids with small amorphous NiNPs (1.7±0.8 nm) included in the polymer "corona".

[1] T.B. Zheltonozhskaya, N.M. Permyakova, A.S. Fomenko, D.O. Klymchuk, V.V. Klepko, L.N. Grishchenko, L.O. Vretik. The process of nickel nanoparticle formation in hydrophilic polymer/inorganic matrices. Mol. Cryst. Liq. Cryst. 2021, *716* (1), 13-28. https://doi.org/10.1080/15421406.2020.1859692.