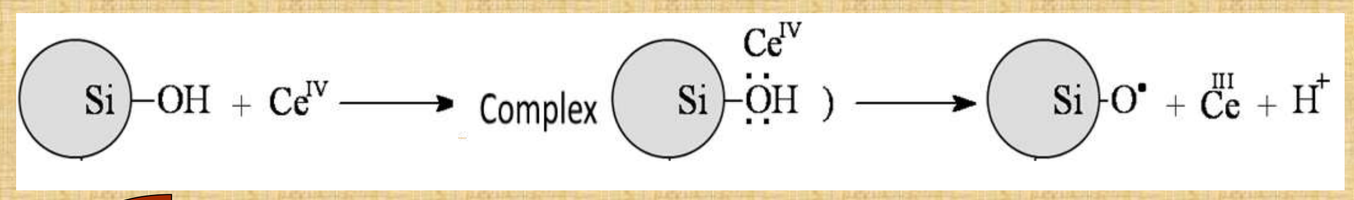
Effect of the structure of silica/polyacrylamide hybrids on cobalt nanoparticles formation

N. Permyakova, A. Fomenko, T. Zheltonozhskaya, D. Klymchuk , V. Klepko

In recent years, cobalt nananoparticles (CoNPs) have attracted considerable attention due to their outstanding magnetic properties as ferromagnetic materials, which use in high-density magnetic storage media, gene deliver and as targeted drug carrier. This paper presents a simple and effective method for producing stable CoNPs in an aqueous medium using polymer/inorganic hybrid (PIH) based on silica nanoparticles and grafted polyacrylamide chains

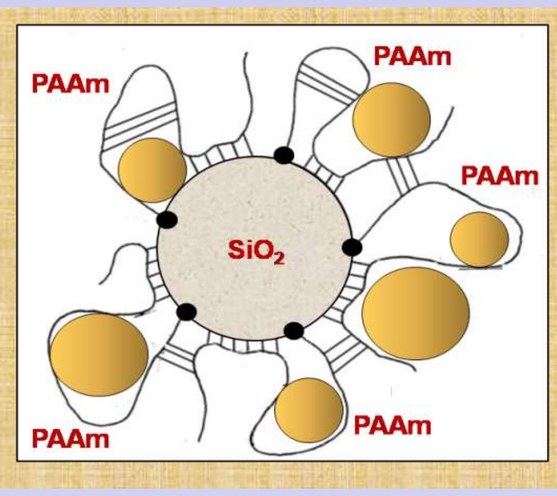
Institute of Macromolecular Chemistry, NAS of Ukraine
Kyiv Taras Shevchenko National University, Ukraine
Institute of Botany, NA S of Ukraine,
E-mail:permyakova@ukr.net

Synthesis of PIH



PIH sample was synthesized by a free-radical grafting polymerization of acrylamide (AAm) "from" the surface of silica hydrosol

Schematic structure of the CoNPs/PIH composition



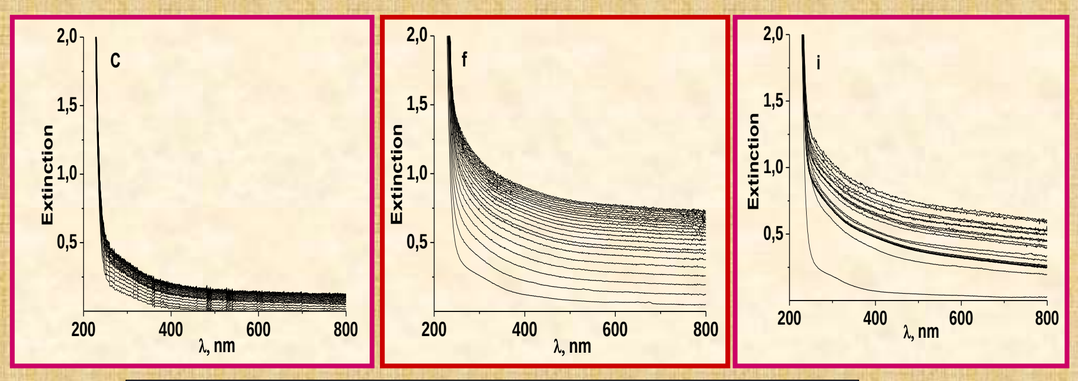
Main characteristics of one from HIP samples found by elemental analysis, DTGA, static light scattering and viscosity

PIH	w_{SiO2} [a], w %	$R_{av\ SiO2}$ [b], nm	w_{PAAm} [c], w %	$M_{v\ PAAm}$ [d], kDa	w_{H2O} [e], w %	N [f]
SiO_2-*g*-PAAm	9.7	7.7	86.1	2824	4.2	8

[a] *The weight fraction of SiO_2 in the hybrid: $w_{SiO2}=1-w_{PAAm}-w_{H2O}$.*
[b] *The average radius of silica nanoparticles found by static light scattering.*
[c] *The weight fraction of PAAm in the sample, calculated according to elemental analysis.*
[d] *The viscosity-average molecular weight of the grafted PAAm chains.*
[e] *The total water content in the sample, determined by DTGA.*
[f] *The average quantity of PAAm grafts per particle SiO_2*

UV-Vis Evolution of the extinction spectra of the Co^{2+}/PIH mixtures after $NaBH_4$ addition.

$C_{Co(NO3)2}$ (c) $0.98\cdot10^{-2}$, (f) $1.96\cdot10^{-2}$, (i) $3.92\cdot10^{-2}$ kg·m^{-3}
C_m 2 kg·m^{-3}



Borohydride reduction of cobalt ions

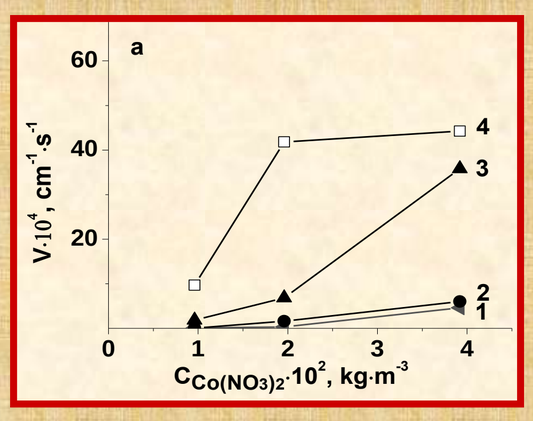
CoNPs in water

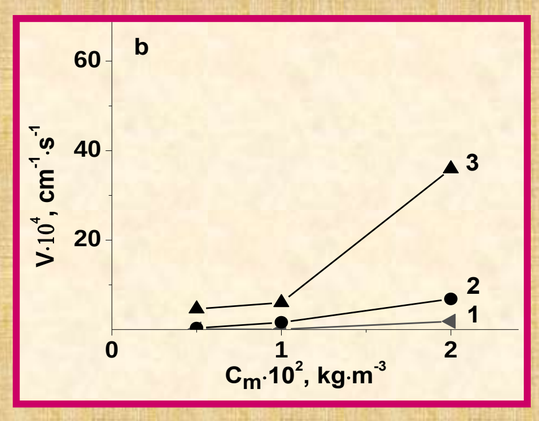
in PIH solution

$$Co^{2+} + 2BH_4^- + 6H_2O \rightarrow Co^{\circ} + 7H_2 + 2B(OH)_3$$
$$2Co^{2+} + 2BH_4^- + 2H_2O \rightarrow Co_2B + HBO_2 + 2H^+ + 4.5H_2$$
$$4Co_2B + 3O_2 = 8Co^0 + 2B_2O_3\ ; \qquad B_2O_3 + 3H_2O = 2B(OH)_3$$

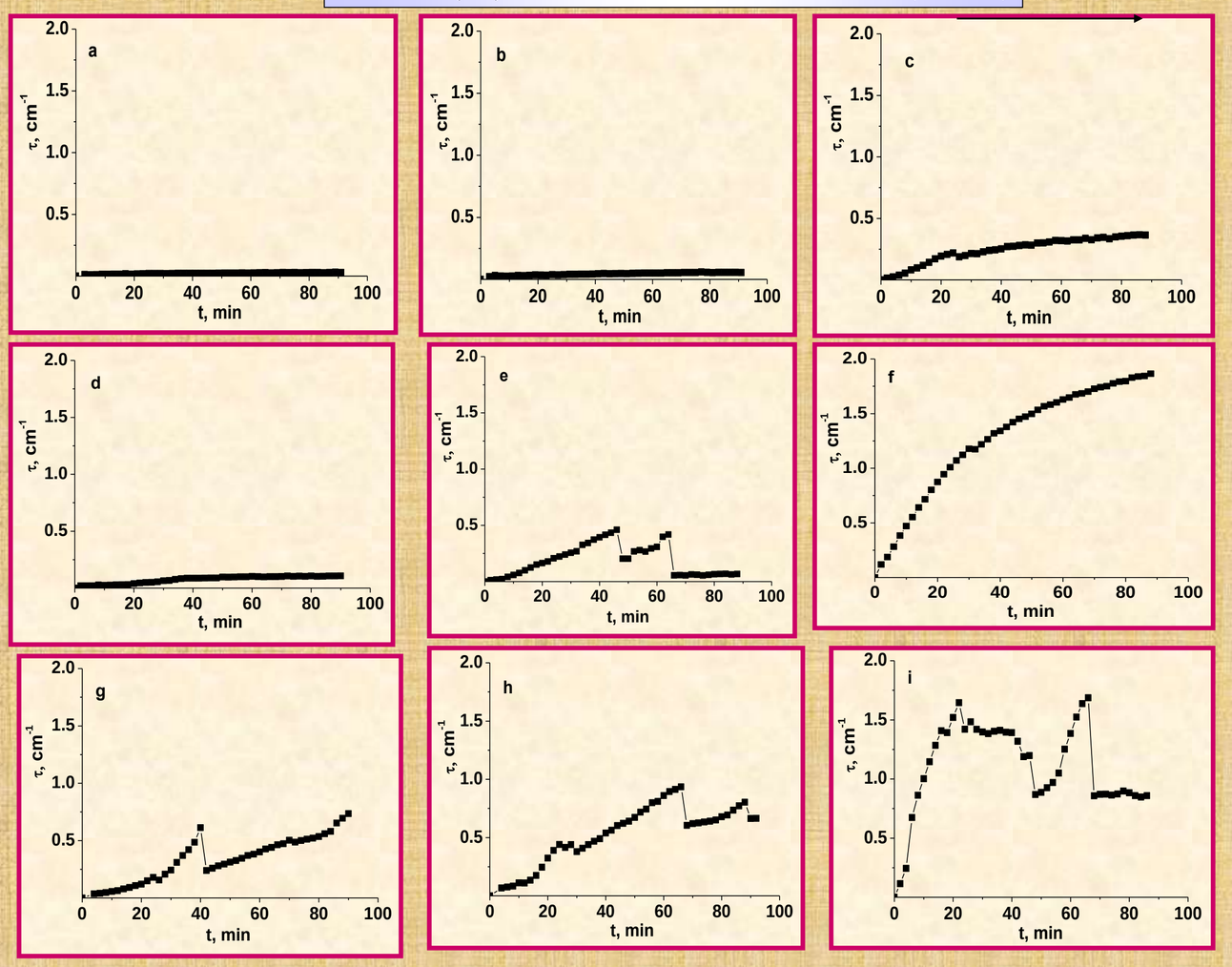
$$\tau = -\frac{1}{l}\ln\left(\frac{I_t}{I_0}\right) = 2.303\frac{D}{l} = \left(\frac{N}{V}\right)\frac{128\cdot\pi^5\cdot a^6}{3\cdot\lambda^4}\left(\frac{n^2-1}{n^2+2}\right)$$

Reaction mixtures:
$C_{(CoNO3)2}$ +PIH+$NaBH_4$ $C_{(CoNO3)2}$ +$NaBH_4$ (twenty-fold molar excess)





Rate changes of the CoNPs accumulation vs (a) Co-salt concentration and (b) PIH concentration in reaction mixtures (a) C_m=0.5 –1, 1.0 –2 i 2.0 kg·m^{-3}–3 and without matrix -4; (b) $C_{Co(NO3)2}=0.98\cdot10^{-2}$ -1, $1.96\cdot10^{-2}$ -2, $3.92\cdot10^{-2}$ -3 kg·m^{-3}; T=20 °C

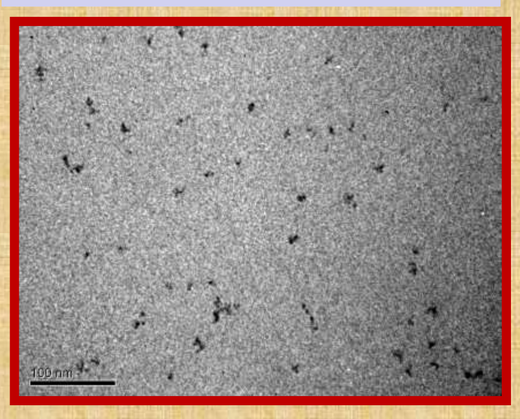


Turbidity changes in the Co^{2+}/SiO_2-g-ПАА mixture after reducing agent adding over 90 min.
$C_{Co(NO3)2}$ (a, b, c) $0.98\cdot10^{-2}$, (d, e, f) $1.96\cdot10^{-2}$ and (g, h, i) $3.92\cdot10^{-2}$ kg·m^{-3};
C_m (a, d, g) 0.5, (b, e, h) 1.0 and (c, f, i) 2.0 kg·m^{-3}; T=18-22°C

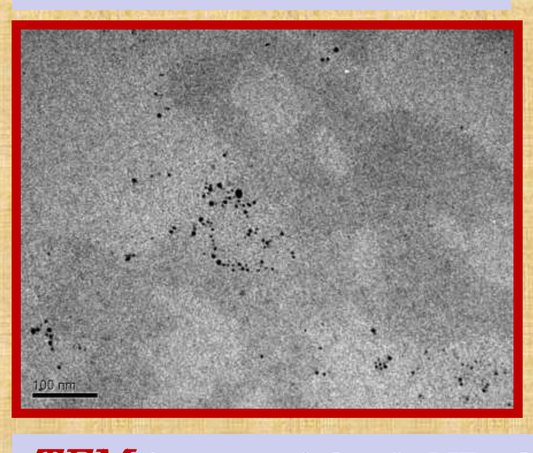
Morphology of CoNPs/ PIH compositionscompositions

a $C_{(CoNO3)2}$ $1.96\cdot10^{-2}$ kg·m^{-3}

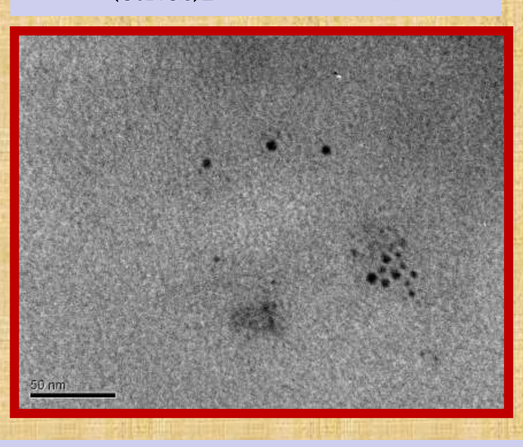
b $C_{(CoNO3)2}$ $3.92\cdot10^{-2}$ kg·m^{-3}



C $C_{(Co\ NO3)2}$ $1.96\cdot10^{-2}$ kg·m^{-3}



d $C_{(CoNO3)2}$ $3.92\cdot10^{-2}$ kg·m^{-3}



TEM images of the CoNPs dispersed within PIH matrices (a, b) and without PIH matrices (c, d)

Conclusion

- Using UV-Vis spectroscopy, TEM we determined the kinetic parameters of the CoNP formation process as well as the yield, size, and morphology of nanoparticles in hybrid solutions and pure water at various concentrations of metal salt and hybrid.
- The growth of both concentrations had a positive effect on the rate of formation of metal nanoparticles and their yield, but in all cases the reduction process developed much slower in hybrid solutions compared to pure water.
- It was revealed that among the PIH samples, the most intense process of CoNPs formation developed in hybrid matrices with a rather loose "corona" of grafted PAAm chains.
- The morphology of the CoNPs/PIH compositions is represented mainly by separate hybrid particles of ~9-35 nm containing metal nanoparticles with a size of ~1-7 nm.