



# GRAFT COPOLYMER-ASSISTED SYNTHESIS OF NICKEL NANOPARTICLES IN AQUEOUS SOLUTIONS



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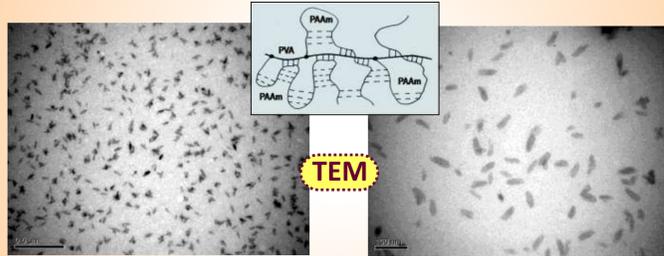
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Nickel nanoparticles (NiNPs) have become one of the most interesting and relatively cheap metallic nanomaterials due to their promising applications in chemical catalysis and electrocatalysis, in nanoelectronics as magnetic fluids, magnetic sensors and storage devices. In the present paper, a special hydrophilic graft copolymer with interacting poly(vinyl alcohol) backbone and grafted polyacrylamide chains (PVA-g-PAAm) was synthesized, characterized and used as a matrix for *in situ* synthesis of NiNPs in aqueous media. The effect of the concentration of initial Ni-salt and copolymer matrix, as well as the structure of NiNPs/PVA-g-PAAm nanocompositions were characterized. To study the borohydride reduction of Ni<sup>2+</sup>-ions in PVA-g-PAAm solutions and pure water, an original method for monitoring the kinetics of the formation of metal nanoparticles was proposed and implemented in the cases where there is no a surface plasmon resonance band (SPRB) in UV-Vis spectra [1,2].

## Parameters of graft copolymer matrices

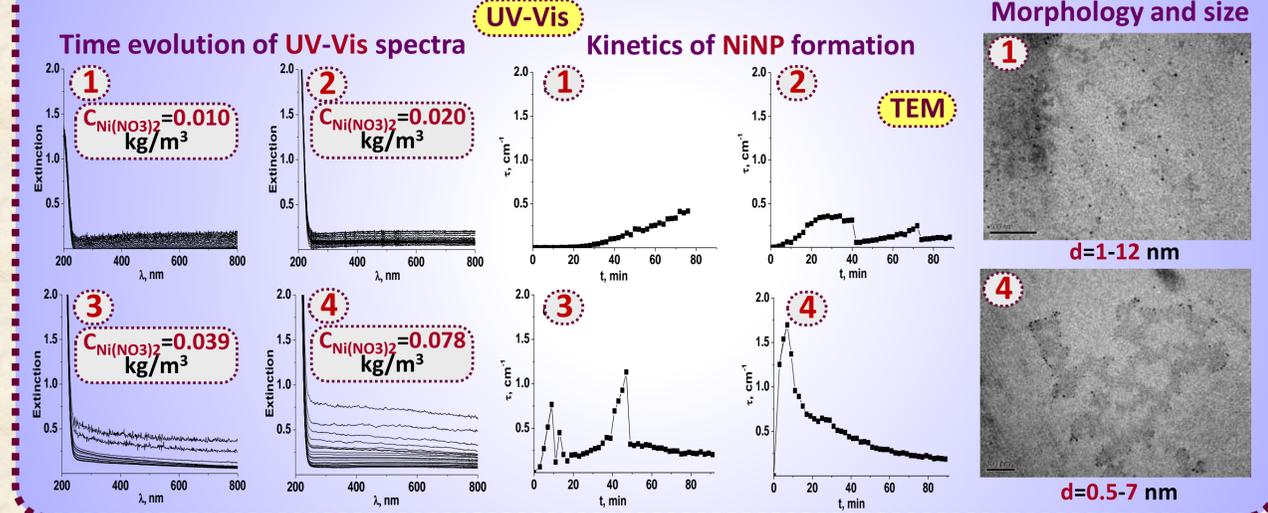
Copolymer	M <sub>wPVA</sub> , kDa	M <sub>wPAAm</sub> , kDa	N
PVA-g-PAAm	90	366	31

## Morphology and size



Copolymer	The shape and length of particles, nm	
	Monomolecular micelle	Fractal aggregates
PVA-g-PAAm	18.6-64.3	64-320

## Synthesis of NiNPs by borohydride reduction of nickel nitrate in pure water



## Determination of the kinetics and yield of NiNPs

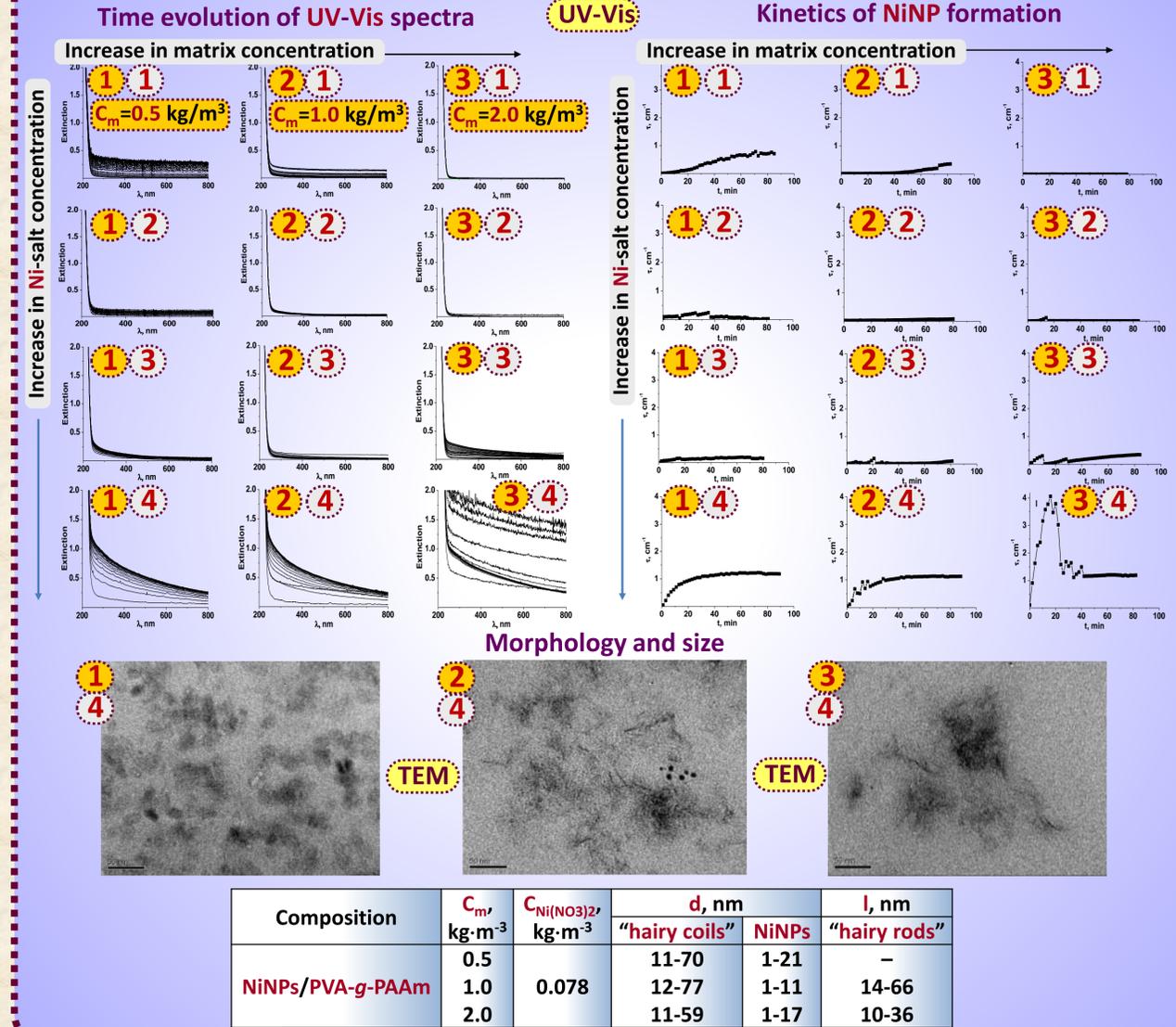
The method is based on the phenomenon of light scattering on the resulting metal nanoparticles < 30 nm in size, which is determined by the turbidity ( $\tau$ ) of the reaction mixture at  $\lambda = 500 \text{ nm}$  (at which there are no absorption bands). Under these conditions,  $\tau$  depends on the size (a) and the number (N) of the resulting nanoparticles [1,2]:

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

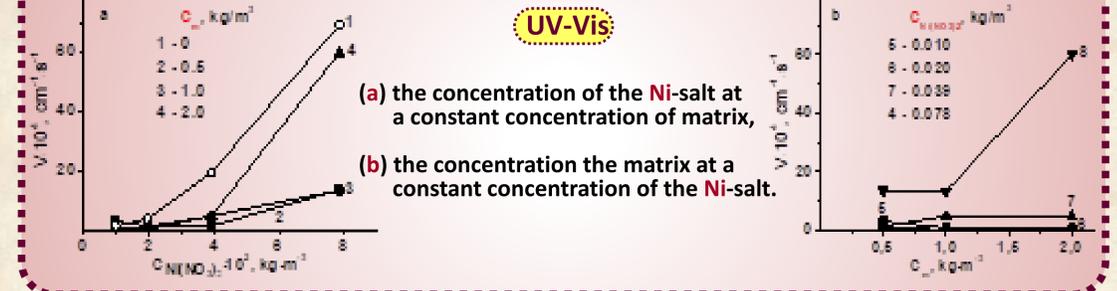
## Conclusions

- The PVA-g-PAAm was synthesized using the known radical matrix polymerization of PAAm from PVA chains in aqueous medium, which was initiated by the Red/Ox reaction between Ce<sup>IV</sup> ions and PVA hydroxyl groups. Its chemical composition and molecular parameters including the number and molecular weight (length) of grafted chains (N=31 and M<sub>wPAAm</sub>=366 kDa) were determined using elemental analysis, DTGA and viscometry.
- Individual macromolecules of the copolymer, which can be attributed to monomolecular micelles, had ellipsoidal shape in aqueous solutions due to the formation of intramolecular polycomplexes between the main and grafted chains. These macromolecules (or monomicelles) also formed bizarre fractal aggregates of various sizes and shapes.
- An original method for monitoring the kinetics of the formation of metal nanoparticles in systems in which SPRB does not appear in UV-Vis spectra has been proposed, physically substantiated, and implemented. Based on this approach, the kinetics of borohydride reduction of Ni<sup>2+</sup>-ions in deionized water and aqueous solutions of PVA-g-PAAm was studied and analyzed depending on the concentrations of Ni-salt and copolymer matrices (C<sub>m</sub>).
- The effects of an increase in the initial accumulation rate and yield of NiNPs with an increase in the concentration of Ni-salt and a deceleration of the reduction of metal ions in copolymer solutions in comparison with pure water (due to the complexation of Ni<sup>2+</sup>-ions with amide and hydroxyl groups of PAAm and PVA) were established. But the accumulation rate and NiNPs yield in a complex way was depended on the matrix concentration that was determined by the ratio of such factors as a decrease in the diffusion rate of NaBH<sub>4</sub> molecules in copolymer solutions and the accumulation of Ni<sup>2+</sup>-ions in matrices due to complexation with active chemical groups at the 1-st stage of reduction process.
- The *in situ* synthesis of NiNPs in copolymer matrices was accompanied by the "detachment" of PAAm grafts from the main PVA chains and led to the appearance of two new structures, such as "hairy coils" and "hairy rods", containing small spherical NiNPs (d~1-21 nm) in isolated and chain states, respectively. The design and size of these structures depended on the relative content of the Ni-salt in the composition. Structures of the "hairy coil"-type with a diameter of ~11-77 nm and small NiNPs, located mainly in the centers of the coils, prevailed in the composition at a high relative content of Ni-salt (0.16 w/w), while the structures of "hairy rods" having a length of ~10-66 nm and containing NiNP chains, appeared at a lower relative content of Ni-salt (0.08 and 0.04 w/w). The appearance of the latter structures was attributed to the formation of complexes of Ni<sup>2+</sup>-ions with active groups of both PVA and PAAm chains at the 1-st stage of the reduction.

## Formation of NiNPs in graft copolymer solutions



## The accumulation rate of NiNPs in water and PVA-g-PAAm solutions depending on:



[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>.

[2] T.B. Zheltonozhskaya, N.M. Permyakova, A.S. Fomenko, L.R. Kunitskaya, V.V. Klepko, L.M. Grishchenko, D.O. Klymchuk Formation of nickel nanoparticles in solutions of a hydrophilic graft copolymer. Polymer Journal 2021, 43 (2), 79-94. <https://doi.org/10.15407/polymerj.43.02079>.