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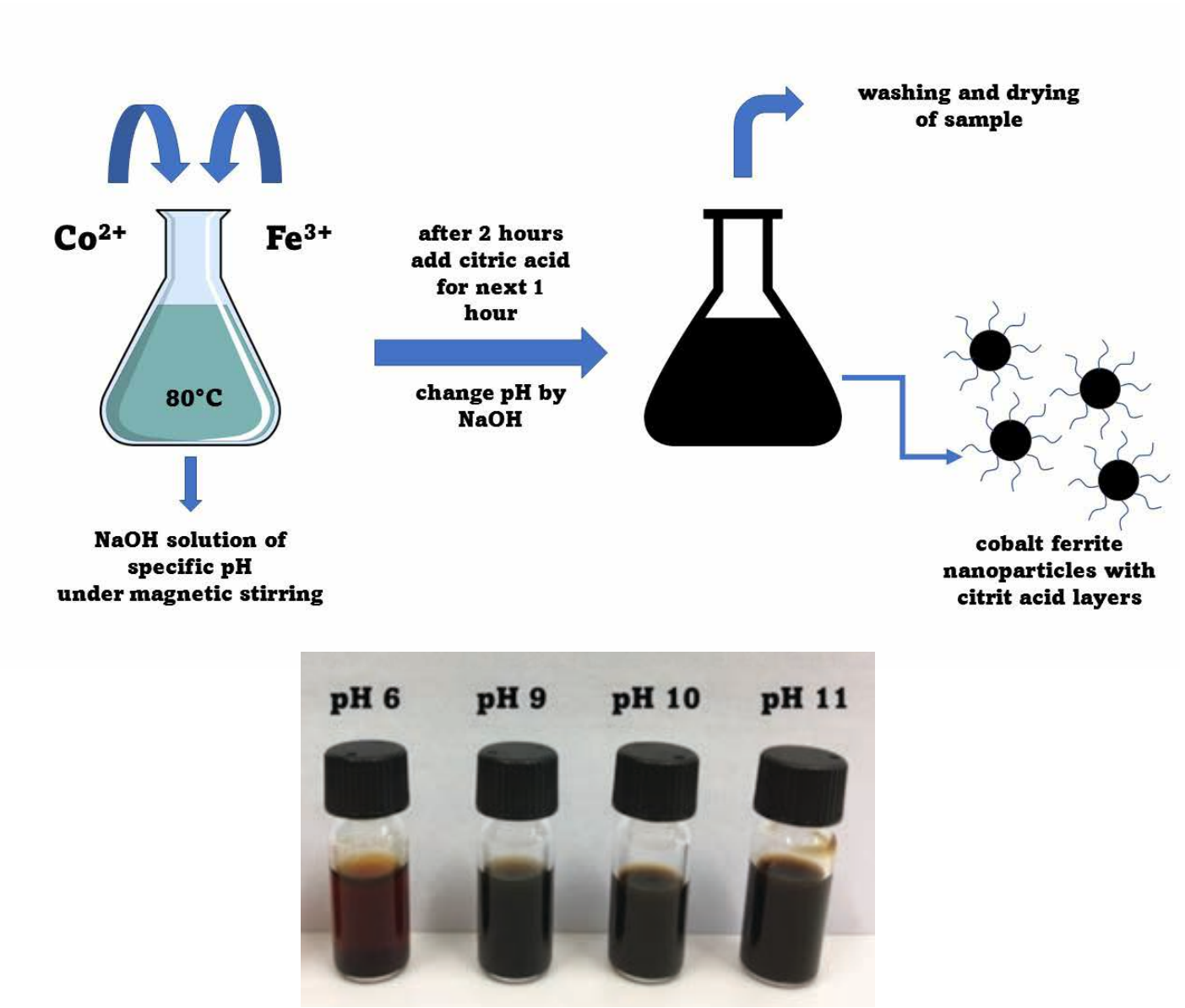
Cobalt Ferite Nanoparticles Modified by Citric Acid: the role of pH on structural and magnetic properties

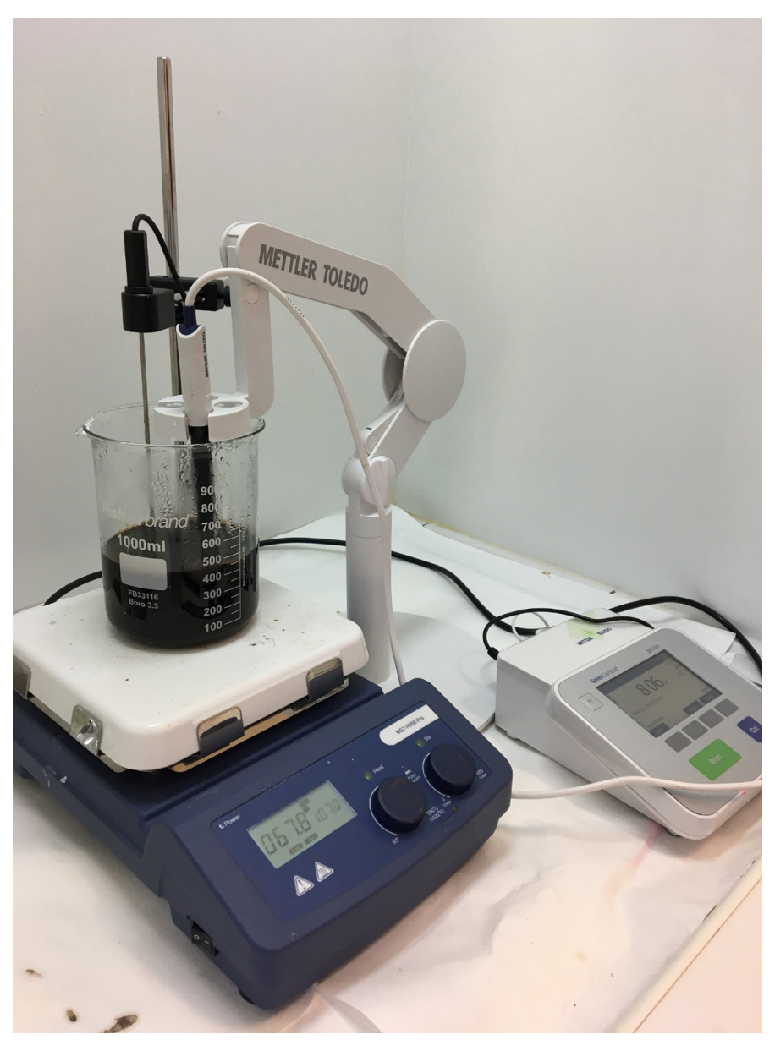
Ľuboš Nagy[1], Adriana Zeleňáková[1*], Pavol Hrubovčák[1],
Michael Barutiak[1], Maxym Lisnichuk[1], Jozef Bednarčík[1, 2]
1 Institute of Physics, P. J. Safarik University, Park Angelinum 9, 040 01 Kosice, Slovakia;
2 Slovak Academy of Science, Institute of Experimental Physics, Watsonova 47, 040 01 Kosice, Slovakia
*** Correspondence: adriana.zelenakova@upjs.sk**

ABSTRACT:

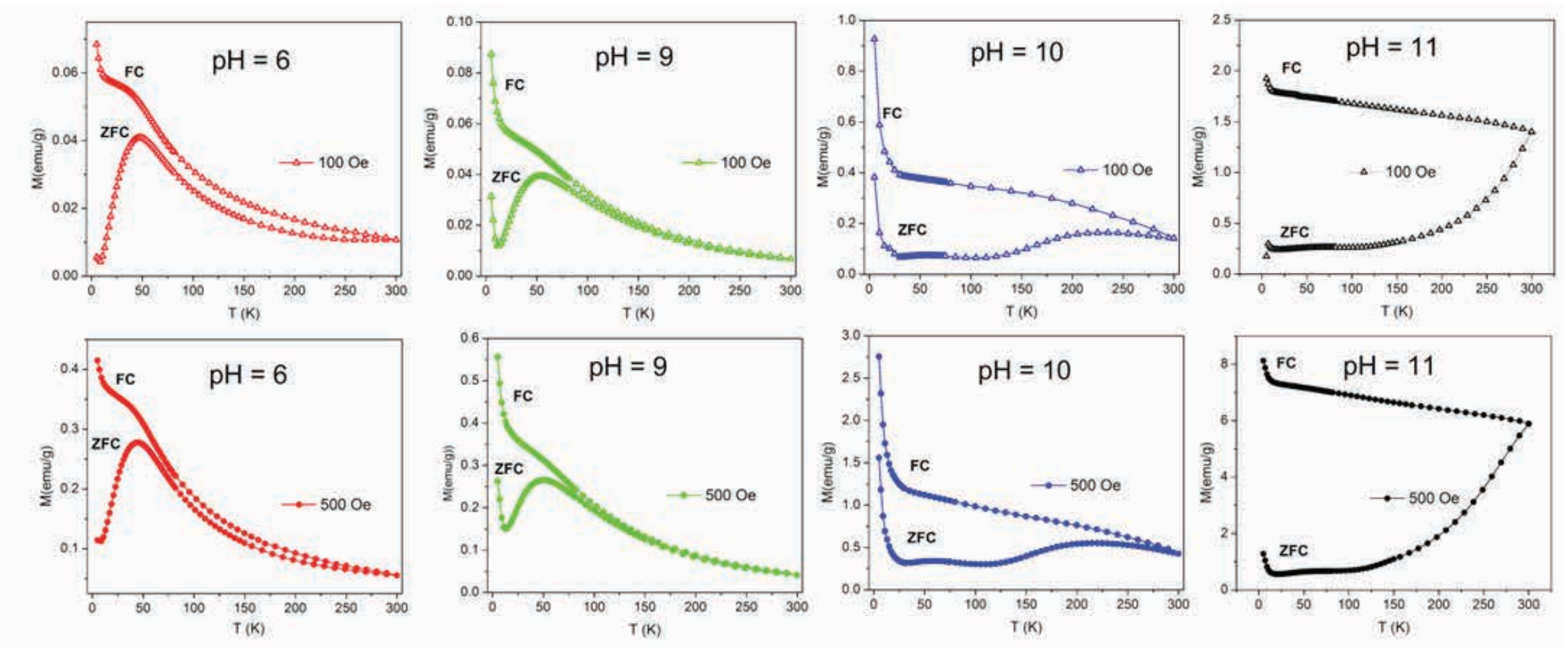
We report the synthesis of fine (~5 nm) citric acid capped $CoFe_2O_4$ (CA-$CoFe_2O_4$) nanoparticles by co-precipitation method at different pH conditions changes gradually from 6 to 11. Structural characterization by TEM and XRD and magnetic measurements providing by SQUID confirm that synthesis under lower pH (6 and 9) leads to the formation of citric acid shell covering the individual nanoparticles, what increases inter-particle distance and decreases the strength of the interactions. On the other hand, higher pH (10 and 11) apparently disrupts citric acid chains resulting in thinner organic capping layer. Therefore, individual nanoparticles are in closer contact and acting of mutual interactions results in the formation of larger agglomerates with pomegranate - like structure.

Preparation of CoFe nanoparticles by coprecipitation method

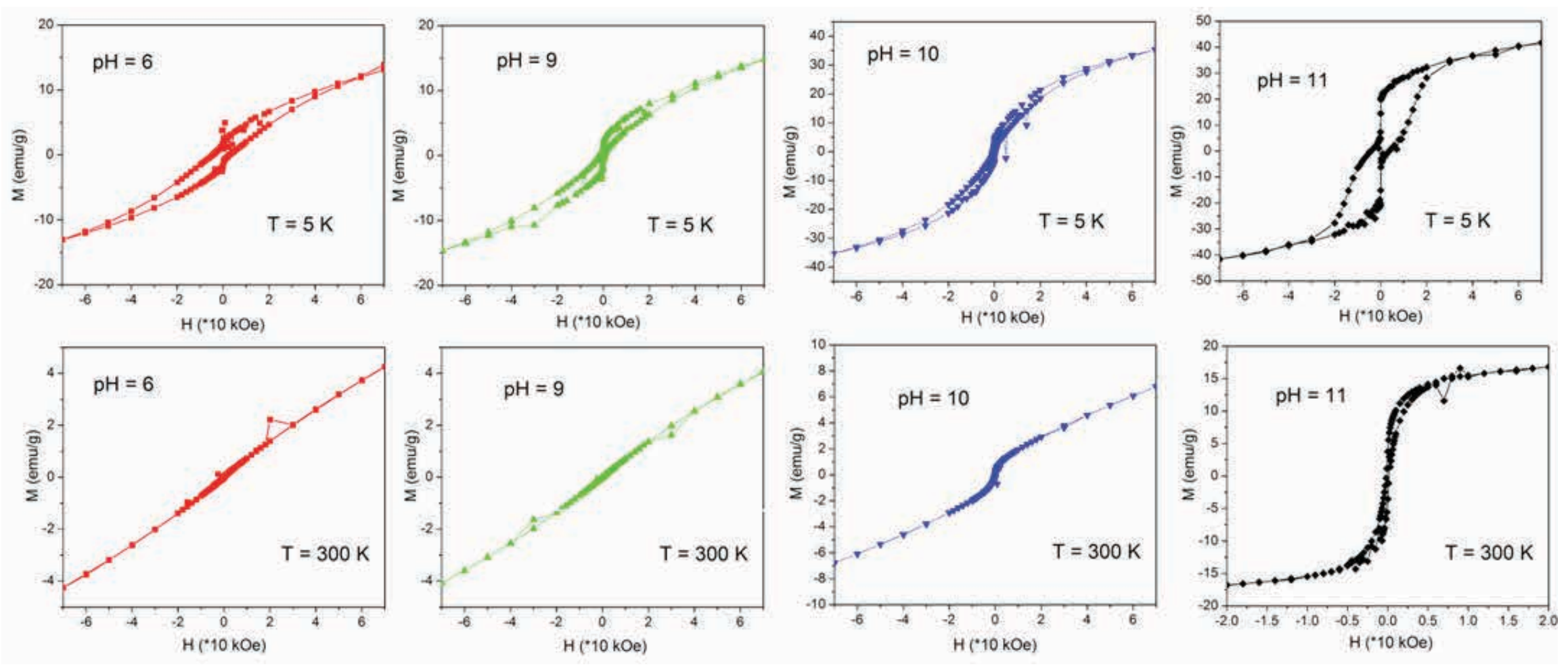




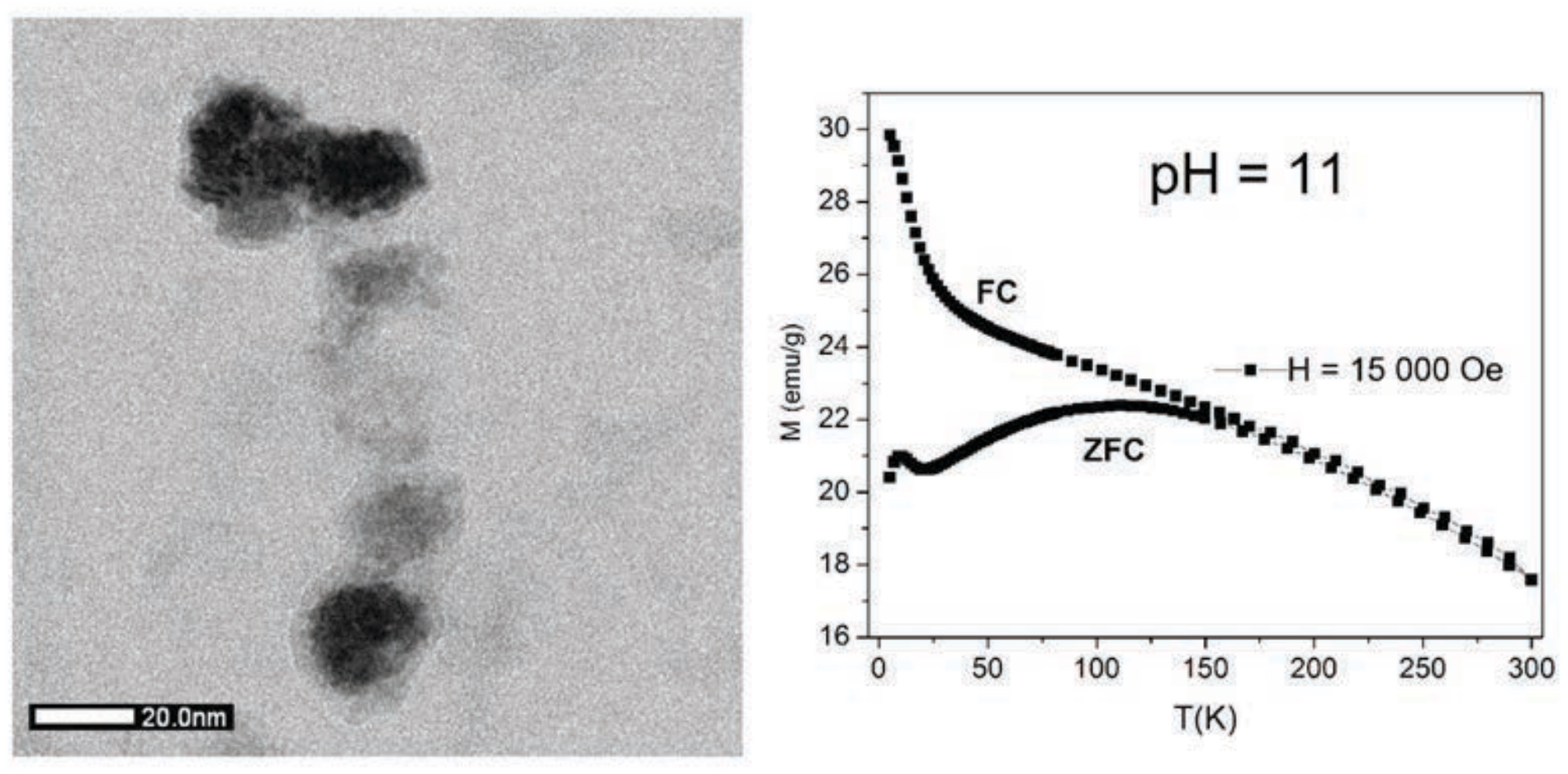
Magnetic measurements



Magnetic dc-susceptibility vs. temperature dependences measured in ZFC/FC protocols in external magnetic field of 100 Oe (upper panel) and 500 Oe (lower panel).

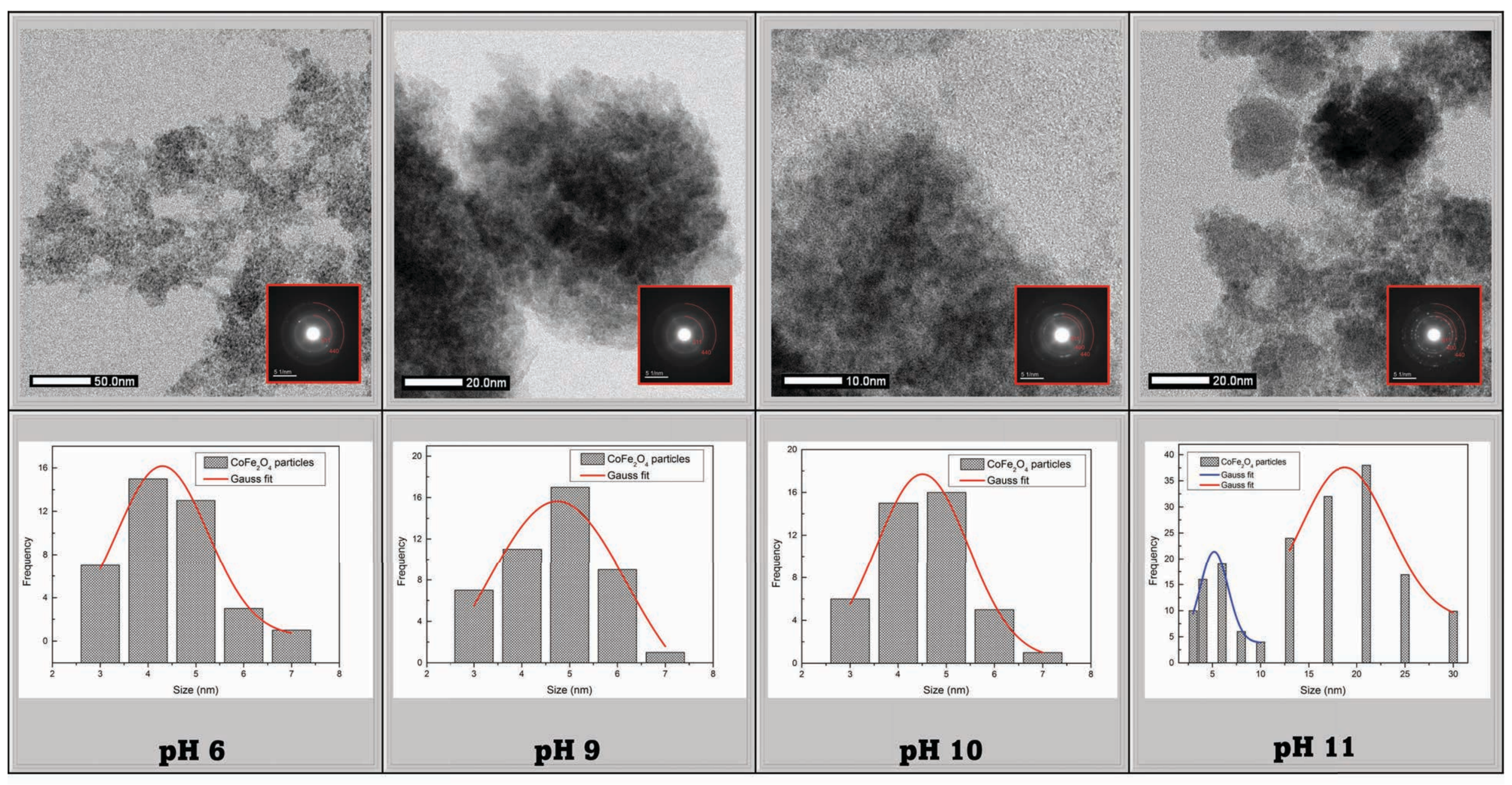


M(H) curves measured at 2 K and 300 K: for sample synthetized at pH=6, sample synthetized at pH=9, sample synthetized at pH=10, sample synthetized at pH=11.

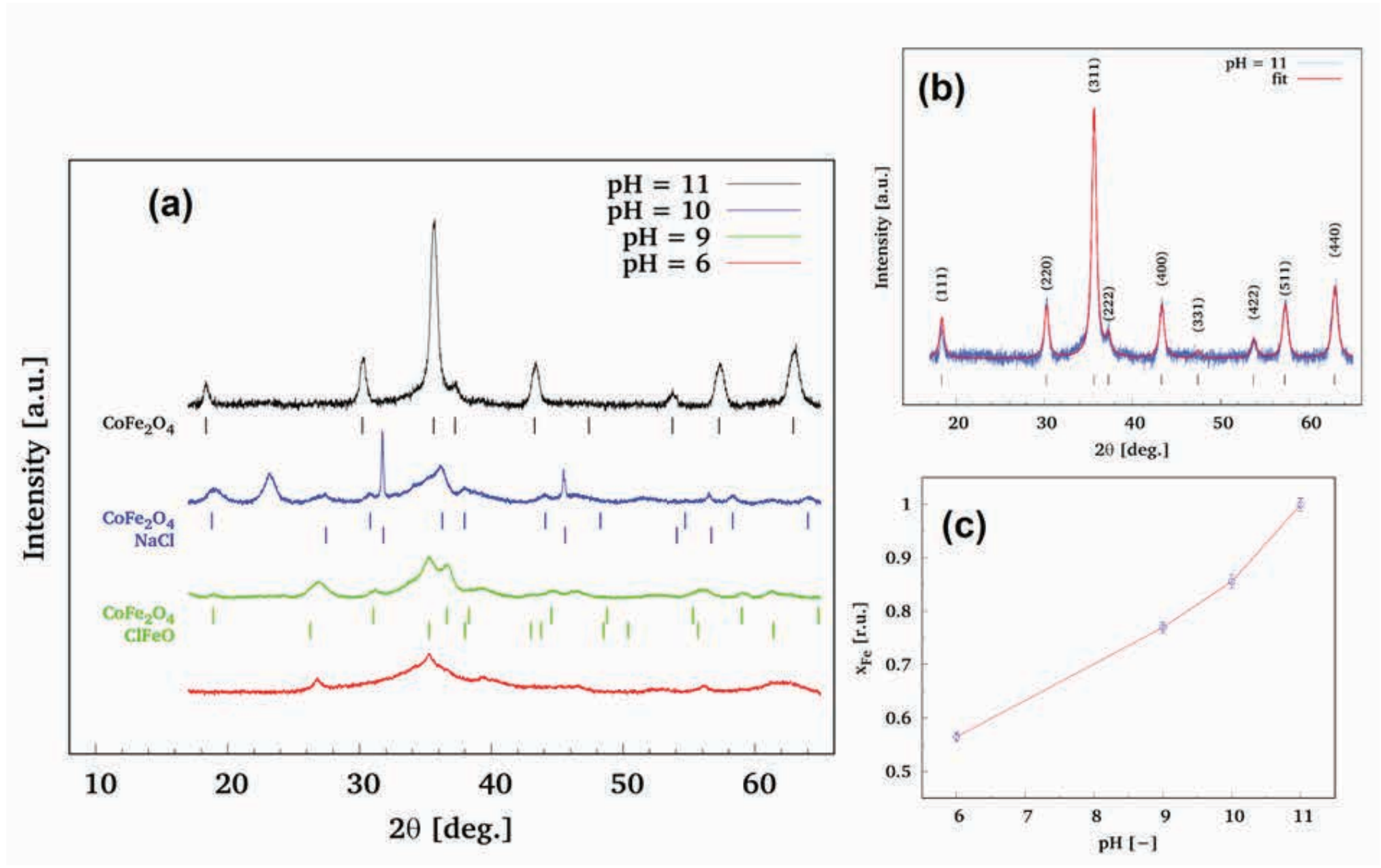


Confirmation of existence of $CoFe_2O_4$ agglomerates capped by citric acid for sample synthesized at pH=11, by TEM (left panel), where the structure of the pomegranate is seen, and by ZFC/FC magnetization measured at very high dc field of 15 000 Oe (right panel).

Structural characterization of prepared samples



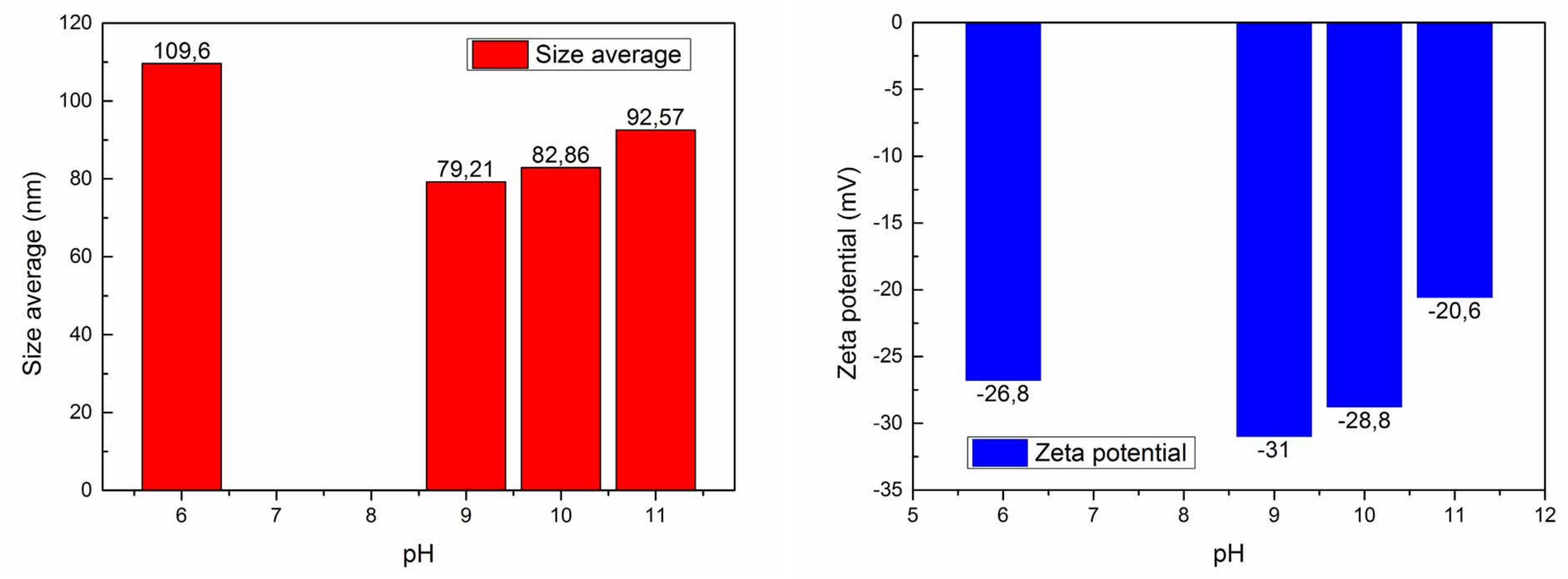
TEM image of studied samples (upper panel), electron diffraction patterns and particles size distribution estimated from TEM pictures (lower panel).



(a) Comparison of XRD patterns for powder samples investigated in this study.

(b) Comparison of experimentally determined XRD pattern (corresponding to the pH 11 sample) and calculated one based on structural model of cubic phase $CoFe_2O_4$. Vertical tics mark positions of Bragg peaks corresponding to cubic $CoFe_2O_4$ phase. Background was removed from the XRD profile.

(c) Relative comparison of Fe level in respective powder materials as calculated from the relative background intensity (calculated on 2θ interval 48°–52°) with respect to the pH 11 sample.



Hydrodynamic size estimated from dynamic light scattering method of samples measured in simulated body fluid at pH=7. Zeta potential of studied samples measured in simulated body fluid at pH=7.

CONCLUSION:

We investigated the structural and magnetic properties of citric acid-coated $CoFe_2O_4$ samples prepared by the coprecipitation method at pH 6, 9, 10, 11. We determined the values of saturation magnetization and blocking temperature from magnetic measurements. The features are characteristic of typical superparamagnetic nanoparticle system with relative narrow size distribution. One can clearly see that magnetic performance for the samples pH 6 and pH 9 differs significantly from the couple of samples synthetized under higher pH (10 and 11). Both samples prepared under lower pH exhibit ZFC maxima at T_{max} ~ 50 K that are well resolved. Synthesis under lower pH (6 and 9) leads to the formation of citric acid shell covering the individual nanoparticles, what increases inter-particle distance and decreases the strength of the interactions. On the other hand, higher pH (10 and 11) apparently disrupts citric acid chains resulting in thinner organic capping layer. Therefore, individual nanoparticles are in closer contact and acting of mutual interactions results in the formation of larger agglomerates. The presence of $CoFe_2O_4$ phase was confirmed from XRD measurements and also the increasing concentration of Fe atoms with increasing pH of the synthesized samples. From the hydrodynamic size measurements, we see an increase in size towards higher pH, which was also confirmed by TEM observations and the particle size distribution calculated from them. The decreasing zetapontial from ph 9 to pH 11 is due to the decreasing thickness of citric acid on the surface of the nanoparticles.

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