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Synthesis and characterization of *in situ* functionalized iron oxide nanoparticles

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Introduction

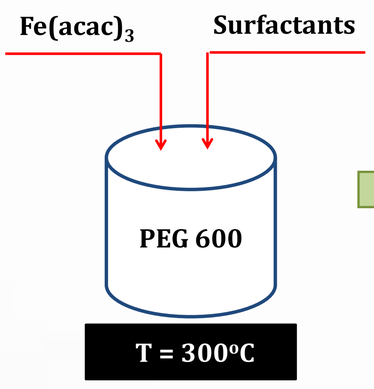
Magnetic nanoparticles are suitable materials for the applications developed in the research fields of catalysis, biomedicine, magnetic resonance imaging, data storage and environmental remediation. In this work, synthesis and characterization of functionalized magnetic nanoparticles surface through polyol process is reported. Thermal decomposition of organic salts in hot organic solvents allows the control of the particle size in the submicron size. In the mixture, two surfactants are added with varying concentrations in order to fabricate organophilic, hydrophilic and amphiphilic nanoparticles. Surface modified magnetic nanoparticles are characterized in respect of their structure, magnetic properties, surface functionalization, hydrodynamic size and z-potential.

Experimental Procedure

Materials

Solvent: Polyethyleneglycol 600 Da (PEG 600), MERCK, Schuchardtt, Germany. Preecursor: Tris(acetylacetonato)iron(III) ($Fe(acac)_3$), Alfa Aesar, Karlsruhe, Germany. Surfactants: Oleic Acid (OA, 90%), Alfa Aesar, Karlsruhe, Germany. 11-Mercaptoundecanoic Acid (MUA, 99%), Aldrich.

Synthesis



a) Uncoated nanoparticles (NPs): a thin layer of the organic solvent (PEG 600) [1] → soluble in H_2O

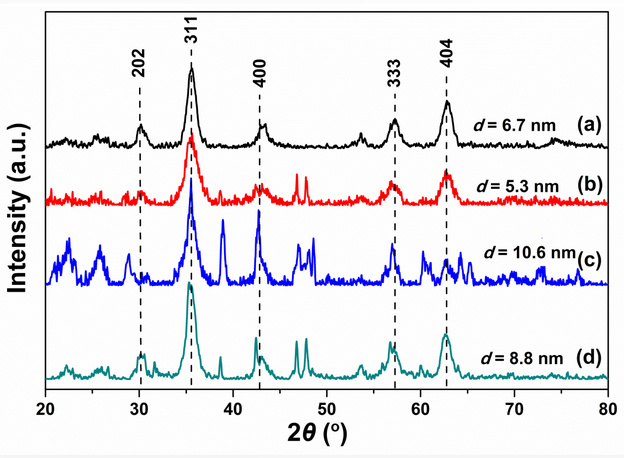
b) Coated with OA → soluble in EtOH, $CHCl_3$.

c) Coated with MUA → soluble in H_2O.

d) Coated with OA & MUA → soluble in H_2O, EtOH, $CHCl_3$.

Results and Discussion

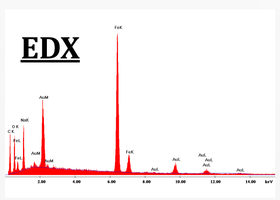
XRD Data



XRD spectra of the uncoated and coated NPs: (a) uncoated, coated with **(b)** OA, **(c)** MUA and **(d)** OA & MUA.

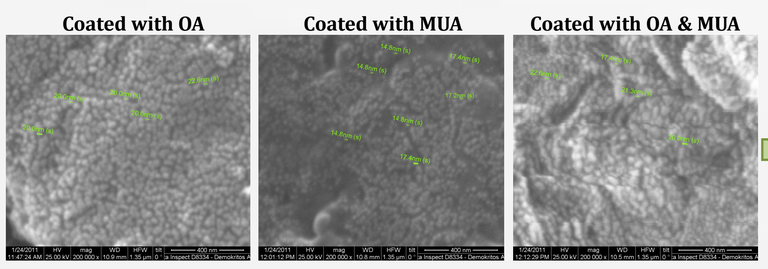
- ✓ Spectrums are indicative of γ-Fe_2O_3 structure, with a chemically disordered face-centered cubic (fcc) structure [2].
- ✓ OA reduces core size.

Scherrer Formula [3]: $d = 0.9\ \lambda/\beta \cos\theta$



→ Fe_2O_3

SEM Images



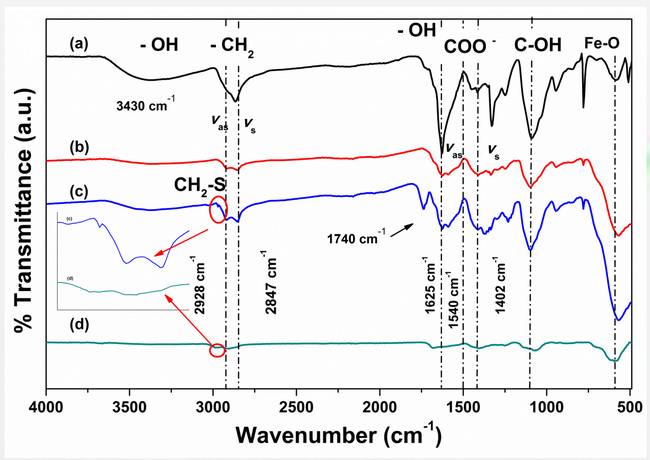
TEM Analysis required

- ✓ Core Size
- ✓ Dispersion

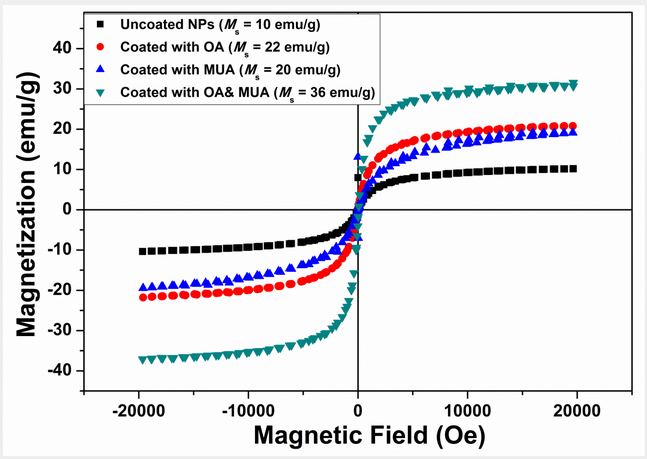
FT-IR Data

FT-IR spectra of the uncoated and coated NPs: (a) uncoated, coated with **(b)** OA, **(c)** MUA and **(d)** OA & MUA.

- ✓ *Uncoated*: characteristic vibrations of -OH, -CH_2 and C-OH, due to PEG layer [3].
- ✓ *Coated with OA*: characteristic vibrations of -OH, -CH_2 , COO^- and C-OH, due to OA and PEG layer.
- ✓ *Coated with MUA*[4]*:* characteristic vibrations of -OH, CH_2-S, -CH_2 , COO^- and C-OH, due to MUA and PEG layer.
- ✓ *Coated with OA & MUA*: mix of spectrums (b) and (c).



Magnetization Data



Hysteresis loops of the uncoated and coated with OA, MUA and OA & MUA NPs.

- ➢ NPs reveal superparamagnetic properties
- ➢ The relatively low magnetization values can result in:
  - ✓ Poor crystallinity
  - ✓ The underestimation of the thickness of the nonmagnetic (organic) layer covering the crystalline core and its paramagnetic contribution to the magnetization [1].

Dynamic Light Scattering Data

Table: Hydrodynamic size and z-potential values of the synthesized samples at room temperature.

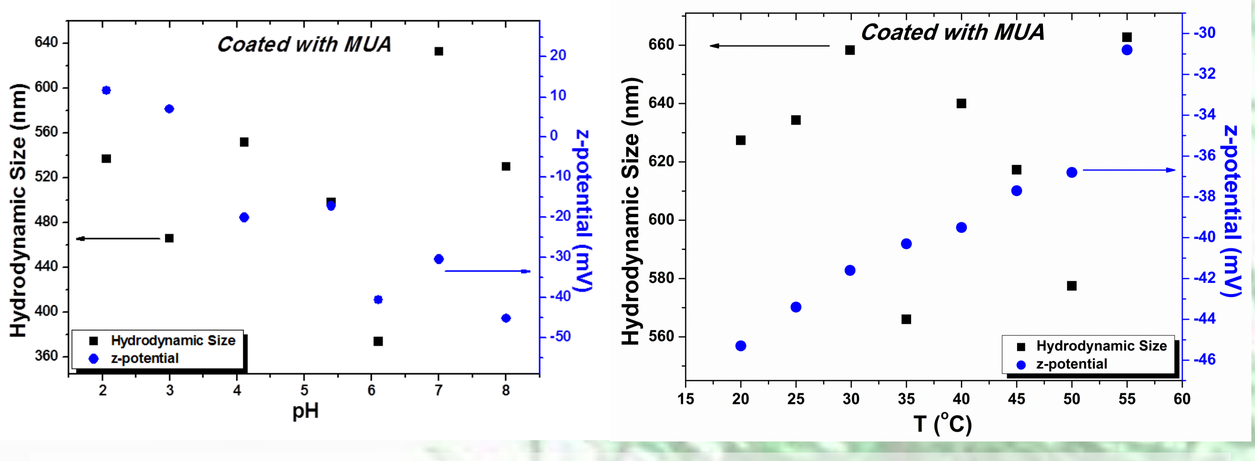
Sample	Hydrodynamic Size (nm)	Z-potential (mV)
Uncoated NPs	156	-33.2
Coated with OA	196	-34.5
Coated with MUA	571	-30.5
Coated with OA & MUA	521	-32

Hydrodynamic size and z-potential of NPS coated with MUA are affected by:

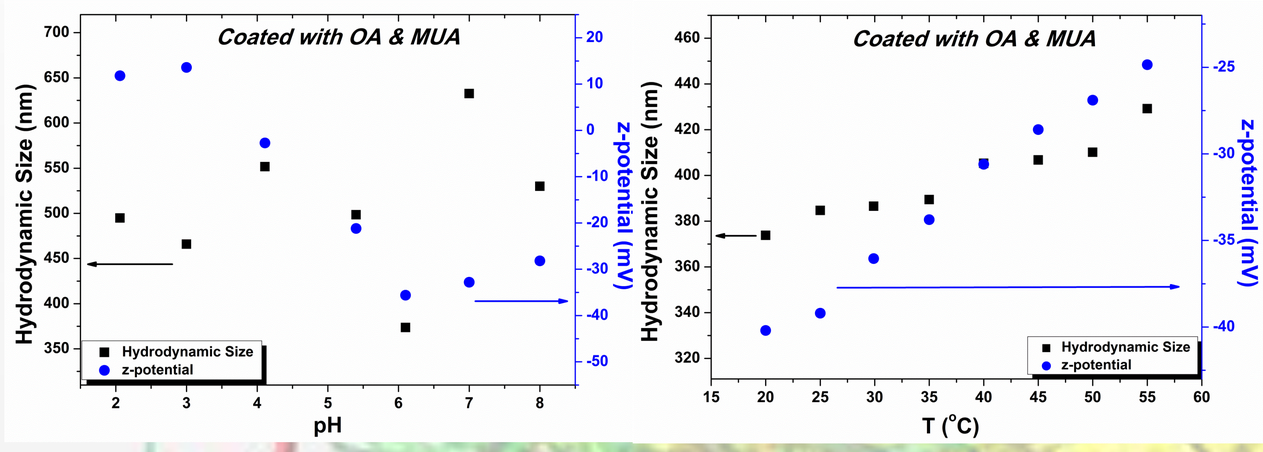
- ✓ *Hydrogen bonding* → increasing size & offering the carboxylic group for further chemical reaction and/or functionalization.

Effect of pH and temperature on the hydrodynamic size and z-potential values of:

(a) Coated with MUA NPs → deprotonation at acidic and basic pH values of –SH and carboxylic acid groups, respectively.



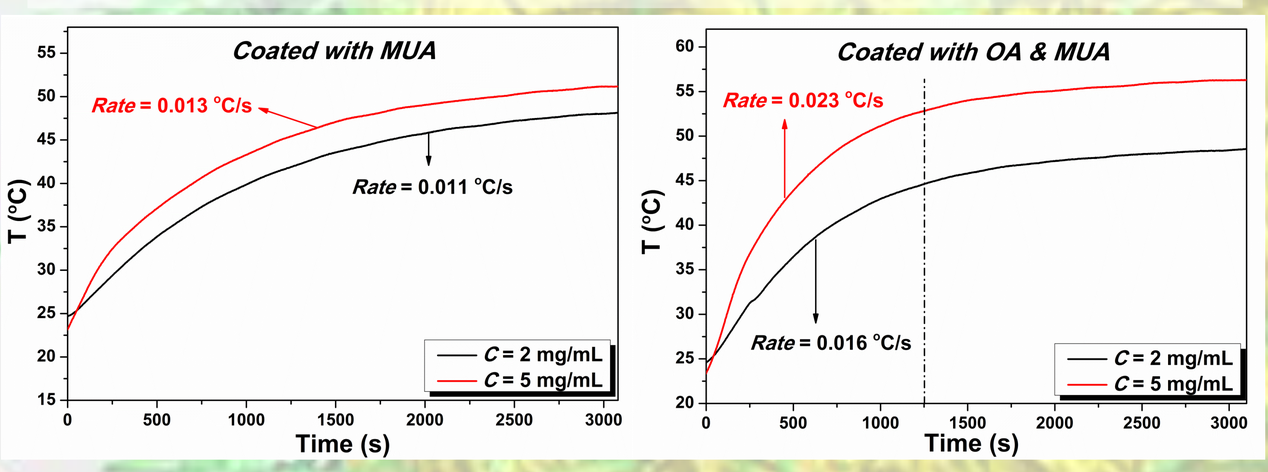
(b) Coated with OA & MUA NPs → deprotonation at acidic and basic pH values of –SH and carboxylic acid groups, respectively.



- ✓ MUA coated NPs can only be well dispersed in basic condition and reveal negative z-potential because of the thiol group coordination of MUA towards the iron cations on the surface of maghemite, which leaves uncoordinated carboxylate groups exposed to the aqueous solution and get deprotonated under basic condition [5].

Hyperthermia

- ➢ Lower concentrations decrease the temperature increase rate.
- ➢ Lower M_s values of MUA coated NPs decrease the hyperthermia rate.
  - ✓ Further TGA experiments required → calculation of organic layer mass → normalized M_s values to the inorganic (magnetic) core.



Conclusions

This work presents the following benefits:

- ✓ An easy procedure to produce *in situ* functionalized magnetic NPs.
- ✓ Induce efficient superparamagnetic properties.
- ✓ Satisfactory hyperthermia rates.
- ✓ Improved nanoparticles solubility in various solvents.

References

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