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Nitrocatechol Dispersants to Tailor Superparamagnetic Fe₃O₄ Nanoparticles

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Application of superparamagnetic iron oxide nanoparticles (SPIONs) as imaging contrast agents and as actuators in smart materials require them to retain high stability even in extremely dilute suspensions, at high salt concentrations and elevated temperatures. Furthermore, many biomaterial applications require close control over SPION hydrodynamic diameter and interfacial chemistry. These requirements can only be met by steric stabilization with irreversibly-binding, low molecular weight dispersants, *e.g.* poly(ethylene glycol) (PEG).

We have shown that a recently described group of catechol derivatives for surface functionalization, nitrocatechols, have vastly higher affinity to Fe₃O₄ than previously proposed bestperforming groups, such as dopamine and DOPA, for grafting of dispersants to SPIONs.^[1] By subjecting SPIONs to strict purification, high salt concentrations and high temperatures we could demonstrate the importance of irreversible dispersant binding for good SPION stability under physiological conditions. These stringent tests led to discrimination between anchors which yielded low dispersant density or reversible binding, ones which had too high affinity and caused particle dissolution, and nitro-DOPA and nitrodopamine which led to unsurpassed dispersant density on the particles as well as irreversible binding up to temperatures >90 °C in physiological buffer. The high nitrocatechol affinity was shown to result from oxidation of Fe²⁺ upon binding and corresponding reduction of the nitrocatechol ring.^[2]

The use of ultra-stable anchors which bind irreversibly to iron oxide and which can be attached to any kind of dispersant, makes it easy to tune independently core and shell size of SPIONs. By synthesizing Fe_3O_4 cores ranging in size from 5–15 nm and using dispersants of different molecular weights, we have demonstrated the effect of changes in core size and shell thickness respectively on nanoparticle overall size, stability and magnetic performance. An important lower cut-off for stability of PEG dispersants molecular weight of 1.5 kDa was found even for densely packed nitroDOPA-PEG when typical core sizes for magnetic resonance imaging contrast agents were used.^[3]

We are now further exploiting the high stability and versatility of this mix-and-match, core-shell SPION system to create multi-functional nanoparticles for biomedical imaging^[4] as well as nanoparticle interfacial assembly into membranous functional materials.^[3]

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Fig. 1. a) Nitrocatechol-PEG dispersants were used to achieve irreversibly stabilized SPIONs (DLS comparison to dopamine shown). b) The high affinity bond results from a redox reaction between Fe²⁺ and the nitrocatechol.

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