

Raft polymerization provides better antifouling coatings on inorganic nanoparticles than grafting through polymerization

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Precise control of particle stability and the nanobiointerface is crucial for bioapplications. Nanoparticle properties are often altered after adsorption of a protein corona in a biological environment. Many applications become complicated due to non-specific binding of nanoparticles to proteins or cells. To avoid these inconveniences, inorganic nanoparticles need to be coated with polymers with antifouling properties, which create an intact surface and stabilize nanoparticles by steric hindrance. ¹ These hydrophilic polymers typically require further modification with functional molecules with defined orientation, and appropriate flexibility to meet specific application needs.

Various hydrophilic polymers have been used for this purpose such as polyethyleneglycol, polyoxazolines, polysaccharides, polyglycerol or poly(N-(2-hydroxypropyl) methacrylamide). ² There are various ways to attach polymers to nanoparticles such as “grafting to”, “grafting from” and “grafting through” methods. The last two approaches offer thicker and denser brushes, since the polymer grows from the particle surface.³

We present methods for coating inorganic nanoparticles with a dense polymeric shell composed of two distinct polymers. The inner layer consists of polyglycerol, synthesized via ring-opening polymerization, followed by an outer layer of poly(N-(2-hydroxypropyl) methacrylamide) (pHPMA). The pHPMA shell is formed using either conventional free radical polymerization or RAFT polymerization. The size and density of the resulting polymer layers are characterized and compared using dynamic light scattering (DLS), nanoparticle tracking analysis (NTA), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). To enable post-synthetic functionalization, two different functional monomers were incorporated into the polymer shell, propargyl methacrylamide or azidopropyl methacrylamide. The efficiency of their integration is evaluated by NMR and infrared spectroscopy. Their accessibility for subsequent “click” chemistry is assessed by conjugation with small molecules (e.g., dyes) and larger biomolecules (e.g., proteins). Finally, the reduction in non-specific binding of the polymer-coated nanoparticles to biomolecular structures is evaluated via surface plasmon resonance (SPR), confocal microscopy and flow cytometry.

As inorganic nanoparticles, we use fluorescent nanodiamonds (FNDs), which are a promising material for the preparation of near-infrared fluorescent probes and sensors for bioimaging due to their unique properties such as exceptionally stable fluorescence, sensitivity to magnetic and electric fields and broad biocompatibility. Unlike many other fluorophores, nanodiamonds do not photobleach and have a long fluorescence lifetime.⁴

References:

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