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Nanoparticle decoration with surfactants: Molecular interactions, assembly, and applications

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ABSTRACT

Nanostructures of diverse chemical nature are used as biomarkers, therapeutics, catalysts, and structural reinforcements. The decoration with surfactants has a long history and is essential to introduce specific functions. The definition of surfactants in this review is very broad, following its lexical meaning "surface active agents", and therefore includes traditional alkyl modifiers, biological ligands, polymers, and other surface active molecules. The review systematically covers covalent and non-covalent interactions of such surfactants with various types of nanomaterials, including metals, oxides, layered materials, and polymers as well as their applications. The major themes are (i) molecular recognition and noncovalent assembly mechanisms of surfactants on the nanoparticle and nanocrystal surfaces, (ii) covalent grafting techniques and multi-step surface modification, (iii) dispersion properties and surface reactions, (iv) the use of surfactants to influence crystal growth, as well as (v) the incorporation of biorecognition and other material-targeting functionality. For the diverse materials classes, similarities and differences in surfactant assembly, function, as well as materials performance in specific applications are described in a comparative way. Major factors that lead to differentiation are the surface energy, surface chemistry and pH sensitivity, as well as the degree of surface regularity and defects in the nanoparticle cores and in the surfactant shell. The review covers a broad range of surface modifications and applications in biological recognition and therapeutics, sensors, nanomaterials for catalysis, energy conversion and storage, the dispersion properties of nanoparticles in structural composites and cement, as well as purification systems and classical detergents. Design principles for surfactants to optimize the performance of specific nanostructures are discussed. The review concludes with challenges and opportunities.

Contents

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1. Introduction

Nanomaterials with specific surface functionality are ubiquitous in nature. Soils, seashells, bone, and teeth contain inorganic/organic nanostructures [1–3]. Small cells like mycoplasma (~200 nm) and cell organelles can be regarded, according to size, as living polymeric nanoparticles [4]. The term surfactant-decorated nanoparticles, as used in the chemical sciences and in this review, is typically associated with manmade nanostructures for applications in imaging, drug delivery, composites, catalysis, energy conversion devices, purification systems, and other technologies (Fig. 1) [5,6]. The terminology "surfactant" is used here for a broad array of surface active agents, according to its true definition (see Section 1.1), and includes classic alkyl-based surfactants, peptides, lipids, DNA, molecular ligands, bioconjugates, and polymers covalently grafted to or non-covalently assembled on nanomaterial surfaces, thereby changing their properties. The term nanoparticles encompasses a broad range of nanostructures of different chemical composition, shape, and size in the 1–1000 nm range. Details of the definitions, a historical perspective, and a full outline of this review follow in the subsections below. The main part of the review consists of general concepts in Section 2, the discussion