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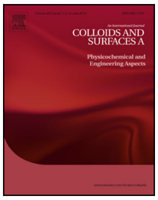

Synthesis and aggregation behavior of hybrid amphiphilic titania Janus nanoparticles via surface-functionalization in Pickering emulsions

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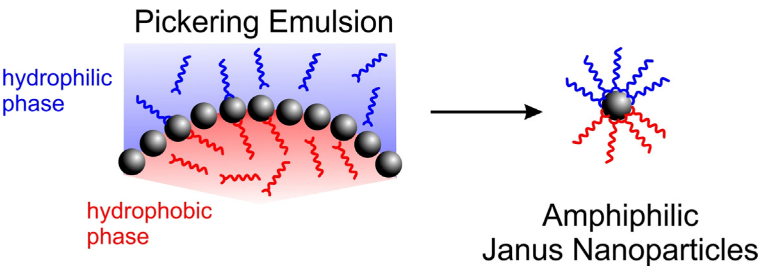
HIGHLIGHTS

- Anisotropic surface modification of titania nanoparticles in a Pickering emulsion.
- Amphiphilic Janus nanoparticles were obtained applying different organophosphonates.
- Amphiphilic Janus nanoparticles show high potential in stabilizing emulsions.
- Amphiphilic nanoparticles form micelles with low critical micelle concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Amphiphilic surface-functionalized titania nanoparticles were prepared in a Pickering emulsion applying hydrophobic or hydrophilic agents containing a phosphonate anchor group. The Pickering emulsion approach allows for the formation of anisotropic nanoparticles with a high degree of surface-functionalization that mimic the behavior of surfactants. Therefore, the efficiency of the formed particles in stabilizing emulsions was studied and it could be shown that the stability of emulsions substantially increases by addition of amphiphilic particles. Due to the photocatalytic activity of anatase nanoparticles the emulsions stability against creaming can be decreased by irradiation with UV light. The critical micelle concentration (CMC) of suspensions of amphiphilically modified nanoparticles was determined by conductivity measurements. The prepared surface-functionalized nanoparticles show similar characteristics as amphiphilic block copolymers.

1. Introduction

In recent years so-called Janus nanoparticles consisting of two hemispheres which are different from a chemical point of view have drawn a lot of scientific attention due to many potential applications of such anisotropic materials [1]. The different chemical composition at the surface of such particles results in variations of polarity, charges, and optical or magnetic properties for the two hemispheres [2]. Preparative methods either lead to particles which are composed of two different materials [3–5], for example magnetic Janus particles that can be obtained from a miniemulsion polymerization approach [6,7], or the surface of the particles presents an anisotropic surface-functionalization [8–11]. The formed Janus systems may be used for drug delivery, catalysis,

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functional coatings, self-agglomeration or stabilization of emulsions [8,10–16].

The synthesis of anisotropically modified particles is quite challenging because isotropic surface-functionalization is often preferred and can only be prevented if there is discrimination between different reaction environments on the particle surface. Typically masking/unmasking techniques, directed fluxes and fields, microcontact printing, and techniques based on reactions at interfaces are described in the literature as preparation methods, mostly for micrometer sized particles [2]. Many of these procedures are quite complex and yield only small amounts of modified particles. A very promising method is the localization of the particles at the interface of two immiscible liquids [17,18]. Particularly emulsions are capable to produce higher quantities of particles because they have a large interface in relation to the volume. The fact that nanoparticles have the ability to stabilize so-called Pickering emulsions [19] can be used to achieve amphiphilically modified particles in a simple one step reaction [8,9,20,21]. Most of the described procedures involve a wax phase as oil phase of the emulsion to lock the particles at their positions. Applying such a procedure, several steps are necessary to produce and purify the particles especially if both hemispheres are modified. Only very few publications deal with the modification at a liquid oil phase [21]. The synthesis of amphiphilically modified silica nanoparticles via simultaneous ATRP in both phases [22] and the amphiphilic surface functionalization of gold nanoparticles in Pickering emulsions are described in the literature [9].

Since Pickering discovered the capability of nanoparticles to stabilize emulsions [19], nanoparticles evolved to an important class of emulsifying agents [23–27]. Many investigations of silica particles stabilized emulsions were realized during the last twenty years. Titania nanoparticles have drawn attention due to their unique properties. Today the most important application of titania nanoparticles stabilized emulsions are in emulsifier-free cosmetics [28]. But properties as the photocatalytic activity, UV-absorption, good mechanical properties, the positively charged surface at pH below 6 open access toward new applications of titania stabilized emulsions. Song et al. were the first to present the possibility of stabilizing styrene-in-water emulsions and at the same time for initiation of styrene polymerization via illumination the emulsions by addition of anatase nanoparticles [29].

The efficiency of nanoparticles in stabilizing emulsions depends on many factors, e.g., size, shape, and hydrophobicity of the particles. Additionally, the state of flocculation, pH, ionic strength, and particle concentration of the emulsion are important factors for the stability [23,25,30,31]. Binks et al. discovered that the wettability of particles is an important factor regarding stabilization of Pickering emulsions. Highly hydrophilic or hydrophobic particles tend to coagulate. Emulsions with particles of intermediate hydrophobicity are stable to coalescence [24]. The nanoparticles need to form a stable interfacial film in order to stabilize emulsions [32]. Finkle et al. found that the efficiency of nanoparticles in stabilizing emulsions depends on the wettability of water and oil phase. The formation of a stabilizing interfacial film is only possible if the particles are wetted by both liquids [33]. Better wetting abilities and consequently better stabilization of emulsions can be achieved by particles with an anisotropic surface-functionalization with hydrophobic and hydrophilic organic coupling agents. These amphiphilic particles resemble surfactants and with this they are potential emulsifiers [10].

The present paper describes an *in situ* strategy for the amphiphilic surface-functionalization of titania nanoparticles in Pickering emulsions. Based on the particles spontaneous organization at the liquid–liquid interface, hydrophilic and hydrophobic coupling agents bind at the respective hemisphere of the particle. The following report discusses the ability of amphiphilic nanoparticles in stabilizing Pickering emulsions. Furthermore, the critical micelle concentrations (CMC) of the formed amphiphilic particles in aqueous suspensions were determined to prove their amphiphilic properties.

2. Experimental

2.1. Materials

Titanium isopropoxide, diethylene glycol monomethyl ether, polyethylene glycol monomethyl ether ($M_n = 750$ g/mol), diethyl phosphate, AIBN, bromotrimethylsilane, allylphosphonic acid diethylester and dry dichloromethane were purchased from Sigma–Aldrich. Hexamethylcyclotrisiloxane (D_3) and chlorodimethylsilane were purchased from ABCR. Allylbromide was purchased from Alfa Aesar and ^{n}BuLi (1.6 M in hexane) from Acros Organics. D_3 was distilled from CaH_2. All solvents and chemicals were dried according to standard procedures or used as received.

2.2. Characterization

Powder X-ray diffraction (XRD) data were recorded on a PANalytical X'Pert Pro diffractometer with PIXcel-detector and Cu$K\alpha$ radiation in Bragg-Brentano geometry on flat samples. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2010 microscope. The samples were attached to Plano S160-3 copper grids by dispersing them in ethanol using an ultrasound cleaning bath, adding one drop (30 μL) on the copper grid and evaporating the solvent. Fourier transform infrared spectroscopy (FT-IR) measurements were performed on a Bruker Vertex 70 Spectrometer under ambient air (40 scans at a resolution of 4 cm^{-1}) in attenuated total reflectance (ATR) mode. Thermogravimetric analysis (TGA) was performed on a Netzsch Iris TG 209C in an alumina crucible heating from room temperature to 700 °C under nitrogen followed by heating to 800 °C under oxygen with a rate of 5 K min^{-1}. Differential scanning calorimetry (DSC) measurements were carried out on a Netzsch DSC 204 F1 Phoenix calorimeter in aluminum crucibles with pierced lids, heating under nitrogen with a rate of 20 K min^{-1}. Dynamic light scattering (DLS) measurements were carried out by noninvasive backscattering on an ALV/CGS-3 compact goniometer system with an ALV/LSE-5003 multiple tau correlator at a wavelength of 632.8 nm (He–Ne Laser) and at a 90° goniometer angle. The dispersing media were purified before use with a syringe filter (200 nm mesh). The determination of the particle radius was carried out by the analysis of the correlation function via the g2(t) method followed by a number-weighting (n.w.) of the distribution function. Nitrogen sorption measurements were performed on a Sorptomatic 1900 instrument from Fisons Instruments at 77 K. The samples were degassed under vacuum at 80 °C for at least 2 h prior to measurement. The surface area was calculated according to Brunauer, Emmett, and Teller (BET). Liquid state NMR spectra were recorded on a Bruker AC 200F spectrometer (^{1}H at 200.13 MHz, ^{13}C at 50.32 MHz). Liquid-state ^{29}Si and ^{31}P NMR spectra were recorded on a Bruker Avance 300 spectrometer at 59.63 MHz and 121.48 MHz, respectively. Solid-state ^{13}C, ^{29}Si and ^{31}P NMR were recorded on a Bruker DSX Avance NMR spectrometer at 125.78 MHz, 202.48 MHz, and 99.38 MHz, respectively. Conductivity measurements were carried out with a Mettler Toledo Seven Multi instrument. UV irradiation was performed in a self-constructed reactor using a Sylvania Lynx-S blacklight compact (BL355, 9 W) lamp.