



Sodium alginate-grafted submicrometer particles display enhanced reversible aggregation/disaggregation properties

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ABSTRACT

In this article, we demonstrate that submicrometer particles with surface-grafted sodium alginate (SA) display enhanced and reversible aggregation/disaggregation properties in aqueous solution. 300 nm silica particles were first functionalized with an aminosilane coupling agent, followed by the grafting of pH-sensitive SA, as confirmed by zeta potential, XPS and FTIR analyses. The SA-modified particles show enhanced aggregation properties at acidic pH compared to unmodified silica, with a 10 times increase in average aggregate diameter. The process is reversible, as the aggregates can be broken and dispersed again when the pH is increased back to 7.0. As a result, the sedimentation rate of SA-modified particles at pH 3.0 is both significantly faster and complete compared to the unmodified particles. This enhanced aggregation is most likely due to the formation of intermolecular hydrogen bonds between neighboring SA-modified particles. This work illustrates how surface-grafted macromolecules of natural origins can be used to tune interparticle interactions, in order to improve separation processes.

1. Introduction

The controlled aggregation and dispersion of colloids is a key step in separation processes involving complex fluids comprised of immiscible liquids and/or micro/nanoparticles (e.g. Pickering emulsions), in fields such as petrochemistry (Doshi, Repo, Heiskanen, Sirvio, & Sillanpaa, 2017; Hosseini et al., 2016; Mohammadi, Rashidi, Mousavi-Dehghani, & Ghazanfari, 2016) and waste water treatment (Bakhteeva et al., 2016; Chai et al., 2015; Leudjo Taka, Pillay, & Yangkou Mbianda, 2017). When particle separation is required, it is often desirable to form aggregates and flocs as large as possible, in order to ease the separation process and decrease costs. Furthermore, if those particles were originally added to the process, for example as supports for much smaller catalytic nanoparticles (Ballauff & Lu, 2007), reversible aggregation/disaggregation behavior would be a desirable feature for recycling purpose.

The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory is a classical framework to understand and analyze the stability of colloidal suspensions (Chin, Yiakoumi, & Tsouris, 2001; Ohki & Ohshima, 1999). It models particle-particle interactions as a combination of repulsive double-layer overlap forces and attractive dispersion (van der Waals) forces (Verwey, 1947). In the energy landscape, the contribution of the electrostatic repulsion superimposes to the Van der Waals attraction

and generates an energy barrier that can reduce or inhibit particle aggregation in a suspension (Rodgers, Velicky, & Dryfe, 2015). Other forces that can also enhance or inhibit aggregation include the hydrophobic effect, hydrogen bonding, steric interactions, and depletion forces (Durand-Gasselin, Sanson, & Lequeux, 2011). As a result, the typical ways to control the aggregation level of micro/nanoparticles in a suspension are via pH and/or ionic strength (salt addition) adjustments (Yan et al., 2013), which control the electrical double layer properties. Grafting water-soluble polymer/polyelectrolyte chains on particle surface, which promote stabilization via steric interactions (Hemraz, Lu, Sunasee, & Boluk, 2014), and/or adding polyelectrolytes (Borkovec & Papastavrou, 2008) or water-soluble macromolecules (Bakumov & Kroke, 2008) are two other approaches.

Recently, nanoparticles responding reversibly to external stimuli, such as changes in pH (Chen et al., 2017; Jia et al., 2016; Stular, Jerman, Naglic, Simoncic, & Tomsic, 2017; Xu et al., 2015) or temperature (Abreu et al., 2016; Qiao, Niu, Wang, & Cao, 2010), have generated an interest for chemical engineering processes, drug delivery and biomedical applications. For example, thermo- and pH-sensitive particles have been employed to stabilize (Kawaguchi, 2008; Morelli, Holdich, & Dragosavac, 2016) and destabilize Pickering emulsions (Binks, Murakami, Armes, & Fujii, 2005), – allowing separation of the liquid constituents. They were also used as carriers for \approx 1–10 nm

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catalytic nanoparticles, easing their separation and recovery process (Ballauff & Lu, 2007). However, separating particles from a liquid phase remains an energy intensive process. As a result, the formation of flocs or aggregates facilitates separation and, if reversible, allows re-dispersing for multiple reuse.

We hypothesize that grafting sodium alginate (SA) polymer chains onto the surface of submicrometer particles can increase interparticle interactions and enhance their aggregation properties reversibly, since SA undergoes reversible gelling at low pH due to the protonation of its carboxylate groups and the formation of intermolecular hydrogen bonding. The main objective of this work is to design, synthesize and evaluate the stabilization and aggregation properties of model sub-micrometer silica particles modified with SA, and to compare the results to unmodified particles in order to confirm if the aggregation/disaggregation process is enhanced.

2. Experimental section

2.1. Materials

Sub- μm silica particles (SP) were supplied by Nippon Shokubai Trading Co., Ltd (average diameter $d = 290 \pm 13.2 \text{ nm}$ by SEM, see Supporting Information Fig. S1; specific surface area $S = 42 \pm 2 \text{ m}^2 \text{ g}^{-1}$, measured by BET with an ASAP 2020 instrument from Micromeritics Instrument Corporation). Sodium alginate (SA) from brown algae was supplied by Sigma-Aldrich (CAS. 9005-38-3, low viscosity, molecular weight $\approx 60 \text{ kDa}$, $\text{pK}_a = 3.5$) (Harnsilawat, Pongsawatmanit, & McClements, 2006). The M/G ratio ($= 1.83$) was measured at 80°C with a 10 mg ml^{-1} solution in D_2O for the ^1H NMR using a Bruker Avance 500 instrument (11.7 T) at a frequency of 500 MHz (Raheilvao, Andriamanantoanina, Heyraud & Rinaudo, 2013). 128 scans using 32 000 data points were acquired with a relaxation time (D1) of 5 s, a 4 kHz spectral window and a 30° impulsion. (3-Aminopropyl) trimethoxysilane (APTMS, 97%), *N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC, $> 98\%$), *N*-Hydroxysuccinimide (NHS, 98%) and urea ($> 98\%$) were all purchased from Sigma-Aldrich and used without further purification. Ethanol (99.8%) was obtained from Thermo Fisher Scientific. HCl 1N and NaOH 12N solutions were of analytical grade and prepared without further purification with Milli-Q water (DI water, 18.2Ω , Synergy 185 system by Fisher Scientific).

2.2. Particle surface modification

2.2.1. Silane coating grafting

In order to graft SA on silica sub- μm particles, a silane coupling agent was first covalently grafted on its surface. In a typical batch, 10 g of SP particles were added in a hydrophobized Erlenmeyer flask containing 100 ml of a 95% v/v ethanol solution and DI water, while stirring at 600–700 rpm with a magnetic stirrer (Arkles, 2006). The pH was then adjusted to 4.5–5.5 using HCl 1N. APTMS was then added dropwise while stirring at room temperature, following three targeted surface concentrations: 0.01 (SP-A), 0.1 (SP-B) and 1 (SP-C) APTMS molecule nm^{-2} (based on particle specific surface) (Pickering, Khimi, & Ilanko, 2015). For example, to treat 10 g of particles with a desired surface APTMS density of 1 molecule nm^{-2} (SP-C), 0.131 ml of APTMS was added to the reaction medium. The reaction was then carried for 12 h. The particles were collected by centrifugation (Sorvall RC 6+, Thermo Fisher Scientific) at 8000 rpm for 15 min, and cleaned by washing twice with ethanol in order to rinse off any remaining unreacted silane. The particles were finally dried in a vacuum oven at 70°C for 2 h.

2.2.2. Sodium alginate grafting

A fraction of the APTMS modified SPs were further modified by grafting SA using two different solution concentrations (Table 1): 0.1%

(1) and 1% (2) w/v. As an example, following this terminology, SP-C-2 particles were modified with a silane coating targeting an APTMS surface density of 1 APTMS molecule nm^{-2} , followed by grafting of SA with a 1% w/v solution. In a typical experiment for the preparation of SP-((B-2) or (C-2)) particles, 0.2 g of SA was first dissolved in 20 ml of DI water (1% w/v). 0.29 g of EDC and 0.17 g of NHS (EDC/NHS molar ratio = 1) were then added to the solution (EDC/-COOH molar ratio = 0.5, relative to the –COOH groups of alginate) (Giani, Fedi, & Barbucci, 2012). Then, 2 g of APTMS modified SPs were added to the mixture and the pH was adjusted to 4.5 with HCl 1N. The reaction proceeded for 15 h at room temperature and the mixture was subsequently centrifuged at 8000 rpm to collect the modified particles, which were washed with DI water 3 times. Finally, the particles were dried in a vacuum oven at 70°C for 10 h. The synthesis conditions of the surface-modified SPs are summarized in Table 1.

2.3. Particle surface characterization

2.3.1. Zeta potential measurements

Particle zeta potential (ζ) was measured with a Zetasizer Nano ZSP instrument (Malvern Instruments Ltd., Worcestershire, UK). Samples were dispersed in DI water at pH 7.0 (adjusted by adding NaOH 12N), and the measurements were performed at 25°C . ζ after modification with APTMS and SA, at different pHs (3.0, 7.0 and 10.0), were measured on at least three different samples by microelectrophoresis at a particle concentration of 0.001 g ml^{-1} . Disposable zeta potential folded capillary cells (DTS1070) were used and all samples tested were freshly prepared. The instrument determined the electrophoretic mobility, and the Smoluchowski model was then applied by the software for the calculation of ζ (Lattuada & Hatton, 2007).

2.3.2. High-resolution X-ray photoelectron spectroscopy (XPS) analysis

Elemental analyses of unmodified and modified silica particles with APTMS were realized with a VG ESCALAB 3 MKII X-ray photoelectron spectroscope (XPS) equipped with a non-monochromatic Mg K α radiation source operated at 300 W (15 kV, 20 mA). XPS analyses were conducted to detect electrons with a takeoff angle normal to the surface of the sample, yielding a probed depth around 10 nm. The pass energy was 100 eV for survey scans and 20 eV for high-resolution scans, at 1.00 and 0.05 eV increments, respectively. The pressure during analysis was kept under 5×10^{-9} Torr (6.67×10^{-11} Pa). Particles were stored under vacuum overnight prior to analysis. The results were analyzed using the Avantage XPS software package. The elemental distribution of the samples was determined on the basis of peak area comparison (C1s, O1s, etc.), normalized to their corresponding sensitivity factors, after the removal of the scattered electron background. In the case of higher resolution spectra, binding energies were referenced to the C1s peak at 285.0 eV to adjust for possible charging effects, and the Shirley method was applied for background noise subtraction. According to the data trend for each distribution of binding energy, the baseline was manually placed. Each curve is represented by its maximum binding energy (BE) in the Supporting information (Fig. S2). The species' elemental distributions are obtained via Gaussian/Lorentzian curve fitting on the original curve. The number of sub-curves and their corresponding species were obtained with full width at half maximum (fwhm) = 1.6, 1.8, 2.2, and 2.4 eV for C, O, Si, and N, respectively.

2.3.3. Fourier transform infrared (FTIR) spectroscopy analysis

A Perkin Elmer Spectrum 65 FTIR spectrometer operating in attenuated total reflectance mode (Zn/Se crystal) in the range of 650–4000 cm^{-1} was used to characterize unmodified SiO_2 sub- μm particles, as well as modified particles with APTMS and SA. For each sample, 32 scans were recorded at a resolution of 4 cm^{-1} . The spectra of SP, SP-C and SP-C-2 are presented as Supporting Information (Fig. S3).

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