3. Preparation of Aminated Silica Colloidal Particles

3.1 Introduction

Colloidal particles play an important role in studies of self-assembly and phase behavior, and can find many applications in practical materials with interesting optical properties.[67] As the individual particles are substantially larger than the atomic scale but still much smaller than a macroscopic size, these materials have unusual thermodynamic and optical properties bridging the gap between the molecular and macroscopic world.[68] This makes colloidal matter interesting, both for the fundamental research of monolayer as well as for their application. In addition, the size of the building blocks makes these materials amenable to relatively simple chemical modifications. Using chemical synthesis techniques a variety of coated colloidal core-shell particles can be prepared. For fluorescence confocal microscopy the core should not absorb any light where as should fluorescence. Recently, significant progress has been made in the preparation of large number of inorganic colloids consisting of particles of different chemical composition, shape, and size.[69] Alternate assembly of ordered multilayers of SiO_2[70] play an important role for charge separation. Krozer *et. al.*[71] work was concentrated on preparing negatively and positively silica particles for multiplayer formation they were used quartz crystal microbalance (QCM), Kunitake *et. al.* worked on the same project preparing protein and silicate multilayers and recently Markowitz *et. al.*[72] described a template-direction molecular-imprinting method to form surface-imprinted silica particles that enantio-selectively catalyze amide hydrolysis. Balladur *et. al.*[73] studied determination of the main forces driving DNA oligonucleotide adsorption into aminated silica wafers. N. A. Mamleeva, A. N. Mitrofanova, and T. N. Kropacheva studied mixed adsorption layers of chlorophylls *a* and *b* on the surface of amino silica. Now days amino silicate particles play an important role in organic as well as inorganic chemistry. The synthesis of colloidal particles is well explored and understood for wide variety of inorganic materials. However, most of the model systems with narrow size distribution consists of spherical particles it appears very difficult to synthesize because to maintain size and smoothness of particles. In other hand non-spherical particles one can synthesized very

easily. van Blaaderen *et. al.*[74] described preparation of spherical amino silicate particles with different sizes and different shapes. Before Blaaderen the synthesis of organosilica sphere is a modification of a method that was first systematically studied by Stöber *et.al.*[72] In the same year monodisperse silica spheres from tetraalkoxysilanes have been used as a model systems in many studies.[37,72-82] Monodisperse, colloidal silica spheres were prepared from tetrethoxysilane (TEOS) in mixtures of ammonia, water and ethanol. The surface of the particles could be coated through a subsequent chemical reaction with the silane coupling agent (3-aminopropyl)-triethoxysilane (APS). APS then forms a propyl amine coating on the silica particles which stabilizes them against water and organic solvents and render the surface reactive forward with acid derivatives. The qualitative reaction of APS on the silica spheres proved to be a very simple test to the presence of amino groups on the surface. If the silica particle was colored yellow in solution, the amine groups could always also be detected on dried silica. We are interesting to use of amino modified silica colloidal particles for preparation of 2 nm gaps. In such studies it is a requirement to use stable, monodisperse, unclustered colloids and also important to be able to adjust the surface properties and chemical composition of the particles. Preparation and study of 2 nm gaps (yoctowells) shall be discussed in three chapters. In this chapter, the preparation and characterization of aminated silica particles shall be discussed.

3.2 Preparation of Amino Modified Silica Colloids

The silicate particles developed by van Blaaderen, are produced by hydrolysis of tetra ethoxysilane (TEOS) with aqueous ammonia in ethanol and are stabilized by subsequent treatment with (3-aminopropyl)-triethoxysilane.[74] Spherical particles with a diameter between 20 nm and 150 nm depending on the concentration and hydrolysis time. The smaller 20 nm particles showed, however, a rough surface in transmission electron microscopy (TEM) which was not appropriate for the self-assembly of rigid membranes and defined nanometer gaps.[23-25] The smallest uniform particles with a perfectly smooth surface had a uniform diameter of 100 ± 10 nm (fig. 3.1).

The conditions to produce such smooth 100 nm particles in 1-10 g quantities included a purification by repeated precipitation at pH 2 and centrifugation, followed by resuspensi--on at pH 11. These particles were stable and could be stored indefinitely as a moist powder. When resuspended in milli-Q water at pH 7-8, transmission electron microscopy (TEM) always showed observed ill-defined networks of 100-nm spheres with a smooth surface.

For preparation of aminated silica colloidal particles we followed Blaaderen[74] method with modified procedure for achieving 100 nm size with smooth surface. The smoothness, size, and chemical self-assembly procedures were optimized in order to establish a closed monolayer with modest curvature and containing functional gaps. Furthermore, the amino silica particles are soluble in water and many solvents, and the chemistry of the amino groups is versatile enough to produce all kinds of modification on surface.

Finally we examined the smoothness and size of particles by transmission electron microscopy (TEM) and observed ill-defined networks of 100-nm spheres with a smooth surface. We applied 100 nm smooth particle for two step self assembly however, smaller than 100 nm particles shows rough surface.
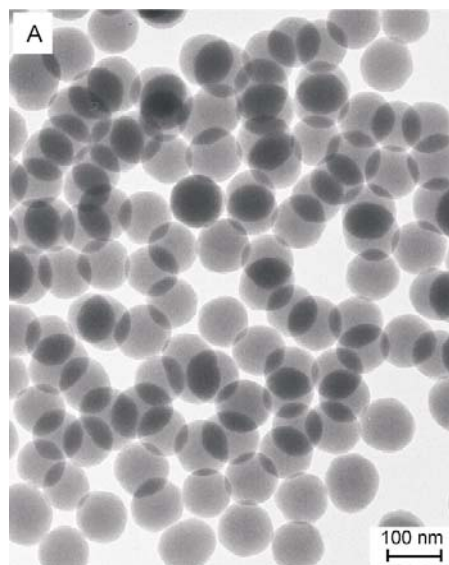
Figure 3.1 Transmission electron micrographs (TEM) of synthetic aminated silica particles.

Protection of the silicate surface by the thin propylamine coating as introduced by van Blaaderen[74] solved the major problems, which were encountered with commercial CabOSil⁻ (i) no detectable roughness or irreversible aggregation occurred, (ii) organic solvents did not cause any swelling or formation of jelly like protrusions, (iii) self-assembly processes on the amino surface gave closed rigid monolayers with form-stable gaps (ill-defined, larger gaps occurred only to an acceptable extent of about 10%) in chapter 4.3 (iv) no disturbing photochemistry of the carrier competed with that of the adsorbed dyes, and (v) the electro neutral porphyrin spots on the amine surface did not intervene with reversible precipitation-dissolution cycles upon pH changes.

3.3.1 Monomeric porphyrin dots on amino silica colloids

In the first step of self-assembly, *meso*-(tetra-*m*-benzoyl chloride) porphyrin **26a**, was applied first it did not work at all. Which were to be expected typical for commercial inorganic CabOSil⁻ particles. This activated porphyrin presumably formed domains on the silicate surface rather than spots of monomeric porphyrins, because it readily formed anhydride dimers upon partial hydrolysis of the acid chlorides, which could not be totally avoided. The more stable mixed anhydrides **26b** made with ethyl chloroformate were much more reliable (fig. 3.2).
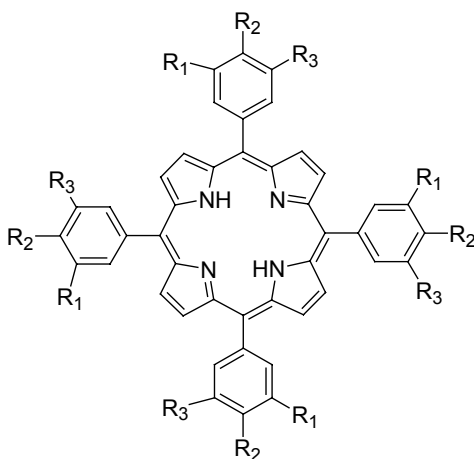
26   a R_1 = COCl, R_2, R_3=H

     b R_1 = COCOOEt, R_2, R_3=H

     c R_1, R_3=COCOOEt, R_2=H

The amino-coated silica particles were first dispersed in ethanol by mild sonication and centrifuged and redispersed 4 times. The same procedure was repeated with dichloromethane suspensions. The particles were finally suspended in 60 mL dichloromethane containing triethylamine (1 mL) and mixed with 1 mg of the *meso*-(tetra-*m*-benzoyl acid) porphyrin **26a** or the mixed anhydride with ethyl chloroformate **26b**. The particles, which are sketched remained soluble in dichloromethane as well as in water. If the corresponding octacarboxy porphyrin (OCP) **26c** with four *meta*-carboxyl substituents on both sides of the porphyrin plane was applied instead, the silicate particles aggregated strongly at all pH values between 2 and 12. It was thus not possible to bind this charged porphyrin onto the surface of the amino silica particles.
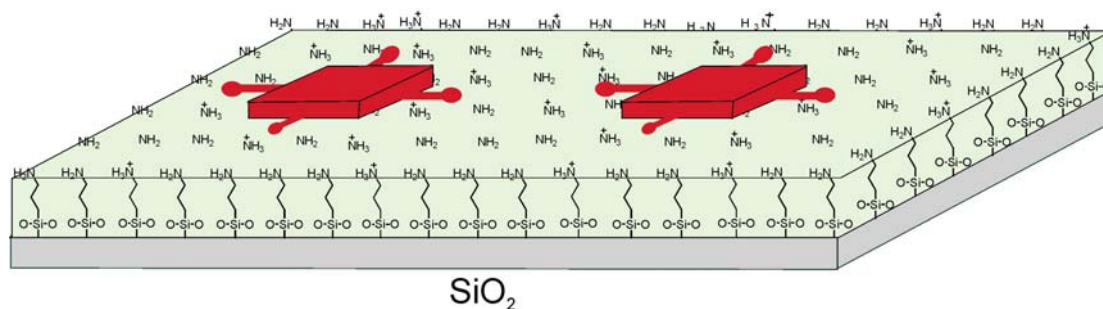
Figure 3.2 Monomeric porphyrin **26b** dots on aminated silica particles

3.3.2 pH Dependent aggregation of particles

Smooth and nonswelling spherical silica particles with a diameter of 100 nm and an aminopropyl coating are soluble in water at pH 11, coagulate quickly at pH 3, and resuspended at pH 9. Electron microscopy as well as visible spectra of covalently attached porphyrins indicate the aggregation state of the particles. The Soret band of the silicate-bound porphyrintetraamide **30** appears at 413 nm (half-width, 17 nm) which is similar to that of the tetraethylester porphyrin **26** in ethanol (418 and 15 nm). The intensity and line-width of the Soret band changed drastically upon aggregation of the aminated silica particles. At pH 11, the particles appear monomeric in TEMs, and the Soret band has a line-width close to that of monomeric TPP derivatives in solution, namely 17 nm. Upon acidification and formation of large numbers of cationic ammonium groups, we expected even better water solubility, but this was surprisingly not the case. At pH 7, the particles began to aggregate as indicated by TEM pictures as well as line-broadening in porphyrin spectra; the Soret band's half-width broadened from 17 to 34 nm. This could have been traced back to $NH_2{\rightarrow}NH_3^+$ hydrogen bonding. At pH 3, however, where only well-hydrated NH_3^+ should be present, the particles even precipitated. Addition of sodium hydroxide lead to a quantitative reversal of the aggregation, and the half-width of the Soret band goes back to 17 nm at pH 11 (Figure 3.3a). The Q-band near 550 nm was more sensitive to changes in the environment than the Soret band (Figure 3.3b). Tetraethylester porphyrin **26** absorbs at 549 nm in ethanol, at 557 in water.
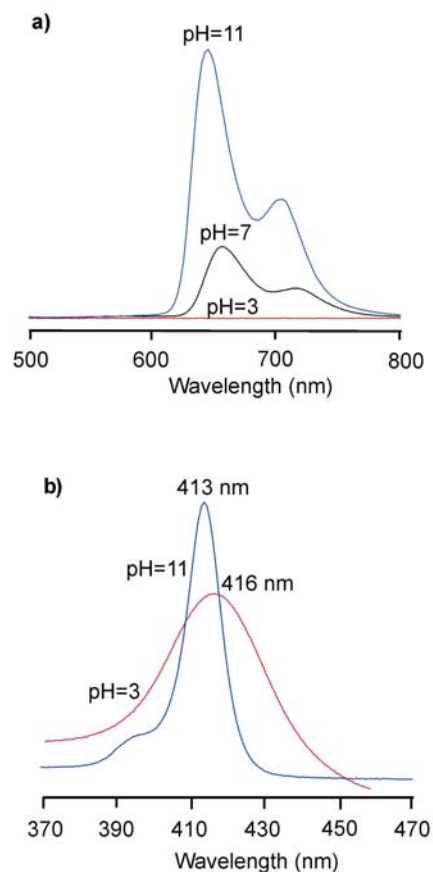
Figure 3.3 (a) Fluorescence of porphyrin **26b** bound to aminated silica particles, at pH 11 aminopropyl coating are soluble in water, coagulate quickly at pH 3 (b) absorption spectra of the silicate particles are shows same behavior.

From figure 3.3a shows that at different pH values more NH_3^+ groups lead to more hydrogen bonds and to aggregation, to a broadening of absorption peaks and to a loss of fluorescence. The aggregation of the particles was fully reversed at pH 11 after addition of sodium hydroxide.

The aminopropyl-coated silica particles flocculated only slowly (>3 h) in water at pH 11 and not at all when 50% ethanol was added to this solution. Ionization of the amino groups had, surprisingly, no stabilizing effect. On the contrary, at pH 3, immediate and complete coagulation took place. Similar observations have been made with propionate-coated gold particles. These particles coagulated rapidly independent of ionization of the coating. Only hydroxylation of naked citrate gold colloids had a strong stabilizing effect

above pH 11.[83] We assume that the aminated silica particles also add hydroxyl ions, which deprotonate some remaining Si-OH groups forming silicate anions next to the NH_2 groups. Repulsive interactions between these hidden negative charges then prevent coagulation. The extra stabilization by ethanol is probably caused by solvation of the propyl groups. At low pH, the silicate layer is probably protonated and loses its repulsive character, whereas the ammonium polyelectrolytes stick together via ion pairs and hydrogen bonding. This corresponds to the cationic analogue of acid soaps.[84]

3.4 Conclusion

Monodisperse, colloidal silica spheres were prepared from tetrethoxysilane (TEOS) in mixtures of ammonia, water and ethanol. The surface of the particles could be coated through a subsequent chemical reaction with the silane coupling agent (3-aminopropyl)-triethoxysilane (APS). APS then forms a propyl amine coating on the silica particles which stabilizes them against water and organic solvents and render the surface reactive forward with acid derivatives. Spherical particles with a diameter between 20 nm and 150 nm depending on the concentration and hydrolysis time. The smaller 20 nm particles showed, however, a rough surface in transmission electron microscopy (TEM) which was not appropriate for the self-assembly of rigid membranes and defined nanometer gaps. The smallest uniform particles with a perfectly smooth surface had a uniform diameter of 100 ± 10 nm and it produced in gram scale and they are soluble in water at pH 11, coagulated quickly at pH 3, and redissolve at pH 9. Applied electron microscopy as well as visible spectra of covalently attached porphyrins indicate the aggregation state of the particles. The aminated silica particles introduced by van Blaaderen proved to be an exceptionally stable and versatile substrate for the establishment of rigid, closed membranes containing form-stable nanometer gaps and photoactive heterodimers in aqueous media and organic solvents. Their photochemical and electronic inertness limits their usefulness to that of a carrier system with a smooth and reactive surface, but in this respect, they are unsurpassed by any other colloidal particle.