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# Aggregation behavior of one-patch inverse patchy particles: an experimental and numerical study

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## Abstract

### Hypothesis

Inverse patchy colloids (IPCs) are promising building blocks to create new materials using their self-organization. For example, the control of the self-assembly of oxide-based IPCs is interesting for ceramic shaping. Thus, the synthesis of silica based IPCs as well as a detailed study of their behavior in suspension are presented in this paper.

### Experiments

Fluorescent silica particles are partially modified in surface by grafting amine groups using a Pickering emulsion route. Zeta potential measurements, sedimentation tests and confocal microscopy observations are carried out to analyze the aggregation of the obtained particles in aqueous suspension as a function of the patch size and of the pH. Brownian dynamics simulations are also performed to better understand the aggregate structures.

### Findings

The aggregation of the synthesized silica-based IPCs can be tuned by modifying both the patch size and the pH of the suspensions. Different aggregate structures, from elongated to compact ones, are obtained. This control of aggregation makes such particles promising to build new ceramic materials.

**Keywords:** Colloid; Aggregation; Inverse patchy particles; Brownian dynamics simulations; Confocal microscopy

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## 1. Introduction

Colloid science is crossing multiple scientific disciplines, such as food and nutrition, cosmetics, biology, soft matter, nanophysics, or nanomaterials [1]. Colloidal interactions depend on the surface chemistry and the chemical environment of the colloids, which both determine their surface charge, and their hydrophilic or hydrophobic properties. Researchers have addressed this field from a long time with both experimental and fundamental studies, as many real problems may be solved through a better understanding and control of colloidal interactions; for example aggregation in biological fluids, or clogging in industrial processes. To describe real systems with more accuracy (for example proteins often carry different surface charges), anisotropic particles with inhomogeneous surface properties have been studied. Various morphologies exist: Janus particles, which present two different hemispheres, or patchy particles, with one or several different chemical functions or materials present on a smaller fraction of the surface. These anisotropic particles are able to assemble in more complex structures to achieve original clusters, mimicking molecular or crystal arrangements at the colloidal scale [2, 3]. The synthesis of Janus and patchy particles remains a challenge. Many different techniques have been proposed in the literature [4], but still, breaking the symmetry at the surface of a colloid remains a hard task. The first approach consists in toposelective modifications. The very first example of anisotropic particles synthesis was described by de Gennes in 1992 [5], and consisted of glass microspheres around  $50\text{ }\mu\text{m}$  in diameter deposited on a solid substrate and embedded in a cellulose varnish of controllable thickness. The unprotected hemisphere was treated with a silane to render it hydrophobic. Since then, this method was applied to many colloids of different nature and size [6, 7, 8].  $1\text{ }\mu\text{m}$  silica spheres could be immobilized in a photoresist layer, before an  $\text{O}_2$  plasma etching was applied to remove partially the masking layer [6]. By controlling the time and the power of the plasma, it was possible to control the photoresist removal. Then gold and titanium nanolayers were deposited by electron-beam sputtering to modify the available surface. More recently,  $15\text{ nm}$  platinum layer was deposited on silica particles by a simple vertical electron-beam method [7]. The resulting Janus colloids showed self-propelling motion under an electric field, and could be used as programmable colloidal shuttles to pick up, transfer and release cargo made of colloidal polymers of opposite surface charges. In a similar way, a monolayer of polymer spheres deposited on a substrate could be covered by a

nanometric gold layer by metal evaporation [9], or by metal sputtering [10]. Another toposelective technique is the microcontact printing, using a PDMS stamp allowing the transfer of molecules to the colloids, such as surfactants [11] or polyelectrolytes [12], and giving the possibility of multi-patches synthesis. Other techniques can be found in the literature such as lithography [13], microfluidics [14, 15], or Langmuir-Blodgett [16]. One limitation of all these methods is the low production yield, as only one monolayer of colloids is disposed at one interface. In that context the use of Pickering emulsions is a different promising approach which deals with much more particles by synthesis [17]. This method consists in preparing an O/W emulsion stabilized by colloids at moderate temperature (50 - 70°C) in order to have a liquid oil phase which solidifies during cooling at ambient temperature. Colloids are then immobilized at the O/W interface, allowing surface modification, before being released by dissolving the oil (in general paraffin). Granicks group first prepared dipolar silica particles with an aminosilane introduced in solution [18], or in vapor-phase [19]. They showed how the silica surface available was directly controlled by the contact angle at the O/W interface and thus by the surfactant concentration [20]. Other authors have then extended this technique to produce fluorinated silica [21], to decorate silica sheets with gold nanoparticles [22], or to create a TiO<sub>2</sub> layer on silica [23] for catalytic applications.

In this paper, the Pickering emulsion synthesis has been selected to produce one-patch inverse patchy colloids (IPCs), also called zwitterionic particles. These are anisotropic particles showing attractive interactions between the patch and the unpatched surface, while patch-patch and body-body interactions are repulsive. Such organic IPC have been for example proposed as drug delivery carriers [24, 25]. Our goal is to present a comparative study with experimental and numerical results on inorganic IPCs, in order to get a better understanding of their interactions, and to control their self-assembly in future applications. Some previous studies have already shown some comparisons between experimental suspensions and numerical simulations. One can cite Hong et al. for example, who have studied experimentally and numerically amphoteric Janus particles [26]. They have shown that aggregation forms compact aggregates, in which particles are oriented. Aggregation of two-patches IPCs has been also studied in details experimentally and numerically by Bianchi et al. [27, 28]

In this paper, first, the synthesis of one-patch IPCs of fluorescent silica will be presented. Then different conditions of aggregation will be studied, by varying the size of the patch,

as well as the surface charges by varying the pH. The aggregates formed will be observed directly in suspension by confocal microscopy. They will be compared to those obtained using Brownian dynamics simulations.

## 2. Materials and experimental methods

### 2.1. Chemicals

Tetraethyl orthosilicate 98% (TEOS) and ammonium hydroxide  $\text{NH}_4\text{OH}$  28% were purchased from Acros Organic. The fluorescein isothiocyanate isomer I 90% (FITC) and the 3-aminopropyltriethoxysilane 99% (APTES) were purchased from Sigma-Aldrich. Absolute ethanol and paraffin wax were provided by BDH Prolabo and Fisher Scientific, respectively. Didodecyldimethylammonium bromide (DDAB) was supplied by Sigma Aldrich and cyclohexane 99% was purchased from Alfa Aesar. All products were used as received.

### 2.2. Particles synthesis

In this study, home-made fluorescent silica particles are surface modified on only one part by APTES to obtain amphoteric particles. For that, a Pickering emulsion route as proposed by Hong *et al.* [18] is used. The different steps of synthesis are described in the following.

*Synthesis of fluorescent silica particles.* Fluorescent silica particles are synthesized according to the protocol described in Reference 29. It is a modified Stöber synthesis consisting in two steps. In a first one, monodispersed silica particles are synthesized by a classical Stöber method which consists in the hydrolysis of TEOS in a mixture of ethanol, water and ammonia. Then the fluorescent dye (here the FITC) previously bonded with the APTES is added. In a second step, in order to minimize the presence of the dye on the particle surface, a silica shell is grown by a dropwise addition of TEOS. Following the protocol presented in Reference 29, fluorescent core-shell silica particles of around 600 nm are obtained.

*Pickering emulsions.* In order to modify partially the fluorescent silica particles, it is necessary to hide a part of them. In this study, the particles are trapped in solid paraffin droplets as proposed in Reference 18. For that, Pickering emulsions are prepared with paraffin wax, water and silica particles [30]. To obtain partially hydrophobic silica, particles were modified by DDAB. 140 mg of silica particles are thus introduced in 14 mL of osmosed water with the DDAB. The suspensions are stirred at least 12 h to allow the DDAB adsorption on the silica

particles. As already shown in References [20, 30] the quantity of DDAB fix the contact angle between the particle and the wax, and therefore the depth of penetration of silica particles in the wax droplets. By modifying the quantity of DDAB, the surface available for modification and therefore the patch size of the future IPCs can be tuned. In the following, three different amounts of DDAB ( $R = m_{DDAB}/m_{SiO_2}$  with  $m_{DDAB}$  the DDAB mass and  $m_{SiO_2}$  the silica mass) will be used:  $R = 5 \times 10^{-4}$ ,  $1 \times 10^{-3}$  and  $1.5 \times 10^{-3}$ . Pickering emulsions are then prepared by adding 1 g of paraffin wax in the DDAB-silica suspension and by heating the whole at 90°C to melt the wax. Emulsification is performed using Ultra Turrax stirring at 19000rpm for 1 minute. Emulsions are then cooled down at room temperature to ensure the solidification of the stabilized wax droplets. At this stage, silica particles are trapped on solid wax droplets embedded in water.

*APTES grafting.* Naturally, silica particles are negatively charged in aqueous suspensions. In order to have amphoteric particles, the not hidden part of particles will be modified by grafting APTES. Generally, this grafting is performed in anhydrous solvents or in ethanol based solvents in order to better control the rate of grafting [31, 32, 33]. Indeed, in water, the APTES molecules can react with themselves limiting the grafting on silica [34, 35]. Many anhydrous solvents dissolve the wax and thus can not be used in this study. Moreover, it is known that ethanol can release silica particles from the solid wax droplets [20, 30] which makes this solvent also not suitable for this study. That is why, even if grafting is not well controlled, APTES will be grafted directly in water. Cuoq *et al.* have indeed shown that a good rate of APTES grafting can be also obtained in water [34]. In this study, APTES is added in the cold suspensions under stirring. Stirring is maintained over 20 minutes. Then the emulsion is filtered on a Buchner funnel using 10 cm diameter Whatman Gr.541 filter paper and rinsed with deionized water. The solid wax droplets are then dried at room temperature during 48 h.

*Wax removal.* The last stage of the synthesis consists in releasing the amphoteric particles from the wax droplets. For that, wax is dissolved using cyclohexane. To try to isolate only the synthesized IPCs, after dissolution, the mixture was centrifuged at 3000 rpm and powder was obtained. However, it appeared that the obtained particles are mixed with small pieces of wax. Moreover, the obtained particles are found hydrophobic because DDAB is still adsorbed on them. Instead of centrifugation, a method using settling has been preferred. In order to

detach the DDAB, a HCl solution at pH 4 has been added in the beaker avoiding swirling and stirred slowly over the night in order to avoid emulsification. After, the mixture is let to settle in a separatory funnel. The two immiscible phases are observed and with time, colloids settle from the upper cyclohexane phase to the lower HCl solution. In HCl, the particles are aggregated which facilitates their sedimentation. At the end, the settled colloids in HCl solution are less hydrophobic because they are not trapped at the interface. The aqueous phase is isolated and centrifuged at 3000 rpm. Powder is then dispersed another time 24 h in HCl solution at pH 4 in order to remove all the remaining DDAB. After that, the powder is centrifuged, rinsed 4 times in osmosed water and dried at 50°C during 16 h. It has been verified that the obtained powders dispersed in water at a basic pH are not able to promote the formation of a wax in water emulsion, which proves that the DDAB has been removed from the particles.

### *2.3. Characterization techniques*

Solid wax droplets are observed by scanning electron microscopy (SEM) on a SEM-Quanta FEG - 450. To avoid charging effects, a thin film of platinum is deposited onto samples. As proposed in References 20 and 30, SEM is used to determine the penetration depth of particles in the solid wax droplets. For that, the emulsions were rinsed by ethanol to remove the silica from the wax. By comparing the diameter of the voids left in the wax and the silica diameter, the penetration depth or the proportion of silica surface area taken up in the wax is evaluated.

Zeta potential is measured using a Zetasizer Nano ZS from Malvern. For that, suspensions of 0.3vol% are prepared in osmosed water and pH was adjusted with NaOH 0.1 M and HCl 0.1 M.

Aggregation is evaluated performing sedimentation tests. Suspensions are prepared with an amount of 1vol% of silica particle at different pH. After preparation, the suspensions are introduced into closed tubes and are allowed to settle. Analyses are performed after 24 h. The cloudier the supernatant and the lower the sediment, the more stable the suspension. Because silica particles are labeled by FITC, suspensions are observed by a confocal microscope LSM880 from Zeiss. Suspensions are deposited between slide and slip cover. Images are treated with ImageJ.

### 3. Simulation methods

Brownian dynamics simulations will be performed considering a 'raspberry' representation of IPCs. Details on this simulation technique can be found in Reference 36. To summarize, each colloid is represented by a hollow sphere decorated by 92 beads (see Figure 4), which will electrostatically interact with each other.

The interaction between IPCs is modeled here through a DLVO potential (Derjaguin, Landau, Verwey, Overbeek) [37, 38], which is the sum of two contributions: one attractive due to van der Waals interactions, and an electrostatic one due to the surface charges of the colloids. In this numerical study, the attractive interaction is applied as a central force and is expressed as:

$$V_{IJ}^{vdW} = -\frac{A_{IJ}}{6} \left[ \frac{2a^2}{r_{IJ}^2 - (2a)^2} + \frac{2a^2}{r_{IJ}^2} + \ln \left( \frac{r_{IJ}^2 - (2a)^2}{r_{IJ}^2} \right) \right] \quad (1)$$

where  $A_{IJ}$  is the Hamaker constant,  $a$  is the radius of the IPCs and  $r_{IJ}$  is the center-to-center distance between IPCs  $I$  and  $J$ . Here  $a = 300 \text{ nm}$  and  $A_{IJ} = 4.6 \times 10^{-21} \text{ J}$  [39]. The electrostatic interaction applied on an IPC is obtained by the sum of the electrostatic interactions applied on its beads, which are represented by a Hogg Healy Fuerstenau (HHF) potential [40]:

$$V_{ij}^{HHF_{bead}} = \pi\epsilon \frac{4a_b}{2} (\psi_i^2 + \psi_j^2) \left[ \frac{2\psi_i\psi_j}{\psi_i^2 + \psi_j^2} \ln \left( \frac{1 + \exp(-\kappa h_{ij})}{1 - \exp(-\kappa h_{ij})} \right) + \ln(1 - \exp(-2\kappa h_{ij})) \right] \quad (2)$$

where  $\psi_i$  is the surface potential of bead  $i$ ,  $h_{ij}$  is the surface-to-surface distance between beads  $i$  and  $j$ ,  $\kappa$  the inverse of Debye length ( $\kappa = 10^8 \text{ m}^{-1}$ ) and  $a_b$  is the bead radius (here  $a_b = 66.58 \text{ nm}$ ). As proposed in Reference 36, a factor 4 is used in the HHF expression, which allows to reproduce the behavior of suspensions, where heteroaggregation occurs. To avoid interpenetration of IPCs at the contact, the attractive interactions are cut at  $-14k_B T$  and a linear repulsive potential is introduced as a central interaction when IPCs are in contact.

Both the translational and the rotational motions of IPCs are introduced in Brownian dynamics simulations. Simulations are performed with 1500 IPCs in a cubic box with periodic conditions. A volume fraction of 3vol% is used. Simulations have been performed with a time step of  $10^{-7} \text{ s}$ . Results are analyzed at 10 s. Because of the large number of beads used in these simulations, simulations have been performed thanks to a parallelized home-made code developed for calculations on GPU (Graphics Processing Unit) based on the strategies presented in Reference 41.



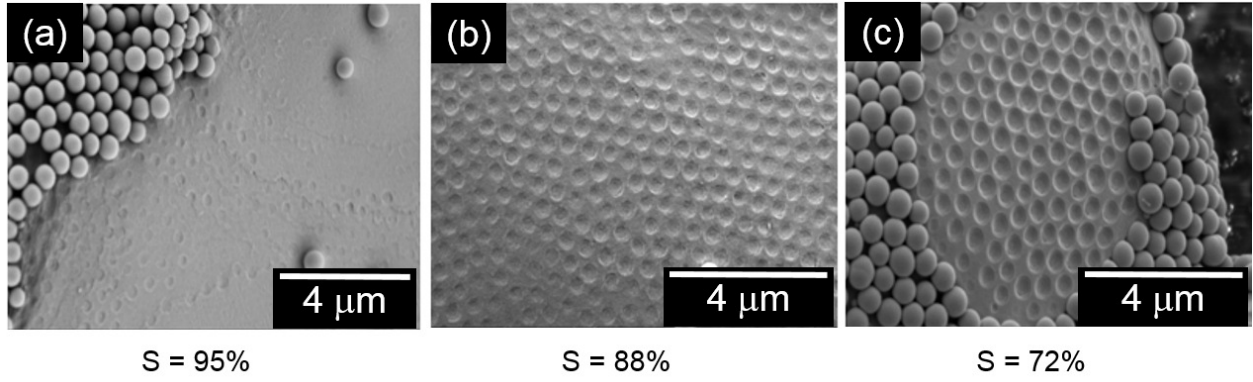


Figure 1: SEM images of solid wax/silica droplets rinsed with ethanol at various concentrations of DDAB: (a)  $R = 5 \times 10^{-4}$ , (b)  $R = 1 \times 10^{-3}$  and (c)  $R = 1.5 \times 10^{-3}$ .  $S$  represents the proportion of silica surface area that will be modified by APTES.

## 4. Results and discussion

### 4.1. Characterization of the synthesized one-patch IPCs

As already mentioned, the quantity of DDAB used to prepare the wax-in-water Pickering emulsion determine the depth of silica penetration in the wax and thus the surface that can be modified by APTES. To quantify this surface, the cold emulsions have been rinsed by ethanol in order to remove some silica particles from the wax. The obtained droplets, observed by SEM, are shown in Figure 1. By measuring the diameter of the indentations, the depth of penetration and therefore the surface area accessible for modification have been determined. Modified surface area proportions of  $S = 95\%$ ,  $S = 88\%$  and  $S = 72\%$  have been obtained with the DDAB ratios  $R = 5 \times 10^{-4}$ ,  $1 \times 10^{-3}$  and  $1.5 \times 10^{-3}$ , respectively. In order to check that the APTES is grafted on the silica during the synthesis, zeta potential measurements have been performed on the synthesized IPCs as reported in Figure 2a. In comparison, the zeta potential measured for the raw silica particles ( $S=0\%$ ) as well as the zeta potential of silica particles whose surface is totally grafted by APTES ( $S=100\%$ ) are also reported. It can be observed that the raw silica have a negative zeta potential over the whole pH range whereas the totally grafted silica particles show an isoelectric point around  $\text{pH}=7.5$ . Below this pH the modified silica particles are positively charged, due to the protonation of the  $\text{NH}_2$  groups of APTES, whereas above this pH they are negatively charged. For the IPCs, zeta potential curves are found in between the curves for  $S=0\%$  and  $S=100\%$ , which is in agreement with partial particle coverage by APTES. Moreover, the greater the

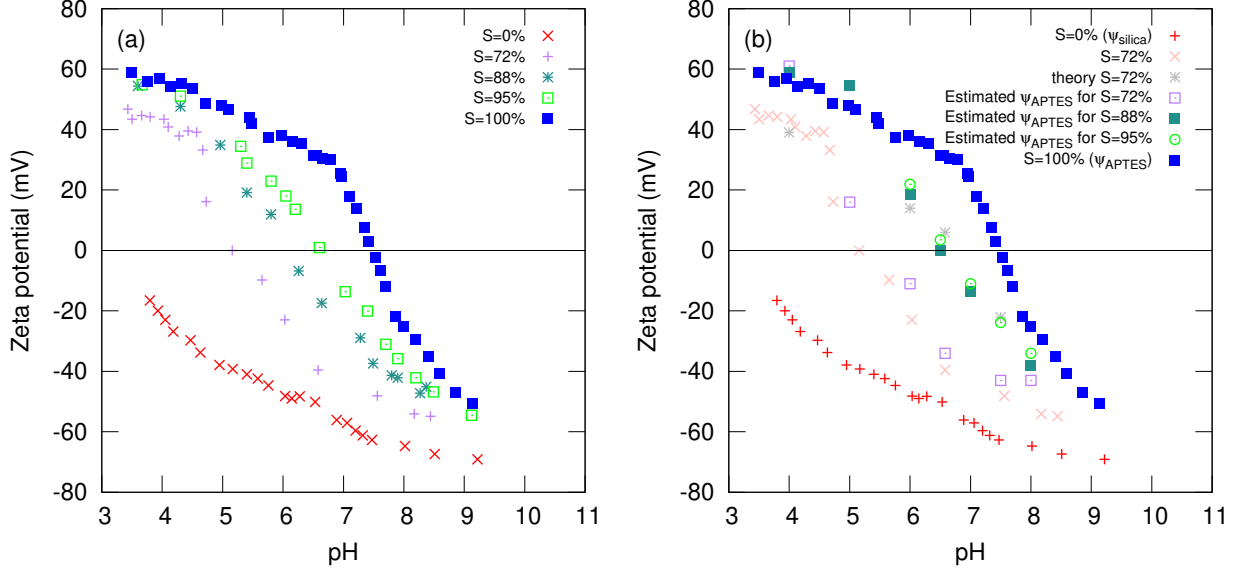


Figure 2: (a) Evolution of the experimental zeta potential of IPCs as a function of the pH. By comparison, results obtained with raw silica particle ( $S = 0\%$ ) and silica fully modified ( $S = 100\%$ ) are reported. (b) Calculated surface potentials for  $S = 72\%$  considering that the patch reacts as the raw silica and the unpatched part as the full APTES modified silica (theory  $S=72\%$ ). Calculated surface potentials of the APTES modified parts of IPCs for  $S=72\%$  (Estimated  $\psi_{APTES}$  for  $S=72\%$ ),  $S=88\%$  (Estimated  $\psi_{APTES}$  for  $S=88\%$ ) and  $S=95\%$  (Estimated  $\psi_{APTES}$  for  $S=95\%$ ).

proportion of modified surface area, the closer the curve is to the case  $S=100\%$ .

To understand the behavior of amphoteric particle suspensions and for their simulation, it is important to know the electric potential at the surface of each part of the particles as a function of the pH: the unmodified part called “silica” and the modified part called “APTES”. We discuss this point in the following.

A reasonable hypothesis would be to consider that the potential of the unmodified part is that of the initial silica,  $\psi_{silica} = \psi_{0\%}$  (the potential measured for  $S = 0\%$ ), and that the potential of the modified part is that measured for the completely modified silica,  $\psi_{APTES} = \psi_{100\%}$  (the potential measured for  $S = 100\%$ ). At this point, at  $pH=7.5$ , we would expect that the suspension would not be stable since  $\psi_{100\%}$  is close to 0, but sedimentation tests show on the contrary that the suspension is stable at this pH. On the other hand, knowing the surface potential, the following formula allows us to go up to the corresponding surface charge

quantity [42]:

$$Z = 4\pi\epsilon \frac{k_B T}{ze^2} \kappa a^2 \left[ 2 \sinh \left( \frac{1}{2} \frac{ze\psi}{k_B T} \right) + \frac{4}{\kappa a} \tanh \left( \frac{1}{4} \frac{ze\psi}{k_B T} \right) \right], \quad (3)$$

where  $e$  is the elementary charge and  $z$  the electrolyte valence (here  $z=1$ ). Thus, by using the surface proportion at  $\psi_{0\%}$  and that at  $\psi_{100\%}$ , we can estimate the number of charges of the unmodified part  $Z_{silica}$  and that of the modified part  $Z_{APTES}$ , i.e., by summing up the total number of charges  $Z_T$ , and thus, by adjustment using equation 3, a theoretical surface potential  $\psi_{theo}$ . This estimate was made for IPCs at  $S = 72\%$  and the result is shown in Figure 2b. It is clearly observed that the calculated curve does not correspond to the measured one.

These two disagreements could be explained by a grafting rate of APTES, while the particles are embedded in the wax, lower than that obtained for completely uncovered particles ( $S = 100\%$ ), without the wax. As already mentioned, the APTES grafting in water is difficult to control because of its self-reaction and moreover, in case of Pickering emulsions, the presence of different phases can also affect this grafting. This would mean that  $\psi_{APTES}$  is different from  $\psi_{100\%}$  and lower.

Another hypothesis for estimating  $\psi_{APTES}$  is to deduce the total number of charges  $Z_T$  from the measured zeta potential, estimate the number of charges of the unmodified part  $Z_{silica}$  from the proportion of unmodified area and  $\psi_{0\%}$  ( $\psi_{silica}$  is assumed to be equal to  $\psi_{0\%}$ ), deduce  $Z_{APTES}$  from this and go back to  $\psi_{APTES}$  by fitting with equation 3.

These estimations, shown in Figure 2b, reveal that the surface potential of modified part may be lower than  $\psi_{APTES}$  in a pH range comprised in [5-7.5] for the case  $S = 72\%$  and in a pH range of [6-7.5] for the cases  $S = 88\%$  and  $95\%$ . For  $S = 72\%$ , the PCN of the modified part is estimated at 5.5 and thus at pH 7.5, both parts of particles may be negatively charged and thus suspension must be stable, which is in agreement with the previous sedimentation tests.

In the following, for each IPC, aggregation will be analyzed for three different pH. The first one,  $pH_a$ , corresponds to the case where the APTES modified surface is positively charged and the unmodified part is negatively charged. The second one,  $pH_n$ , corresponds to a pH where the APTES surface modified has surface potential around 0. And the third one,  $pH_b$ , corresponds to the case where both parts of IPCs are negatively charged. In the following, a pH in the range [4.5-5] is chosen as  $pH_a$  and a pH in the range [7.5-8] as  $pH_b$  whatever

the size of the modified surface. Because of the difficulty to evaluate precisely the PCN of the modified part due the rough estimations used in the model as well as the experimental difficulties to obtain precise measurements of zeta potential near the isoelectric point,  $\text{pH}_n$  is chosen in a larger range [5.5-6.5]. At  $\text{pH}_n$  it is verified by sedimentation tests that the suspension aggregate and that, for higher pH, it becomes stable.

#### 4.2. Study of one-patch IPC aggregation

Sedimentation tests are performed with colloidal suspensions prepared with a volume fraction of 1vol% for the different pH reported in the previous section. Figure 3 shows the results obtained at 24 h. Moreover, because particles are labeled with FITC, the suspensions are observed by confocal microscopy as also shown in Figure 3.

For  $\text{pH}_b$ , it is observed that all the suspensions are stable. The sediments are low and only individual particles are observed by microscopy. According to Figure 2, at  $\text{pH}_b$  both parts of IPCs are negatively charged and thus aggregation of IPCs is unlikely. For  $\text{pH}_n$ , the raw silica is stable and negatively charged. However, this pH is near the isoelectric point of the APTES part of the IPCs, which aggregate because of the van der Waals interactions. For IPC suspensions, higher sediment is observed in the sedimentation tubes and aggregates are clearly observed by confocal microscopy whatever the patch size. As for  $\text{pH}_a$ , the totally modified particles ( $S=100\%$ ) and the raw silica particles ( $S=0\%$ ) are stable. Nevertheless, in case  $S=100\%$ , particles are positively charged and in case  $S=0\%$  particles are negatively charged (see Figure 2). For IPC suspensions at  $\text{pH}_a$ , the sediments are slightly lower than those obtained at  $\text{pH}_n$ . However they are higher than the sediments obtained at  $\text{pH}_b$ , which is explained by an aggregation of IPCs in suspension. Aggregates are indeed observed by confocal microscopy. At this pH, the patch and the unpatched parts of IPCs are oppositely charged and aggregation can be explained by the attractions between the two parts of IPCs. For the largest patch ( $S=72\%$ ), confocal microscopy observations reveal that aggregates are compact (see Figure 3). To better understand the aggregation mechanisms in IPC suspensions, Brownian dynamics simulations have been used.

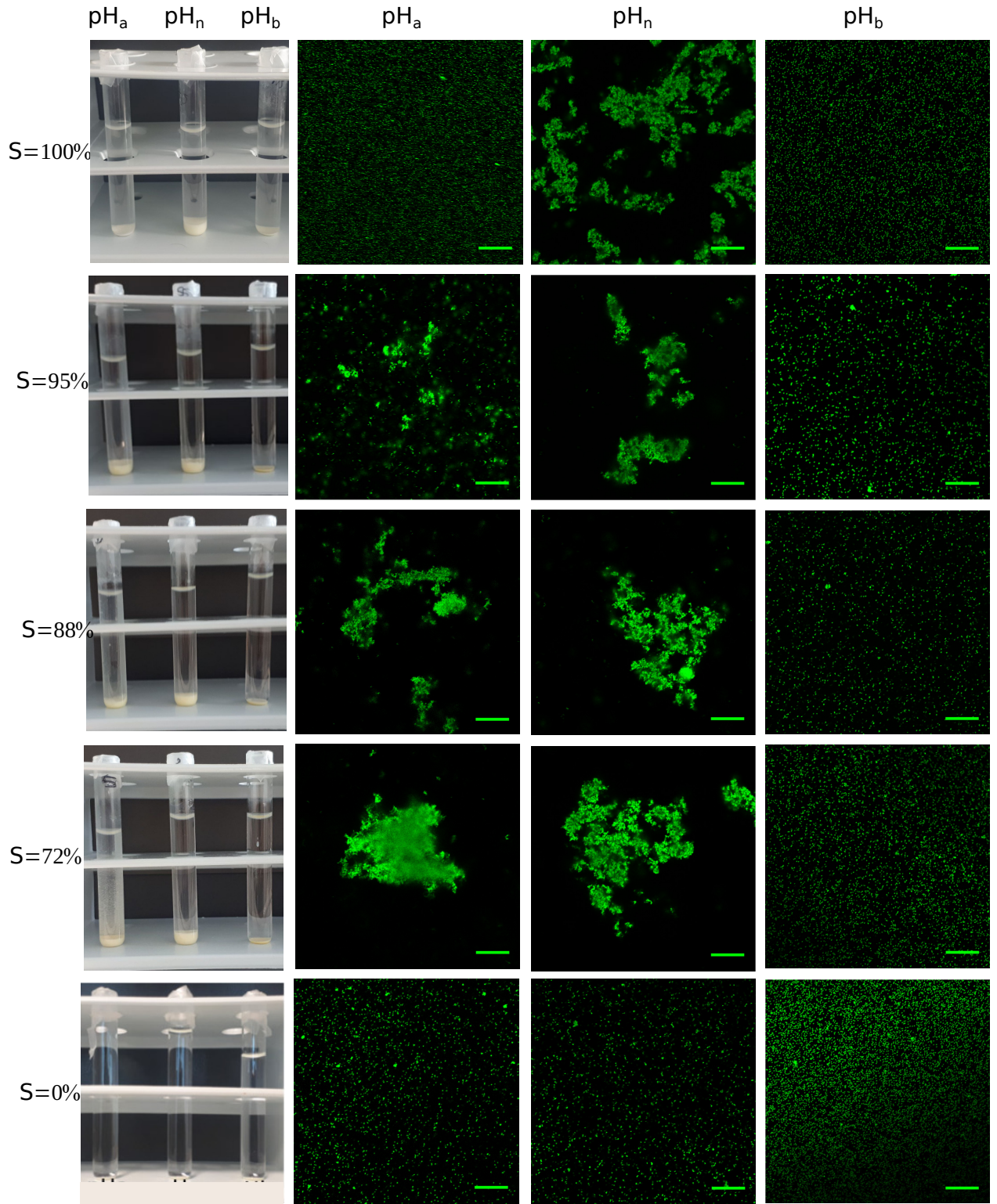


Figure 3: Picture of sedimentation test and corresponding confocal microscopy images for the different pH as a function of the size of the modified part of IPCs ( $S$ ). The scale bar is for  $20\ \mu\text{m}$ .

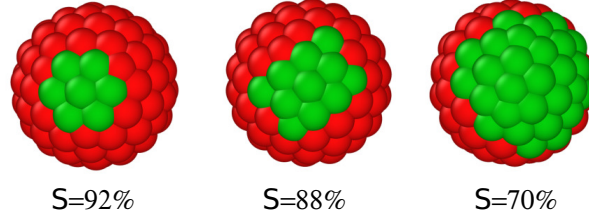


Figure 4: Snapshots of IPCs used in Brownian dynamics simulations with their proportion of red surface area (corresponding to the APTES modified part).

	S=92%		S=88%		S=70%	
	$\psi_{silica}$ (mV)	$\psi_{APTES}$ (mV)	$\psi_{silica}$ (mV)	$\psi_{APTES}$ (mV)	$\psi_{silica}$ (mV)	$\psi_{APTES}$ (mV)
pH <sub>a</sub>	-40	50	-40	50	-40	20
pH <sub>n</sub>	-60	0	-60	0	-50	0
pH <sub>b</sub>	-65	-25	-65	-35	-65	-45

Table 1: Summary of the different values of surface potentials ( $\psi$ ) used in simulations.

#### 4.3. Brownian dynamics simulations of one-patch IPC aggregation

Figure 4 shows the one patch IPCs used in simulations. The green part corresponds to the unmodified part of silica particle and the red part corresponds to the APTES modified part. Patches are defined in order to fit with the experimental patch sizes. The surface potentials used in the HHF potential (Equation 2) are assimilated here to the surface potential of the raw silica ( $\psi_{silica}$ ) for the unmodified part and to the estimated APTES surface potential ( $\psi_{APTES}$ ) for the modified part. Table 1 summarizes the values of surface potential used in simulations.

For a comparison, a simulation has also been performed with particles without patch, which interact only via the van der Waals attraction (case where  $S = 100\%$  at pH<sub>n</sub>). Figures 5 and 6 show the results of simulations at  $t = 10$  s for the different patch sizes. The aggregation kinetics as well as the evolution of the aggregate shape as a function of time are shown in Figure 7.

At pH<sub>b</sub>, for all patch sizes, no aggregation is observed in the simulations in agreement with the experimental observations. Both parts of IPC are negatively charged. Particles repel each other leading to stable suspensions.



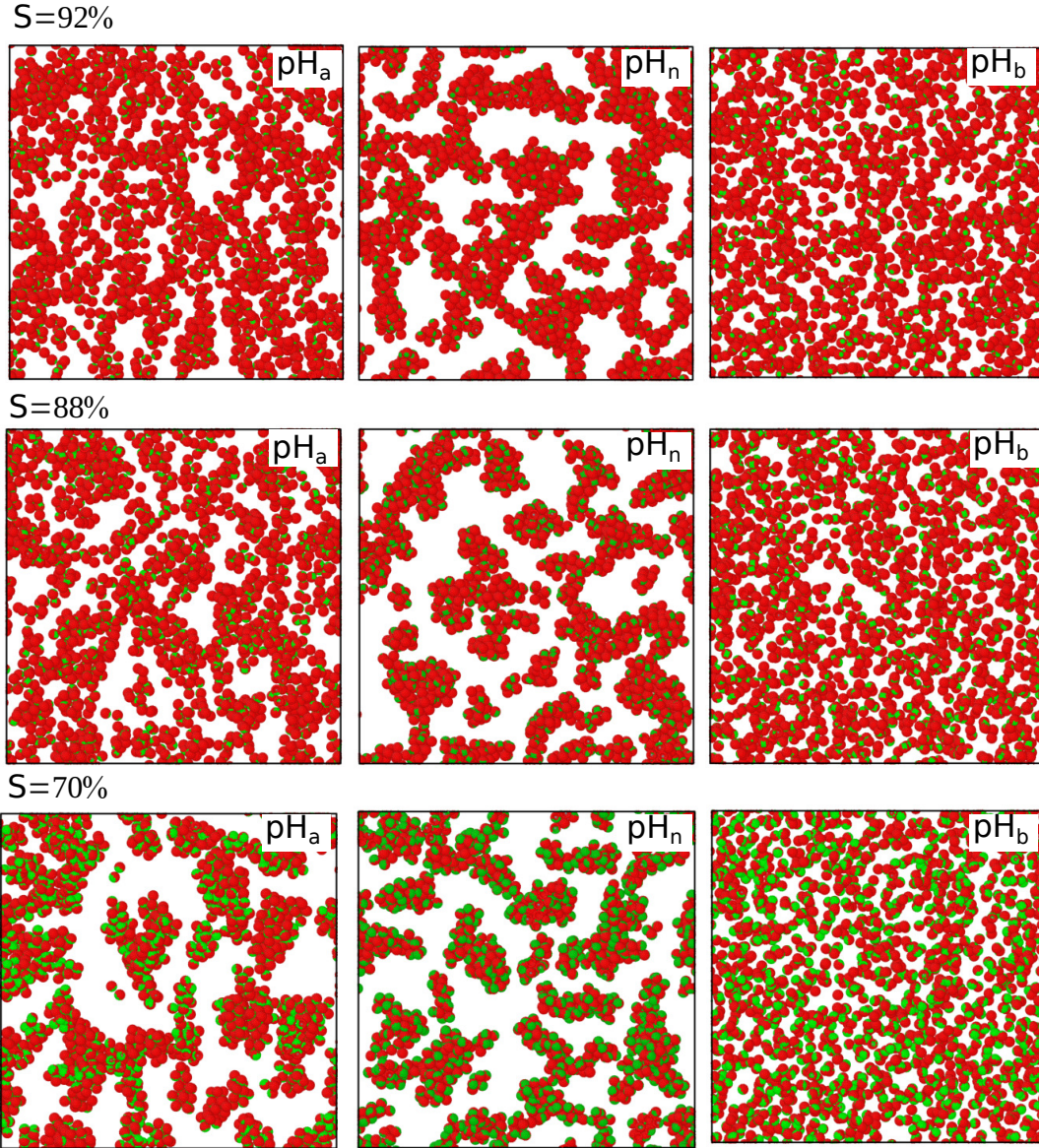


Figure 5: Snapshots of Brownian dynamics simulations obtained at  $t = 10$  s for the different pH as a function of the size of the unpatched part (APTES modified).

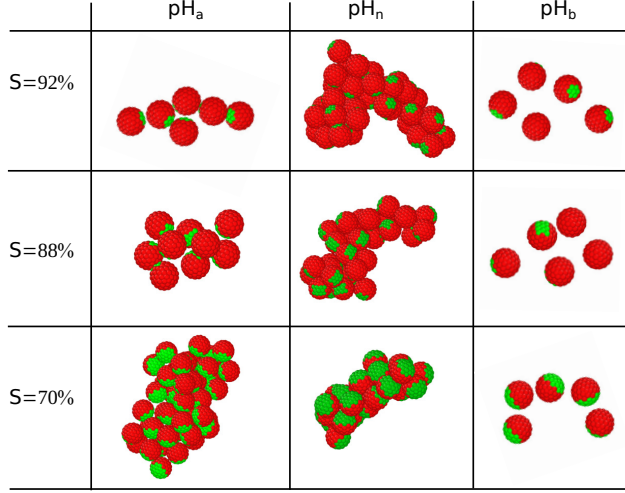


Figure 6: Snapshots of isolated aggregates extracted from the Brownian dynamics simulations performed with different pH and different sizes of the unpatched part ( $S$ ). At pH<sub>b</sub> no aggregate were formed.

At pH<sub>a</sub>, for which the two parts of IPCs are oppositely charged, aggregation is observed regardless of  $S$ . Aggregates are formed by contacts between the modified and the unmodified parts of particles, which are oppositely charged (see Figure 6). However aggregate size and shape differ depending on  $S$ . Figure 7a shows the evolution of the number of aggregates composed of at least two IPCs as a function of time. As already observed in Reference [36], the aggregation kinetics slows down when  $S$  increases. Thus, at the end of simulations, when  $S$  increases, the aggregate size decreases. This observation is in good agreement with the confocal microscopy pictures reported in Figure 3. To characterize the aggregate structure, the coordination number of aggregated particles is plotted in Figure 7c. For all the values of  $S$ , at the beginning of simulations, this number is equal to 1. At this stage, it is observed in Figure 7a that the number of aggregates increases which corresponds to the dimer formation regime and thus the coordination number is equal to one. Then, when the number of aggregates decreases due to their coalescence, the coordination number increases. For  $S = 70\%$ , this number is around 6 at  $t = 10$  s, which corresponds to quite compact aggregates as observed in Figure 6. However, for the smaller values of  $S$ , this number is smaller, around 2 or 3 for  $S = 92\%$  and  $S = 88\%$  respectively. In this case the aggregates are more linear (see Figure 6). To characterize the shape of aggregates, the asphericity parameter has been calculated, according to [43, 44]:

$$A_s = \frac{(\lambda_1 - \lambda_2)^2 + (\lambda_2 - \lambda_3)^2 + (\lambda_3 - \lambda_1)^2}{2(\lambda_1 + \lambda_2 + \lambda_3)^2} \quad (4)$$



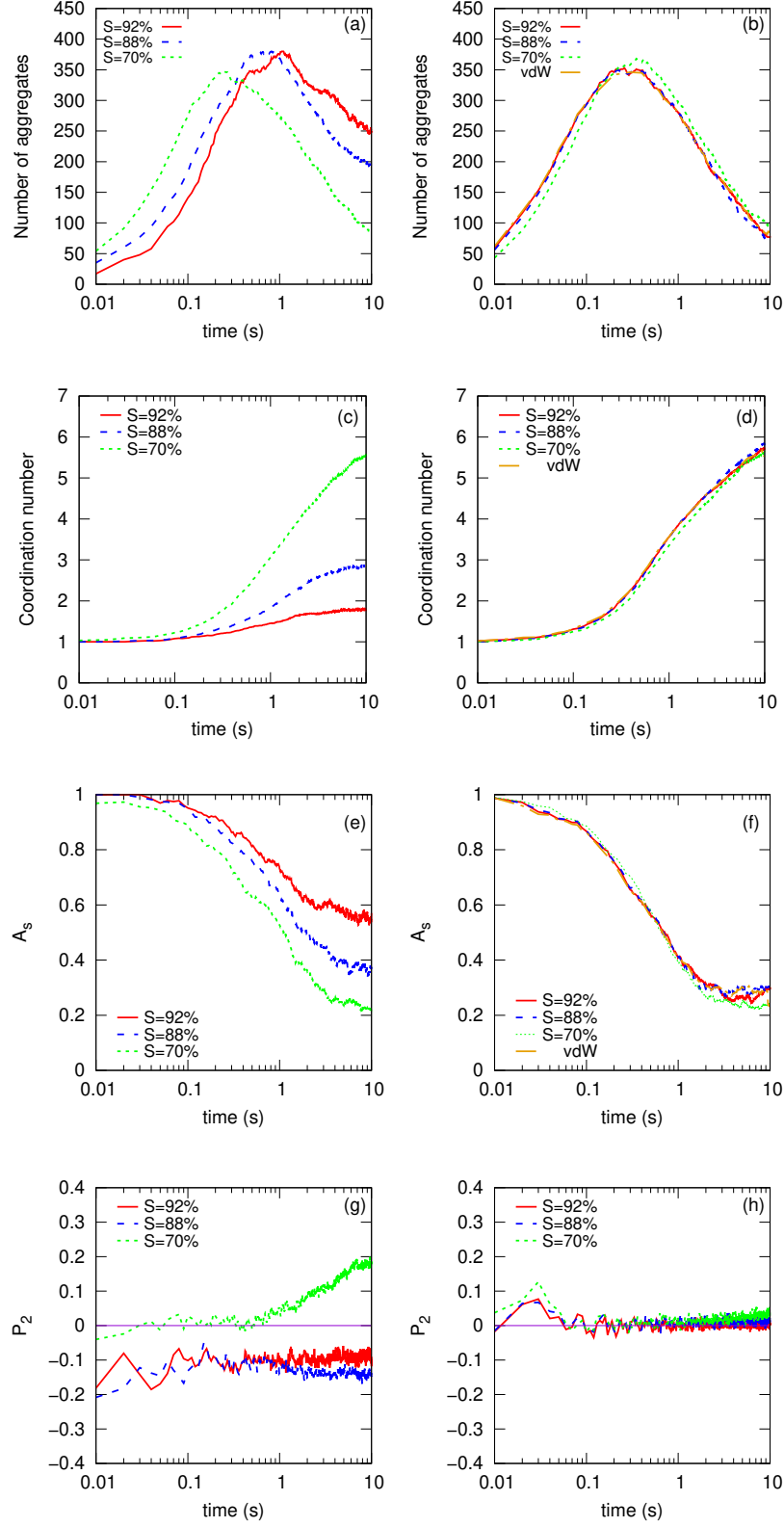


Figure 7: Characterization of the aggregation in the Brownian dynamics simulations performed for different sizes of the silica modified part ( $S = 92\%$ ,  $S = 88\%$  and  $S = 70\%$ ) and for uniform particles interacting only via van der Waals attractions ( $S = 100\%$  at  $\text{pH}_n$ ): number of aggregates for  $\text{pH}_a$  (a) and  $\text{pH}_n$  (b); evolution of the coordination number for  $\text{pH}_a$  (c) and  $\text{pH}_n$  (d); evolution of the asphericity parameter ( $A_s$ ) for  $\text{pH}_a$  (e) and  $\text{pH}_n$  (f) and evolution of  $P_2$  for  $\text{pH}_a$  (g) and  $\text{pH}_n$  (h).

309 with  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  ( $\lambda_1 \geq \lambda_2 \geq \lambda_3$ ) the eigenvalues of the radius of gyration tensor defined as:

$$T_{\alpha\beta} = \frac{1}{N} \sum_{I=1}^N (r_{\alpha,I} - r_{\alpha,center}) (r_{\beta,I} - r_{\beta,center}) \quad (5)$$

310  $r_{\alpha,I}$  is the coordinate of the particle  $I$  and  $r_{\alpha,center}$  the center of mass coordinate of the  
 311 aggregate containing  $I$ .  $\alpha$ ,  $\beta$  represent the Cartesian coordinates (x, y or z), and  $N$  is the  
 312 number of particles contained in the aggregate. Asphericity is null for a sphere and equal to  
 313 one for a rod-like structure. The evolution of  $A_s$  is reported in Figure 7e. At the beginning  
 314 of simulations, whatever  $S$ ,  $A_s = 1$ , which is explained by the dimers formed at this stage  
 315 of aggregation. At  $t = 10$  s,  $A_s$  is smaller when  $S$  decreases and therefore aggregates are  
 316 more spherical. Fractal dimensions ( $D_f$ ) obtained by plotting the number of particles of the  
 317 aggregate as a function of its radius of gyration confirm this observation.  $D_f = 1.34 \pm 0.03$ ,  
 318  $1.54 \pm 0.03$  and  $1.96 \pm 0.04$  have indeed been found for  $S = 92\%$ ,  $88\%$  and  $70\%$  respectively.  
 319 An other important parameter for aggregated patchy particles is their mutual orientation in  
 320 the aggregate. To characterize it, the nematic order parameter defined by the second-order  
 321 Legendre polynomial is used [45, 46]:

$$\langle P_2 \rangle = \left\langle \frac{3 \frac{1}{N_I} \sum_{J=1}^{N_I} (\mathbf{u}_I \cdot \mathbf{u}_J)^2 - 1}{2} \right\rangle \quad (6)$$

322 with  $N_I$  the number of neighbors of particle  $I$  and  $\mathbf{u}_I$  the unit vector of particle  $I$  directed  
 323 from the center of the particle to the center of its patch (here the non-modified part of par-  
 324 ticle). Values of  $\langle P_2 \rangle$  are in the range  $[-0.5; 1]$  [47, 48]. When all vectors of neighboring  
 325 particles are perfectly aligned,  $\langle P_2 \rangle$  is equal to 1. If all the neighboring particles are  
 326 randomly oriented,  $\langle P_2 \rangle$  is null. And a value of -0.5 corresponds to an orthogonal orien-  
 327 tation. Figure 7g shows the evolution of  $\langle P_2 \rangle$  as a function of time. Values of  $\langle P_2 \rangle$   
 328 are small, which indicates that IPCs are poorly oriented in the aggregates. However it is not  
 329 zero. When  $S = 70\%$ ,  $\langle P_2 \rangle$  becomes positive which corresponds to a beginning of align-  
 330 ment of particles in the same direction. However, for the smaller  $S$ ,  $\langle P_2 \rangle$  is negative, the  
 331 unmodified parts are rather orthogonally oriented. All these observations are in agreement  
 332 with previous observations from the literature [36, 49, 50].

333 At  $\text{pH}_n$ , simulations show a strong aggregation of particles whatever  $S$ , which is in agreement  
 334 with the experimental observations (see Figure 3). Contacts in aggregates are obtained essen-  
 335 tially between the modified parts or between the modified and unmodified parts. At this pH,

there is not much difference in the aggregation kinetics for the different  $S$  (see Figure 7b). It is also observed that this kinetics is similar to the kinetics observed in the simulation where particles only experience van der Waals attraction. At this pH, the modified parts of IPCs are not charged and aggregation is mainly due to van der Waals interactions between them. For all values of  $S$ , aggregates are compact with a coordination number around 6, and they have an asphericity around 0.25 (see Figures 7d and 7f). Fractal dimensions are found at  $D_f = 1.74 \pm 0.04$ ,  $1.72 \pm 0.04$  and  $1.81 \pm 0.04$  for  $S = 92\%$ ,  $88\%$  and  $70\%$  respectively. It is also observed that particles are randomly oriented in the aggregates unlike at  $\text{pH}_a$  (see Figures 7h and 6).

In Figure 3, for  $S = 72\%$  at  $\text{pH}_a$ , aggregates seem more compact compared to the aggregates obtained with  $S = 100\%$  at  $\text{pH}_n$ , which is the more common aggregation in oxide suspensions. To see if the simulations could provide an explanation for this observation, complementary calculations have been performed until  $t = 20$  s for  $S = 70\%$  at  $\text{pH}_a$  and  $\text{pH}_n$  and for particles interacting only through van der Waals attractions (similar to  $S = 100\%$  at  $\text{pH}_n$ ). Snapshots of the simulations obtained at  $t = 20$  s as well as the evolution of  $A_s$  are shown in Figure 8. After 10 s, it appears that  $A_s$  slightly increases in simulations where particles interact only with van der Waals interactions contrary to the IPCs. In this case, aggregates are thus more elongated. Fractal dimensions measured at  $D_f = 1.89 \pm 0.06$ ,  $1.73 \pm 0.05$  and  $1.63 \pm 0.05$  for  $\text{pH}_a$ ,  $\text{pH}_b$  and for the van der Waals interactions respectively, confirm this observation. From previous works, it is known that the shape of aggregates is explained by the competition between the kinetics of aggregate coalescence and the kinetics of aggregate reorganization [51]. Since the kinetics of aggregate coalescence is similar in the three simulations (at  $t = 20$  s, 54, 55 and 54 aggregates are found for  $\text{pH}_a$ ,  $\text{pH}_b$  and for the van der Waals interactions respectively), this difference should be explained by the aggregate reorganization. Reorganization of the aggregates is indeed expected in order to maximize the number of contacts between the attractive parts of particles, which minimizes the potential energy and gives compact configurations. The reorganization kinetics has been assessed by following the reorganization of an isolated aggregate obtained just after the coalescence of two small aggregates (see Figure 9). The reorganization has been characterized by the asphericity  $A_s$  and the mean coordination number of aggregated particles as a function of time

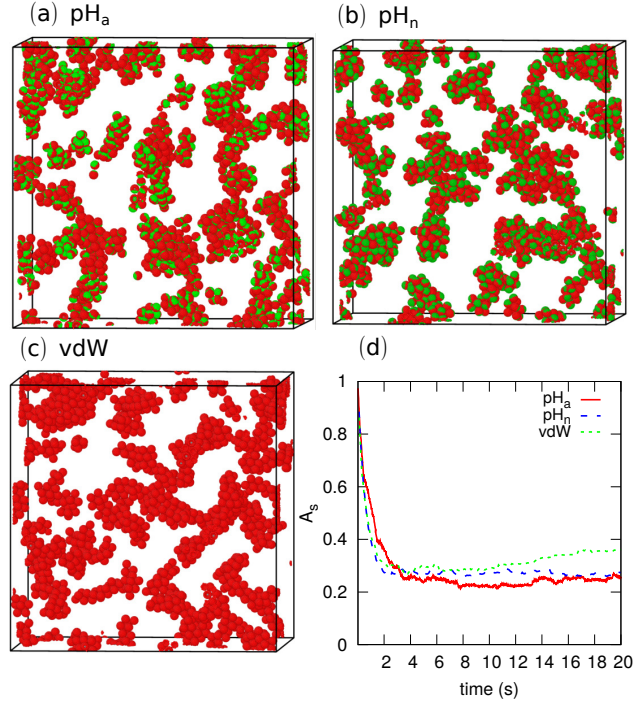


Figure 8: Snapshots of simulations obtained at  $t = 20$  s: (a)  $S = 70\%$  at  $\text{pH}_a$ , (b)  $S = 70\%$  at  $\text{pH}_n$  and (c)  $S = 100\%$  at  $\text{pH}_n$  (particles interact only via van der Waals interactions). (d) Evolution of the asphericity as a function of time in these simulations:  $\text{pH}_a$  ( $S = 70\%$  at  $\text{pH}_a$ ),  $\text{pH}_n$  ( $S = 70\%$  at  $\text{pH}_n$ ) and  $\text{vdW}$  ( $S = 100\%$  at  $\text{pH}_n$ ).

(see Figure 10). It should be noted that, after 1 s, asphericity and coordination no longer evolves in the case of the aggregate of particles interacting via van der Waals, whereas for the IPCs a continuous reorganization of the aggregates is observed. Indeed, for IPCs,  $A_s$  as well as the averaged coordination number vary all along the simulations. The coordination number sometimes decreases, which corresponds to the dissociation of particles and promotes the aggregate reorganization. Nevertheless, in our simulations, the coordination overall increases reflecting the aggregate reorganization in a more compact shape. Bochicchio *et al.* have shown that long dissociation times (e.g.  $\approx 150$  s) prevent from the aggregate reorganization leading to “branched” aggregates, whereas short ones (e.g.  $\approx 0.3$  s) allow an important aggregate reorganization leading to compact, even crystallized aggregates in Brownian dynamics simulations [52]. In previous simulations, the dissociation time of two aggregated patchy particles with  $S$  in the range [60;70]% was measured at around 3 s [36]. This value is low and may explain an important aggregate reorganization in the IPC simulations. The relatively easy dissociation of the IPCs is due to repulsions between some parts of the IPCs. Thus, in the present simulations, when particles interact only via van der Waals interactions, the reorganization is slow and this leads to elongated aggregates. On the contrary, IPC aggregates can be reorganized much more easily to maximize the contact number between the attractive parts, leading to more compact aggregates.

## 5. Conclusion

One patch silica-based IPCs have been synthesized with different patch sizes. Their aggregation in suspension has been studied both experimentally and numerically at different pH. A good agreement is obtained between the simulation results and the experimental characterizations. For pH where both parts of IPCs are negatively charged ( $\text{pH}_b$ ), no aggregation is observed. At acidic pH, where the two parts of the particles are oppositely charged ( $\text{pH}_a$ ), aggregation is observed in all cases. The size of the patch has a strong influence on the aggregate structures. The smaller the patch, the more the aggregates are elongated. For the patch sizes studied here, a slight organization of the particles is found in the aggregates. All of these observations are consistent with the findings in the literature [49, 50]. For pH where the modified part of the particles is weakly charged ( $\text{pH}_n$ ), a strong aggregation is obtained whatever the size of this part. Aggregation is mainly due to van der Waals attractions and no

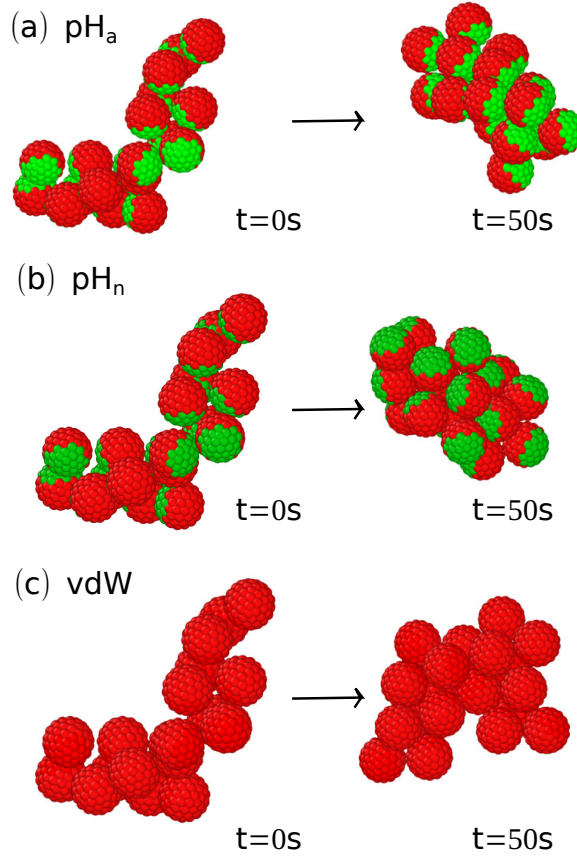


Figure 9: Snapshots of simulations performed on an isolated aggregate: (a)  $S = 70\%$  at  $pH_a$ , (b)  $S = 70\%$  at  $pH_n$  and (c)  $S = 100\%$  at  $pH_n$  (particles interact only via van der Waals interactions).

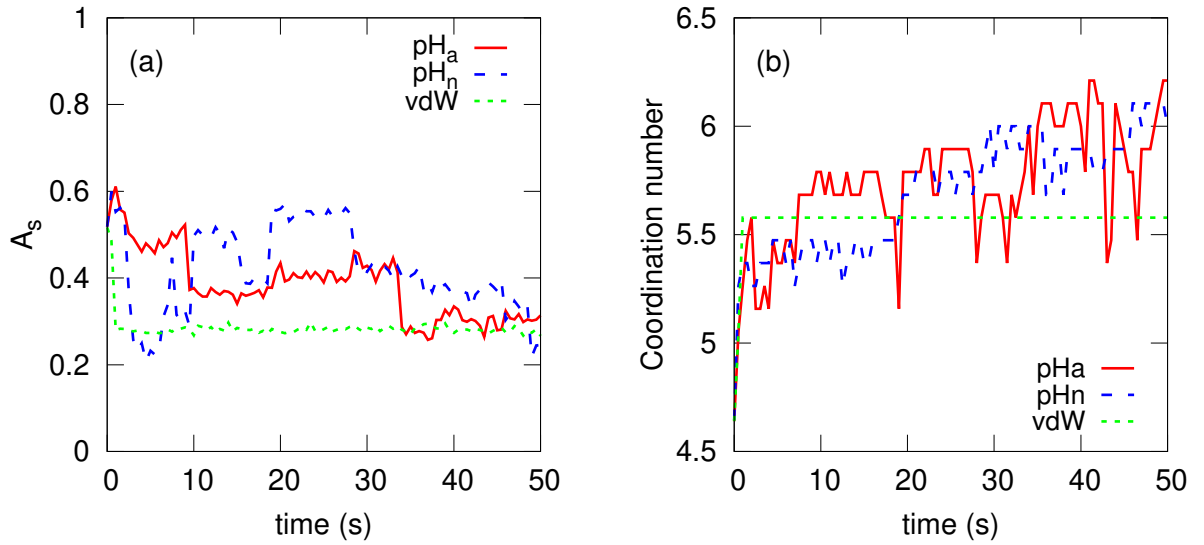


Figure 10: Evolution of the asphericity (a) and of the averaged coordination number (b) as a function of time in simulations performed on an isolated aggregate:  $pH_a$  ( $S = 70\%$  at  $pH_a$ ),  $pH_n$  ( $S = 70\%$  at  $pH_n$ ) and  $vdW$  ( $S = 100\%$  at  $pH_n$ ).

organization is found in the aggregates. It is also observed experimentally, that the largest patch size leads to compact aggregates especially at acidic pH. Numerically, this may be explained by an important reorganization of the aggregates due to the presence of repulsive parts on the colloid surface.

All these results show that the aggregation of the synthesized silica based amphoteric particles can be tuned by modifying both the proportion of the modified part of the particles and the pH. Such particles can be used to obtain either elongated or compact aggregates in which the particles may have a preferential orientation, which makes them promising to build new ceramic materials.

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