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Chapter 11 - Pickering emulsions based on Layered double hydroxides and metal hydroxides.

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Abstract: As previously underlined in this book, Pickering emulsions have in recent years gained increasing attention due to their interesting properties related to the replacement of surfactants by solid microparticles or nanoparticles. Such change in the nature of the stabilizer confers higher stability and lower toxicity to the emulsions. This chapter focus on the recent advances in the specific use of a peculiar class of inorganic bidimensionnal particles the Layered Double Hydroxides (LDH) and hydroxides salts in Pickering emulsion process. The properties of the two main classes of LDH involved in the stabilization of emulsion that is pristine materials and modified LDH with organic anions, are described. Then the different results obtained for oil-in-water, water-in-oil and water-in-water involving LDH or hydroxides salt particles are discussed. At last, the interest of Pickering emulsion stabilized by LDH in various applications are also reviewed.

Keywords: Layered double hydroxides, hydroxides salt, Pickering emulsion, stabilization, Pickering emulsion polymerization.

1- Introduction

In the past two decades, there has been an increasing interest in the development of Pickering emulsion systems for various applications. As described in the pioneer works of Ramsden (Ramsden and Gotch 1904) and Pickering (Pickering 1907), solid particles can adsorb at the liquid interface upon partial wetting of the particle surface avoiding droplet coalescence and conferring stability to the emulsion. Some of the reported benefits of

inorganic particles instead of surfactant to stabilize emulsions are a higher stability, functionality and a lower toxicity especially in terms of irritancy and cytotoxicity. Many factors influence the properties of Pickering emulsion, including particle size, wettability (often expressed as a contact angle θ at the three-phase boundary), initial location, and interparticle interactions. Comprehensive chapters are provided in the first part of this book on formation, stability and applications of Pickering emulsion and reviews have already been published (Chevalier and Bolzinger 2013, Gonzalez Ortiz, Pochat-Bohatier et al. 2020, Lu, Gou et al. 2021, Machado, Benyahia et al. 2021) in particular by Binks (Binks 2002) and Aveyard et al. (Aveyard, Binks et al. 2003).

According to a recent review, (Gonzalez Ortiz, Pochat-Bohatier et al. 2020) various solid particles with different chemical compositions and morphologies can efficiently be involved in emulsion stabilization, ranging from spherical shape (SiO_2 , TiO_2 , Fe_2O_3 , polystyrene (PS) latexes), to 2D structures (graphene oxides, hexagonal boron nitride, graphitic carbon nitride, ...), nanosheets (kaolinite, montmorillonite, illite, layered double hydroxides), disk-like shape (Laponite[®]), nanotubes (carbon nanotubes, halloysite) to fibrous shape (sepiolite, zein particles). Their nature affects both the emulsion formation and their subsequent properties. Among all the inorganic particles used for Pickering emulsion stabilization, 2-D structure with platelet shape such as clay minerals have properties leading to plates lying flat at the interface and more strongly held compared to spherical particles.

Compared with the well-established use of 2D particles from the smectite group such as montmorillonite, kaolinite and Laponite[®], preparing Pickering emulsion in presence of layered double hydroxides (LDH) has only recently attracted attention due to the peculiar physical and chemical properties of LDH. (Rives 2001, Duan, Evans et al. 2006, Forano, Costantino et al. 2013) The structure of LDH is related to that of brucite, $\text{Mg}(\text{OH})_2$ in which a portion of the Mg^{2+} has been replaced by Al^{3+} . Anions along with water, are intercalated between the layers to maintain electroneutrality. Based on a combination of a large variety of divalent and trivalent metal cations, the general formula for the LDH family can be written as $(\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2)(\text{A}^{m-}_{x/m} n\text{H}_2\text{O})$ where $(\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2)$ represents the layer, and $(\text{A}^{m-}_{x/m} n\text{H}_2\text{O})$ represents the interlayer species. Contrary to clay minerals, LDH are naturally rare, however they can be easily prepared in a large quantity and organically modified. According to the synthetic method and parameters used, LDH particles size can be tuned over a large range with lateral dimensions ranging from 30 nm (Xu, Stevenson et al. 2006, Xu, Stevenson

et al. 2006, Gunawan and Xu 2009) to more than 5 μm (Okamoto, Iyi et al. 2007) and thicknesses from 1 nm to 20 nm. It should be underlined the most of the reported synthetic LDH lead to high level of intergrowth of the platelets and secondary aggregation of several micrometres.

Even if LDH display many interesting features such as wide-ranging chemical compositions, variable layer charge densities, ion-exchange properties, reactive interlayer spaces and hydroxylated surfaces, their colloidal stability is difficult to control mainly due to the high charge density of the layers avoiding spontaneous swelling in water.

The present review chapter intends to present the current-state of the art in the Pickering emulsion stabilized by LDH particles. Special attention will be paid to the properties of the LDH particles involved in these emulsion and the interactions at the nanoscale level, since these are crucial for the stability of the final Pickering emulsion. Three main categories of Pickering emulsions will be distinguished: water-in-oil, oil-in-water and water-in-water with a focus of the nature of the LDH particles involved in term of hydrophilicity and hydrophobicity. Finally, the last part is devoted to the use of the LDH Pickering emulsions in applications, particularly for adsorption, catalysis and to produce nanocomposite colloids with enhanced properties. This chapter concludes with some perspectives for future research in the field of LDH-based Pickering emulsions.

2- LDH and LH stabilizing particles used for Pickering emulsions

Common LDH containing simple inorganic anions such as CO_3^{2-} , Cl^- , NO_3^- , SO_4^{2-} display layers with high charge density due to structural constraints. Indeed, LDH with chemical formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2][\text{X}^{\text{q-}}_{x/q}\cdot n\text{H}_2\text{O}]$ for which most encountered x values range from 1/5 to 1/3, develop layer charge densities (LCD) in between 2.5 to 4.2 positive charge per nm^2 ; LCD values that are far higher than those shown by other 2D ion exchangers (smectite, titanate). These intrinsic charge properties lead to robust layer/interlayer interactions and a very strong hydrophilic character, properties that may limit exfoliation and solvent dispersion. Because the formation of LDH-based stable Pickering emulsions needs to overcome LDH inter-particles interactions and favor interactions at liquid-liquid interfaces, it is recommended not only to control the size of the LDH particles but also to chemically tune

their surface properties (anionic species, charge density, hydrophilic lipophilic balance (HLB), wettability). It is well established that amphiphilic molecules are used to stabilize oil in water emulsions as they reduce the surface tension at the liquid-liquid interface. Many of these surfactants, preferentially anionic and non-ionic surfactant, may undergo surface adsorption or bulk intercalation by LDH, then rendering them lipophilic. Some of these amphiphilic molecules have been used as co-emulsifiers or chemical modifiers of LDH for Pickering emulsion stabilization. Few organic molecules were tested yet: an anionic surfactant (dodecyl sulfate)(Wang, Yang et al. 2008), a short amphiphilic molecule (glutamate) (Li, Song et al. 2017), a dye molecule (Methyl orange) (Li, Zhao et al. 2013) and two polymer Tween 80 (Kura, Hussein-Al-Ali et al. 2014) and Span 80 (Wang, Yang et al. 2010).

Sodium Dodecyl sulfate (SDS) ($C_{12}H_{25}SO_4Na$), one of the most used surfactant in emulsion formation, is also the amphiphilic anion (DS) that has been most combined with LDH for many applications. Adsorption of DS on the LDH layer surface leads to a dense epitaxial packing of anions, the $-O-SO_3^-$ groups attached to the positive layers with the hydrophobic tails orientated far away from the bulk, then reversing the zeta potential from positive values, usually +30/+40 mV, to neutral or negative values depending on pH. This surface modification lowers the wettability of the LDH platelets favoring the interaction with oil phase.

Many papers report the adsorption and the intercalation of Methyl orange by LDH, mainly for purpose of depollution. Tween-80 and Span-80 are non-ionic surfactants, derived from the condensation of oleic acid and polyethoxylated sorbitan or sorbitol molecules, respectively, with different HLB value of 15 and 4.3. They aid in minimizing the interfacial tension of the W/O primary emulsion and stabilize oil in water droplets of 12 μm size. Few papers (Wang, Yang et al. 2010, Kura, Hussein-Al-Ali et al. 2014) reported that Tween-80, and Span-80, may adsorb to the LDH surface through their polar part. Such coating preserves the structure while changing their wettability.

Fluorescent confocal laser scanning microscopy analysis is the common technique used for imaging nanoparticles in Pickering emulsions at the liquid-liquid interface. Thanks to their anion exchange properties and hydrophilic properties, LDH are able to intercalate or adsorb anionic fluorescent probes for imaging (Yan, Zhou et al. 2017, Ma, Li et al. 2020). For such application, LDH were functionalized mainly with Rhodamine B and Fluorescein (Musumeci, Mortimer et al. 2010, Legentil, Leroux et al. 2019) (Fig.1).

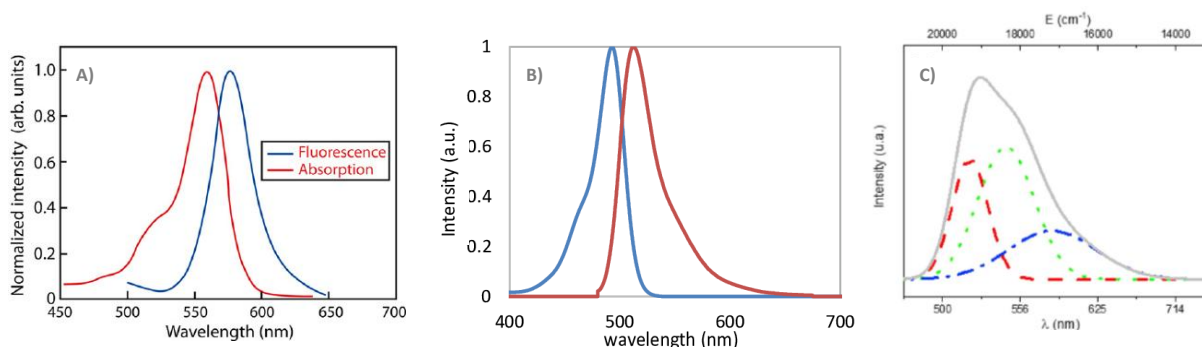


Fig. 1 : A) Excitation and emission spectra of rhodamine B ($\lambda_{exc} = 556$ nm, $\lambda_{em} = 578$ nm). B) Excitation and emission spectra of fluorescein and silica nanoparticles doped with rhodamine B ($\lambda_{exc} = 488$ nm, $\lambda_{em} = 518$ nm). C) Emission spectra at 20 °C with excitation at 450 nm of LDH-fluorescein (0.05%) powder with deconvolution in three contributions. Reproduced with permission from ref (Legentil, Leroux et al. 2019). Copyright 2019 Elsevier.

3- Pickering emulsion involving LDH and LSH particles

3.1 Oil in water emulsions

As described above, the unique properties of LDH such as a variable anion exchange capacity allowing tunable surface properties and hydrophile/lipophile balance (HLB), added to a 2D morphology, with controlled platelet size and aggregation, make them prime candidates for the preparation of stable emulsions for various applications (Machado, de Freitas et al. 2019). However, since the pioneering works of G. Lagaly and S. Abend (Abend and Lagaly 2001) that reported in the early 2001 the interest to use LDH to stabilize o/w emulsions, surprisingly there has been very few studies on LDH-based Pickering emulsions (Table 1). o/w emulsions stabilized by LDHs were more investigated than w/o emulsions in agreement with the hydrophilicity of the LDH particles. In most of the studies reported in the literature, LDHs are never used alone but they are either surface modified or used with a co-emulsifier because due to their hydrophilic properties, LDH particles preferentially favor the formation of o/w emulsions. Pure LDHs display attachment (Aveyard, Binks et al. 2003) energy too low to prevent emulsion coalescence. In addition, reversible o/w \leftrightarrow w/o process was described for few LDH systems (Zhang, Zhang et al. 2015). Chemical composition of LDH investigated was limited to Mg_RAl (with R = 2 and 3) probably due to the ease to prepare colloidal solutions for this chemical composition.

Table 1 : Reported studies on LDH-based Pickering emulsions

LDH	Oil phase	Co-emulsifiers / Additives	Emulsification conditions	Ref.
Mg ₂ Al-NO ₃	Paraffin oil	Bentonites (Wyoming; Ordu) Montmorillonite-Na	Bentonite:LDH wt: 1:1;1:2 LDH+Bentonite : 0.3-3 wt% o/w : 0.38/0.62	(Abend and Lagaly 2001)
Mg ₃ Al-CO ₃	Paraffin oil (C ₁₆ -C ₂₆ isoalkane)	NaCl	LDH: 0.5-4 wt% / NaCl: 10 ⁻³ -2M	(Yang, Liu et al. 2006)
Mg ₂ Al-Cl	Paraffin oil (C ₁₆ -C ₂₆ isoalkane)	NaCl	LDH: 0.5-2 wt% / NaCl: 10 ⁻⁴ M / o/w : 0.5/0.5/ pH 9-12.5	(Yang, Niu et al. 2007)
Mg ₂ Al-Cl	Paraffin oil (C ₁₆ -C ₂₆ isoalkane)	Sodium dodecylsulfate (SDS)	LDH: 0.5-1.5 wt% / SDS: 1-10 ⁻¹ M / o/w : 0.5/0.5	(Wang, Yang et al. 2008)
Mg ₂ Al-Cl	Paraffin oil (C ₁₆ -C ₂₆ isoalkane)	Sorbitan monoleate (Span 80)	LDH: 1 wt% / Span 80: 1-10 ⁻¹ M / o/w : 0.5/0.5	(Wang, Yang et al. 2010)
Mg ₂ Al-NO ₃	paraffin oil (C ₁₆ -C ₂₆ isoalkane)	Methyl orange (MO)	LDH: 0.25 wt% / MO: 0-10 ⁻¹ M / o/w : 0.1-0.9/0.9-0.1	(Li, Zhao et al. 2013)
Mg ₃ Al-NO ₃ Mg ₃ Al- Glutamate	Alkyl ketene dimer wax (AKD)	Glutamate	LDH:Glu 0-3mmol.g ⁻¹ / LDH: 0.25 wt% / MO: 0-10 ⁻¹ M / o/w : 1/9	(Li, Song et al. 2017)
Mn ₂ Al-SO ₄ /K ₂ SO ₄ (K-Shigaite)	Liquid paraffin		LDH: 0.01-0.75 wt% / o/w : 0.18-0.74/9	(do Amaral, de Freitas et al. 2020)
Mn ₂ Al-SO ₄ /K ₂ SO ₄ (Na-Shigaite) Zn ₂ Al-SO ₄ /K ₂ SO ₄ (Na-Natroglaucocerinite) Mg ₂ Al-	Liquid paraffin		LDH: 0.1-1.0 wt% / o/w : 0.54/0.46 / pH 6.5-8.0	(do Amaral, Wypych et al. 2021)

SO ₄ /Na ₂ SO ₄ (Na-Motukoreaite)				
Mg ₃ Al-CO ₃ /CNT/Ru	Toluene		LDH: 1.3 wt% / w/o : 1/2	(Shan, Yu et al. 2015)
Mg ₂ Al-SDS	Paraffin oil (C ₂₀ -C ₃₃ isoalkane)	SDS	LDH: 0.2-3.0 wt% / MO: 0-10 ⁻⁴ M / o/w : 0.1-0.5/0.9-0.5	(Zhang, Zhang et al. 2015)
Co ₂ Ni- CO ₃ /PVDF	soybean oil, petroleum ether, 1,2- dichloroeth ane, n- hexadecane	Polysorbate 80 (Tween80)	Tween80: 0 or 0.5mg.ml ⁻¹ / o/w : 1:99	(Cui, Zhou et al. 2019)

Among the key factors ruling out the particle adsorption at the o/w interface, surface charge density has an important role. It favors not only the steric hindrance that impedes droplet coalescence but also the attachment of particles to the interface, although the mechanism still needs to be clarified. Changing the M²⁺/M³⁺ molar ratio in LDH is a way to control the zeta potential and the electrostatic forces with the interface. An additional strategy consists to add salts in the LDH colloidal solutions. Two papers (Yang, Liu et al. 2006, Yang, Niu et al. 2007) report the effect of NaCl salt addition on o/w emulsion stabilization by LDS, namely Mg₂Al-Cl. Due to both the positive charge and the high charge density of the layers, LDH display high zeta potential values (+30 - +40 mV). Zeta potential has a crucial role on the dispersion state of particle suspensions. Such positive electrochemical field favors LDH platelets repulsion and prevents particle aggregation leading to stable colloidal solutions. As it controls the particle wettability, it may also help to the attachment of the LDH platelets at the o/w interface that displays intrinsically a negative charge due to the local concentration of OH⁻ ions. However, salt addition is needed to reduce the interface charge potential, in order to overcome the energy barrier for LDH adsorption and stabilize the emulsion. A reduction of the zeta potential is also necessary to better control the LDH-LDH repulsions and favor their concentration at the o/w interface. Addition of salt is a key factor as it affects

both the potential of o/w interface but also it impacts the LDH zeta potential. Indeed, as already mentioned by Lagaly et al. (Abend and Lagaly 2001), and confirms by Yang Fei et al. (Yang, Liu et al. 2006, Yang, Niu et al. 2007), the ζ value of Mg_2Al -Cl decreases under addition of increasing NaCl concentrations. As suggested by these authors, increasing the ionic strength leads to a contraction of the Stern layer of the diffuse electrical double layer, modifies the surface charge and decreases ζ . It may be note that the transition between sol and gel phases of the LDH suspensions occurs at concentration between 0.2 to 1 M, depending on the LDH weight % (respectively from 4.0% to 0.5%). Increasing NaCl concentration favors flocculation and LDH particle attachment at the o/w interface. Consequently, adsorption of Mg_2Al -Cl platelets at the o/w interface were found to be optimal for NaCl concentrations in between 0.1 and 1M whatever the LDH wt% and emulsions were stable for 3 months. In such NaCl concentration range, drop sizes vary from 50 μm to 10 μm when LDH wt% is increased from 0.5 to 4% respectively. Increase in pH has a similar effect (Yang, Niu et al. 2007), when the pH of Mg_2Al -Cl suspension is increased from 9.25 to 12.0, ζ decreases from 40 to nearly 20 mV enhancing the stability of the emulsion and decreasing the oil drop size up to a stable gel-like state.

The synthetic minerals Na,K-Shigaite, Na-Natroglaucocerinite, Na-Motukoreaite display layered structures ($[M^{2+}_6Al^{3+}_3(OH)_{18}][Na(H_2O)_6(SO_4)_2]$) with respectively $M^{2+} = Mn^{2+}, Zn^{2+}, Mg^{2+}$ that are related to the LDH structure with additional Na^+ or K^+ and SO_4^{2-} intercalated ions. Compared to classical LDH, the difference in surface composition corresponds to an enhanced anion exchange capacity and an excess of surface charged species. They can disperse easily in aqueous solutions as for LDH in solutions containing high concentrations of NaCl. Stable Pickering o/w emulsions stabilized with these 3 minerals were obtained (do Amaral, de Freitas et al. 2020, do Amaral, Wypych et al. 2021) for high oil fractions (> 0.74) and a critical coverage concentration of particles of 0.25 wt% ($\Phi_e = 0.54$) after 14 days of storage as shown on Fig. 2 were Rhodamine-labelled K-shigaite particles are shown to adsorb at the o/w interface. Oil fraction increases with increasing particle concentration leading to a droplet size reduction. Stabilization of K^+ -shigaite-based Pickering emulsions was attributed to both partial reduction of interfacial energy with increasing shigaite particle content. That was confirmed by surface tension measurements and kinetic limitation due to steric hindrance to coalescence. Emulsion inversion from o/w to w/o occurs at high emulsion fraction, $\Phi_o > 0.5$ and $\Phi_o > 0.75$ for respectively oil fraction $\Phi_e < 0.20$ and $\Phi_e > 0.15$.

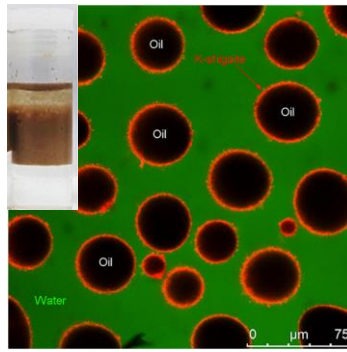


Figure 2: CLSM image of paraffin/water emulsions ($\Phi_o = 0.38$) for 0.75 wt% K-shigaite particles after 24 h. Insert: Corresponding photograph of emulsion after 14 days. Reproduced with permission from ref (do Amaral, de Freitas et al. 2020). Copyright 2020 Elsevier.

Pickering emulsions were also obtained for analogous structures (Na-Motukoreaite, Na-Natroglaucocerinite, Na-shigaite) in nearly similar conditions (do Amaral, Wypych et al. 2021). Differently than what was obtained for MnAl LDH-based Pickering emulsion, for the MgAl and ZnAl counterpart the emulsified volume increase with particle concentrations up to $\Phi_e = 0.6$ and 0.4 respectively.

In another hand, stable Pickering o/w emulsion may be prepared by tailoring the wettability of the particles by surface modification with lipophilic molecules. Adsorption of ionic and non-ionic surfactants, or polyelectrolytes at the particle surface allows to control the Hydrophilic Lipophilic Balance (HLB) of the emulsifier, a key parameter for emulsion stabilization (Binks 2002). Short amphiphilic molecules such as low molecular weight organic carboxylic acid, have also been used in combination with hydrophilic metal oxides nanoparticles for the preparation of stable o/w emulsions (Akartuna, Studart et al. 2008). Following this approach, LDH in-situ modified by glutamic acid was used to stabilize oil in water emulsion for application in papermaking sizing process (Li, Song et al. 2017). The oil used was a wax oil made of alkyl ketene dimer (AKD). The use of organophilic molecules such as glutamate, a zwitterion with short hydrophobic chain and moderate wettability is an alternative to long chain surfactant that may causes an unfavorable increase in emulsion viscosity, therefore requiring lower O/W ratio and much energy. Glutamate-modified LDHs was efficient to stabilize AKD/w emulsions. Emulsion volume fraction of 100% was obtained for glutamate concentration greater than 1.5 mmol/g after 24h and stable over more than 30 days. Fluorescent confocal laser scanning microscopy analysis confirm the adsorption of

glutamate-modified LDH particles at the surface of the oil droplets and the formation of a stable steric shell that inhibits the droplet coalescence. It must be noted that unlike what authors claimed, glutamate was not intercalated in the Mg_3Al-NO_3 structure but only adsorbed at the surface which was sufficient enough for emulsion stabilization. Indeed, a short basal spacing value of 0.863 nm measured for Mg_2Al -Glutamate cannot account for glutamate intercalation as reported recently by Wei Wu et al. (Wu, Song et al. 2021).

Laser confocal scanning microscopy (LCSM) is mostly used to image the particles adsorbed at the droplet surface. However, it needs to label particles with fluorescent probes. Rhodamine or Fluorescein are the most used fluorophore molecules with LDH. Wei Li et al. (Li, Zhao et al. 2013) reported the addition of methyl orange (MO) to the preparation of Mg_2Al-NO_3 -based Pickering paraffin/water emulsions. Adsorption equilibrium of the methyl orange by Mg_2Al-NO_3 platelets was reached for a pH 10.0 after 24h contact time (25°C). Zeta potential decreases from +45 mV to +32 mV with increasing MO concentration up to 10 mM. Adsorption of the amphiphilic molecule modified noticeably the wettability as evidenced by the change in contact angle from 29° to 42.5° for pure LDH and LDH-MO (10 mM), rendering the particles partially hydrophobic. The ability of LDH surface to structurally orientate the amphiphilic MO molecule perpendicular to the surface with the anionic group electrostatically attached to the layer exposing the hydrophobic part to the liquid phase is favorable for the stabilization of the o/w interface. Emulsions are stabilized with volume fractions up to 80% and droplet size reduction from 300 μm to 25 μm for pure and 10 mM MO modified LDH. The dye molecule was used at the same time as a co-emulsifier, tuning the wettability of LDH particles and as a fluorescent probe for LCSM imaging as shown in Fig. 3. (Li, Zhao et al. 2013)

3-2 Water in oil emulsions

The role of surfactant as co-emulsifiers for the stabilization of Pickering emulsions is well known since the works of Binks et al. (Binks, Clint et al. 2005). Addition of ionic (SDS) (Wang, Yang et al. 2008) and non-ionic (Span80, Tween 80) surfactants to Mg_2Al LDH-based Pickering emulsions has been studied. Addition of lipophilic emulsifier changes the wettability of the particle and helps to stabilize the emulsion.

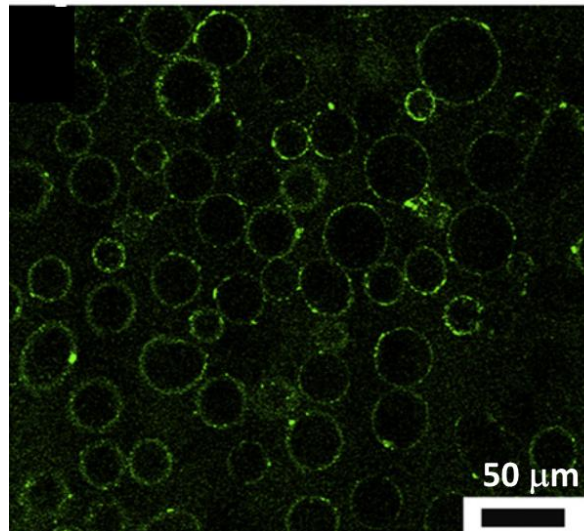


Figure 3 : LCSM images of o/w emulsion stabilized by 0.25 wt% LDH modified with 10 mM. Reproduced with permission from ref (Li, Zhao et al. 2013). Copyright 2013 Elsevier.

At a critical concentration it may reverse the contact angle of the particles adsorbed at the interface leading to an emulsion inversion. As discussed by B.P. Binks (Binks and Rodrigues 2007), water in oil (W/O) emulsion are obtained when the contact angle of particles adsorbed at the interface is slightly greater than 90° . Consequently, W/O Pickering emulsion inversion into O/W Pickering emulsions can be obtained by changing the wettability of solid particles and then the contact angle. This can be obtained by under close control of the hydrophilic/hydrophobic balance of the particle surface, water/oil ratio and surfactant addition. Reversible inversion, also called double inversion, can be obtained by combination of hydrophilic inorganic particles (SiO_2 (Binks, Isa et al. 2013), BaSO_4 (Schulman and Leja 1954), CaCO_3 (Cui, Shi et al. 2008)) and molecular surfactants (dodecylsulfate (Aveyard, Binks et al. 2003), oleate (Sadeghpour, Pirolt et al. 2013), stearate (Tambe and Sharma 1993), didecyldimethylammonium (Binks and Rodrigues 2007)). Cause of emulsion inversion is attributed to the adsorption of surfactant at the particle surface provided the wettability of the particles is enough reversed. In case of LDH particles, adsorption of ionic or non-ionic surfactants at their surface reverse the HLB leading to the stabilization of w/o emulsions.

Jun Wang et al. (Wang, Yang et al. 2008) reported that water/paraffin oil emulsions can be stabilized by Mg_2Al LDH (0.1 – 1%) when SDS are added at concentrations higher than 40 mM. Interestingly, reversible inversion (water/paraffin oil \leftrightarrow paraffin oil/water) was

described for such LDH-based Pickering emulsions. Even though, mechanisms of particle/surfactant emulsion formation and inversion are not yet fully understood they may involve both competitive adsorption of SDS at LDH surface and oil/water interface. SDS surface adsorption change the wettability of LDH particles. As suggested by the authors, inversion could be due to the packed adsorption of the single chain surfactant dodecylsulfate (SDS) onto the densely surface-charged Mg_2Al-Cl LDH.

In the case of Mg_2Al LDH-based water/paraffin oil Pickering emulsions, not only SDS surface adsorption enhanced LDH hydrophobicity but also the intercalation of SDS by replacing interlayered Cl^- anions favors even more the o/w to w/o inversion. Then, increasing the SDS concentration causes an inversion from o/w to w/o at low SDS concentration, provided the right oil/water ratio is insured. At optimized LDH/SDS concentration droplets have the smallest size ($2 \sim \mu m$) and regular spherical shape.

A second inversion from w/o to o/w may occur at higher SDS concentration leading to a double inversion phenomenon. This second inversion may be favored by the adsorption of SDS double layer increasing the compactness of the surfactant molecules and reversing the surface charge. At high SDS concentration the w/o emulsion is no more stabilized by organically-modified LDH that dissolved in oil phase but by the excess of SDS that adsorbs at the o/w interface. A critical emulsification speed was needed to afford the inversion.

Nana Zhang et al. (Zhang, Zhang et al. 2015) demonstrated that the effect of the emulsification process may affect the stability of the w/o emulsion. They compare the stability of water/liquid paraffin (liquid paraffin : $C_{20}-C_{33}$ isoalkane) stabilized by 100 nm size SDS-modified Mg_2Al-Cl platelets emulsified prepared either by ultrasonication or vortex mixing. Clearly, compared to the later, ultrasonication allows a longer time stability. Moreover, gel-like bridging Pickering emulsions were obtained (Fig. 4) at high v/v w/o ratio (50/50) for emulsion volume fraction of 100% whatever the particle concentration (0.2 – 1%). Rheological experiments show that bridging emulsions display similar viscoelastic properties than colloidal gels due to strong adhesions between bridged droplets, leading to infinite percolated fractal networks when particle concentration increases. The authors related the stability of the ultrasonicated emulsions to the formation of a percolating network of neighboring droplets with increased elasticity while emulsion prepared by vortex mixing is made of dispersed droplets.

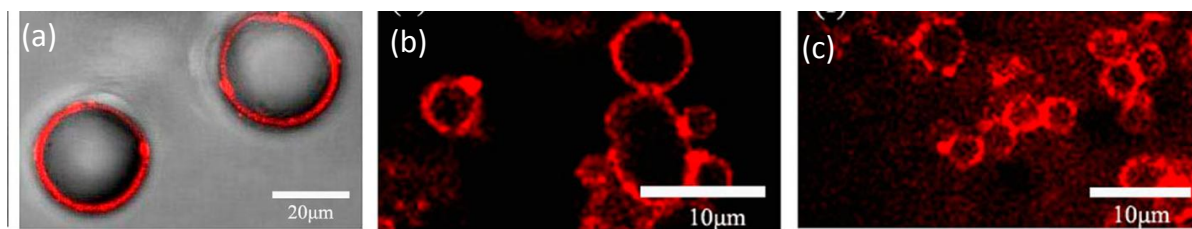


Figure 4: CLSM images of simple (a) and bridged emulsion at 0.2% (w/v) (b) and 0.7% (w/v) (c) Reproduced with permission from ref. (Zhang, Zhang et al. 2015) Copyright 2015

American Chemical Society.

Span 80 is a non-ionic surfactant used to form w/o emulsions due to a low HLB value (4.3) (Nollet, Boulghobra et al. 2019). Combination of Mg₂Al-Cl LDH and Span 80 stabilized w/o emulsions in all conditions above Span 80 concentration of 1 mM (LDH 1 wt%). Increase in Span 80 concentration favors the rise in emulsion fraction volume and the stabilization of the emulsions. As expected, size and size distribution both decrease with increasing Span 80 concentrations, enhancing the emulsion stability. Due to a strong synergistic effect, addition of LDH particle to Span 80 strengthens the long-term stability over more than 3 months. Effect of addition of Span 80 on the wettability of LDH particle was clearly evidenced by contact angle measurements, a proof that Span 80 adsorbs at the LDH platelet surface across the o/w interface rendering LDH more hydrophobic. The greater adsorption capacity of Span 80 by LDH compared to Laponite[®], explains why LDH stabilize w/o rather than o/w emulsions unlike Laponite[®]. No emulsion inversion was observed for such LDH/Span 80 system. Long-term stability may be explained by i) the tight attachment of densely-packed particles at the water droplet surface, ii) the resistance to coalescence thanks to the presence of LDH particles in the continuous phase, iii) the formation of 3D-network of droplet flocs.

Pickering emulsions may offer advantageous confined environments and controlled mass transfers for applications in catalysis for fine product synthesis. However, because many catalytic systems operate at high or medium temperatures there is a need for thermostable LDH-based Pickering emulsions with enhanced attachment energy. Increasing the amphiphilicity of the emulsifier is a strategy to reach this target. Shan et al. (Shan, Yu et al. 2015) reported a thermostable LDH nanohybrid system combining Mg₂Al-CO₃ LDH and

carbon nanotubes (CNT) that produce smaller droplets (30-150 μm) and 100% emulsion volume fraction compared to LDHs or CNT used alone as emulsifiers. The LDH-CNT Pickering emulsion remains stable over time at room temperature and more than 5h at 85°C.

3.3 Water in water emulsions

Water-in-water (w:w) emulsions are obtained by mixing two water-soluble but mutually incompatible macromolecules in solution. This kind of emulsions is commonly found in a variety of food products. These systems have been known for a long time and been described many years ago (Beijerinck 1910). The behavior of a mixture of two hydrophilic polymers is now well documented and numerous papers and reviews have been published (Esquena 2016, Nicolai and Murray 2017, Dickinson 2019). Water-in-water emulsions arise from different combinations of macromolecular compounds that interact attractively or repulsively with each other leading to water-water phase separation. Attractiveness creates structured regions in the medium through complexation, aggregation and coacervation mechanisms, forming a polymer-rich phase in and a polymer-depleted phase. Such a phenomenon is called associative separation. On the other hand, repulsiveness generates different regions containing predominantly one of the polymer involved. The latter is the most commonly found. (Piculell and Lindman 1992, Grinberg and Tolstoguzov 1997, Matalanis, Jones et al. 2011) At low polymer concentration, a competition between the entropy of mixing and enthalpy is responsible for the co-solubility. However, when increasing the polymer concentration, a two-phase system is formed as the enthalpy prevails. This behavior is found in numerous aqueous polymer solutions. As an example, mixtures of polysaccharides of close chemical nature, such as dextran and pullulan, separate if the concentration is high enough. Phase separation of a mixture of a neutral polymer and a polyelectrolyte is inhibited by the entropy of mixing of the counter-ions but is therefore enhanced by the addition of the salts. (Grinberg and Tolstoguzov 1997, Dickinson 2019) Only around 1% wt of polymers, amount depending of their molar mass and chemistry, are needed to generate the phase separation. Polymers with high molar masses require lower concentration to obtain a phase separation due to the lower entropy of mixing. Proteins and polysaccharides are most likely to undergo phase separation by segregation because their affinity for water is very different. (Tuinier and de Kruif 1999)

For w/w emulsions, usually, the internal phase of the dispersed droplet is made of the phase with the smaller volume fraction. Bicontinuous emulsions can be formed with 50:50 polymer ratio, placing the emulsion near the inversion point as shown in the thermodynamic phase diagram. Fig. 5 shows the diagram of w/w emulsions made with the water/gelatin/maltodextrin system. This diagram is composed of a curve (the bimodal curve) separating cosolubility (one phase) and phase separation (two phases). Another important curve shown on this figure is the spinodal curve representing the boundary between unstable and metastable systems. Tie-lines indicate the pairs of phases in thermodynamic equilibrium. These lines all merge at the critical point. Beyond this point, the two phases are totally miscible and only form a single phase.

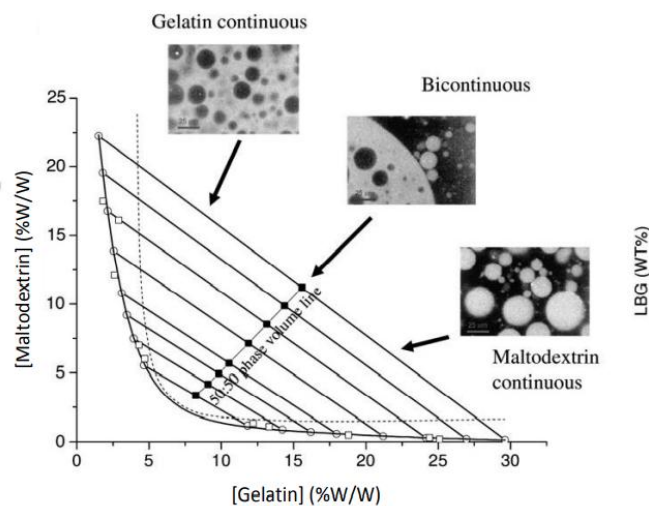


Figure 5: Scheme of w/w emulsion formation in the gelatin/maltodextrin system. Reproduced with permission from (Esquena 2016). Copyright 2016 Elsevier.

Some factors can influence the interactions between two incompatible polymers, among them, the pH and ionic strength, if at least one of the polymer involved in the system is charged. In this case, salts can play an important role by shielding the charges. Finally, temperature can also play a role by modifying the phase diagram changing the quality of the solvent. (Vis, Peters et al. 2014)

Even though w/w emulsions have been studied for many years, these systems are less known than their o/w and w/o counterparts principally due to increase in complexity. The first obvious difference is the presence of a single solvent which means that the two phases possess similar physical properties. These similarities between the phases lead to a slower

rate of creaming compared to O/W droplets of the same size. This also leads to an extremely low interfacial tension and microstructures more sensitive to stirring, shaking and other external flow fields. But it also means that it is almost impossible to stabilize the droplets with surfactants. Stable water-in-water emulsions are still possible by gelation of the continuous phase, thus preventing the coalescence. Due to the fragility of the droplets, with gelation, deformed anisotropic droplets are stabilised. (Nguyen, Wang et al. 2015) Consequently, the major differences with o/w or w/o emulsions comes from the fact that w/w emulsions display a large interfacial thickness and a low surface tension, and consequently a low adsorption energy, that cannot be overcome by the addition of small amphiphilic emulsifiers. Large uniform colloids or particles over hundredths of nanometers are required to stabilize such fragile systems.

During the last 15 years, it has been observed that particles added to w/w emulsions such as two incompatible polysaccharides tend to accumulate at the water-water interface which lead to an increase of the stability of the emulsion by slowing down its coarsening. Since then, various kinds of nano and microparticles have been studied to stabilize w/w emulsions for food applications. (Murray and Phisarnchananan 2016, Peddireddy, Nicolai et al. 2016, Gonzalez-Jordan, Nicolai et al. 2018, Laranjo, Costa et al. 2019)

Almost all of the particles tested are of organic origins. Among them we can cite carboxylated latex particules (Gonzalez-Jordan, Nicolai et al. 2018), or cellulose nanocrystals (Peddireddy, Nicolai et al. 2016, Ben Ayed, Cochereau et al. 2018) used in a PEO/Dextran system, β -lactoglobulin microgels in Xyloglucan/Amylopectin (Machado, Benyahia et al. 2021) system or zein particules, a protein from corn, in Gelatin/Dextran (Chatsisvili, Philipse et al. 2017). However, really few inorganics (Vis, Opdam et al. 2015) were tested but the use of LDH has not yet been investigated despite their use for o/w emulsions.

Silica nanoparticles (SiO_2 NP) are interesting candidates for the preparation of Pickering emulsions because both particle size and surface properties can be easily controlled respectively by tuning Sol-Gel process conditions and surface functionalization. Consequently, SiO_2 NP were successfully used for the preparation of o/w and w/o emulsions. In order to face the difficult problem to stabilize w/w emulsions through the mandatory enhancement of interfacial attachment energy, functionalization of SiO_2 surface may be an appropriate strategy to tailor the hydrophile/lipophile balance and the wettability of SiO_2 NP. In 2018 Griffith et al. (Griffith and Daigle 2018) functionalized, through an easy sol-gel condensation process, SiO_2

NP surface with 2-(methoxy(polyethyleneoxy)6-9propyl)trimethoxysilane. The organically modified particles were tested as an emulsifier for the stabilization of w:w emulsion made of polyethylene glycol and magnesium sulfate. They observed that droplet stability was related to the size of the silica particles used, achieving better stability with 50 nm particles than with 6 nm particles. The larger the particles, the greater the attachment energy. Nevertheless, they obtained a stable emulsion using 6 wt% particles for up to seven days (regardless of particle size).

Ganley et al. (Ganley, Ryan et al. 2017) investigated the stabilizing effects of montmorillonite platelets for a Polyethylene oxide(PEO)/Pullulan system. The PEO adsorbed strongly on the clay mineral platelets, thus favoring the formation of pullulan droplets in PEO. The droplets obtained were stable to both creaming and coalescence for at least 21 days.

In 2015, Vis et al.¹⁸ studied the behavior of Al(OH)₃ (gibbsite), a 2D inorganic structure not far from the LDH structure, at the interface of w/w emulsions formed by mixtures of gelatin and dextran. Gibbsite platelets display anisotropic shape with lateral size ranging from 85 nm to 170 nm and a thickness of about 7 nm leading to a high aspect ratio (0.08-0.04). Theoretical calculations¹⁸ concluded that such bidimensional particles display a higher free energy of adsorption than spherical particles $\Delta G_{ads}(\text{platelet}) = -(\pi/4)d \gamma(1 - |\cos \theta|)$ and should act as better stabilizers. Consequently, nanoplatelets orientate flat to the interface with a poor effect of contact angle (Fig. 6 a, b, c, g) unlike SiO₂ nanospheres.

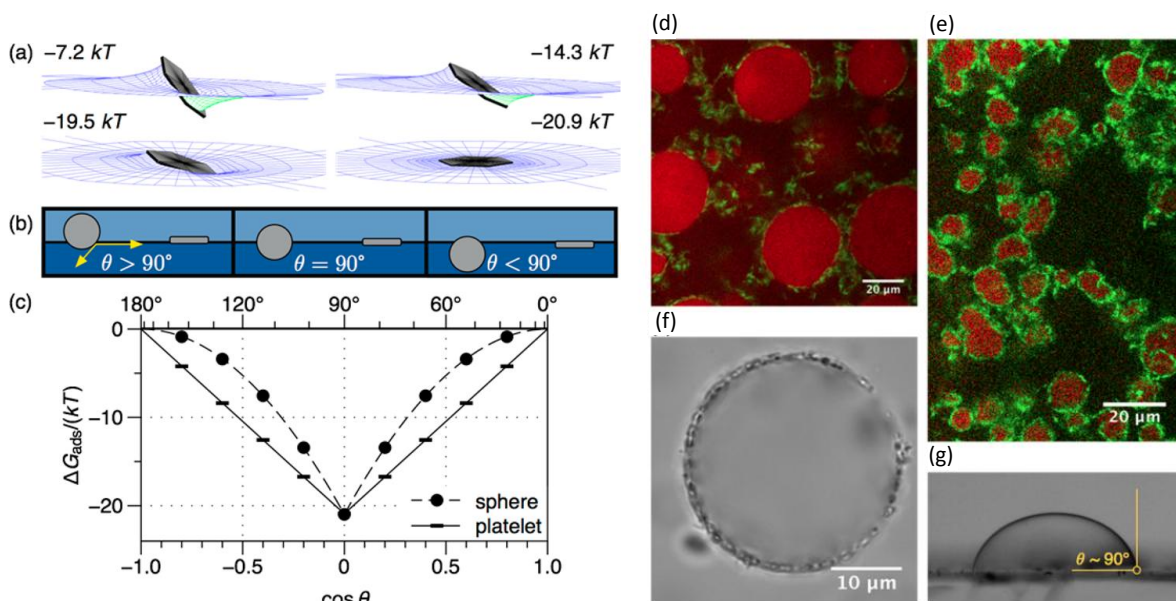


Figure 6. (a) Calculated adsorption energy of nanoplates (167 nm) at the water–water interface ($\gamma = 4 \mu\text{N/m}$). Platelet vs sphere contact angle effect on (b) adsorption area and (c)

adsorption energy. CLSM images of dextran (9%)/gelatin(3%) emulsion stabilized by gibbsite platelets (d) 0.4 wt% and (e) 1 wt%. (f) Gibbsite plates (700 nm) at the surface of a dextran-rich droplet. (d) Gelatin-rich droplet in a dextran-rich continuous phase on a gibbsite-covered glass substrate with permission of ref. 18.

Stable w/w emulsions were obtained for 0.4 w% gibbsite particles content, 1 wt% was needed for a full coverage of the droplets (Fig 6 d,e f). No coalescence neither sedimentation was observed after 3 weeks. This effect was explained by the fact that the gibbsite nanoplatelets were localized at the interface of the w/w emulsions aggregated with each other, thus forming a weak gel of droplets.

This last example highlights the interest of 2D metal hydroxide nanoplatelets to stabilize w/w emulsions. LDH display similar hexagonal platelets to gibbsite and appear as good candidate for such application.

We recently studied the effect of LDH, more specially, nanoplatelets of Mg_3Al of around 100 nm, for the stabilization of three different emulsions systems (data not published). PEO droplets in Dextran, Dextran droplets in PEO and finally Gelatin droplets in Dextran.

For each system, it has been noted that up to 1% wt of LDH, the droplets were more numerous and of smaller size (Fig. 7). Functionalization of LDHs by fluorescein isothiocyanate-dextran (FITC-Dextran) allows to show that LDH nanoparticles may adsorb at the w/w interface while leading to a strong aggregation between droplets. These emulsions could resist in solution for over a week.

However, such LDH based Pickering emulsions are not easy to stabilize. Depending of slight changes in emulsion preparation (stirring speed, temperature) strong affinity between LDH and both dextran and gelatin leads to the partitioning of LDH nanoplatelets in both liquid phases, dextran and gelatin and at the dextran/gelatin interface. While LDHs are very promising candidates for Pickering emulsion systems, more studies are required to found a sustainable way to stabilize droplets with LDH in W/W emulsions.

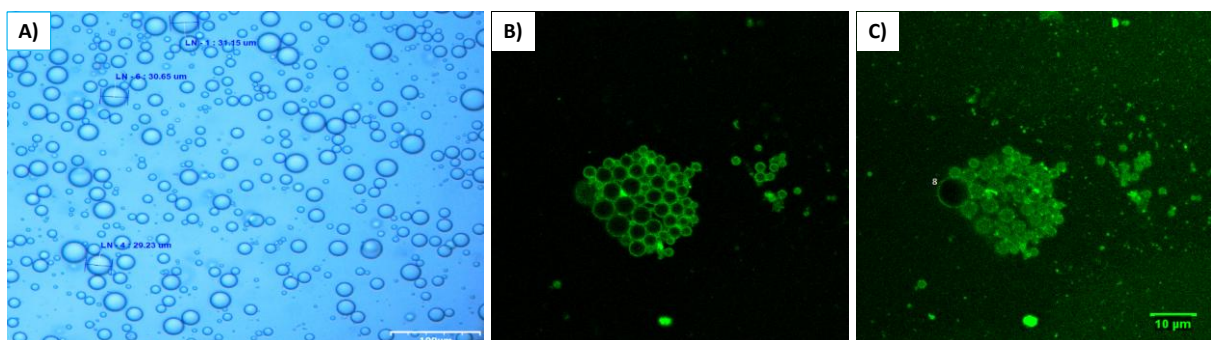


Figure 7: A) Images from optical microscopy of w/w emulsions composed of 5% gelatin, 15% dextran and 1% Mg₃Al LDH. B) and C) Fluorescent confocal laser scanning microscopy images of w/w emulsions composed of 10% gelatin, 10% dextran and 1% Mg₃Al LDH.

4- Applications of Pickering emulsion stabilized by LDH/LSH particles

Pickering emulsions are stable, easy-to-prepare systems that can be used in a variety of fields due to their unique characteristics and can be a good alternative to conventional emulsions in most applications. The large interfacial areas of Pickering emulsions can be efficiently involved for nanoparticles formation, catalysis and photocatalysis reactions while the homogeneous coating of emulsion droplets can act as a barrier to diffusion of great interest in encapsulating active compounds and the development of drug delivery systems or for other applications in life science. In addition, the dense coating at the droplets interface also opens the way for the fabrication of various types of materials including nanocomposite colloids through Pickering emulsion polymerization or functional porous materials by template processes. In the case of LDH however, only a few papers focused on the relevance of Pickering emulsion for applications, probably because for this class of 2D materials research is still at the stage of understanding Pickering emulsion formation and behavior.

4-1 LDH preparation

Pre- formed LDH particles stabilizing emulsion, it is not the only way to associate emulsions and LDH. Indeed, the synthesis of LDH nanoparticles can be quite challenging, specially the fine control of the particles size. An alternative method has been developed using double hydrophilic block copolymers (DHBC) and pickering emulsions. In this method, the DHBC acts as both, growth control and stabilizing agents. For example, as shown by Layrac et al. (Layrac, Destarac et al. 2014) for the formation of Mg-Al LDH, the metallic cations were first mixed with the copolymers thus forming micelles constituted of almost only Al³⁺ by preferential complexation of the trivalent cations. Then, Al³⁺ were transformed into aluminum hydroxide by hydroxylation allowing the incorporation of Mg²⁺ into the micelle by further hydroxylation leading to the Mg-Al phase²¹. Such technique has been also

recently extended to synthesize a Cu-Al LDH phase with an efficient control of the size of the nano particles (Layrac, Harrisson et al. 2020).

4-2 Catalysis

As Pickering emulsions are versatile systems, their ability to be used in catalytic reactions has emerged as a promising and recent research field. (Rodriguez and Binks 2020) Multifunctional particles or modified particles can be involved in the stabilization process and then participate in the catalytic process leading to interesting selectivity and conversion. Shan et al. (Shan, Yu et al. 2015) reported a thermostable water/toluene Pickering emulsion involving LDH nanohybrid system combining Mg_2Al-CO_3 LDH and carbon nanotube (CNT). A large emulsion volume fraction and small droplets size (30-150 μm) were readily formed, producing high emulsion interfacial surface areas compared to LDH or CNT used alone as emulsifiers. The LDH-CNT Pickering emulsion remains stable over time at room temperature and more than 5h at 85°C. LDH-CNT modified with Ru particles were involved in Pickering emulsion and were then tested for the selective oxidation of benzyl alcohol to benzaldehyde, showing a high catalytic conversion.

4-2 Porous LDH materials

Pickering emulsions have been described as an efficient soft template approach to generate a porous structure. (Zhu, Wang et al. 2020). For instance, Li et al. (Li, Zhao et al. 2013) reported from Pickering emulsion stabilized by methyl orange (MO) modified LDH particles (0.25 wt%), the fabrication of hollow colloidosomes composed of fluorescent Mg_2Al -LDH particles. The adsorption of MO-modified LDH onto the surface of liquid droplet has also been exploited to produce hollow colloidosomes. To produce porous materials from the Pickering emulsions, the emulsion was washed with acetone to replace the external aqueous phase and then with ether to dissolve the oil core of droplets. Although most of the colloidosomes were unable to maintain their structural integrity under the high capillary forces developed during the washing step and ether evaporation, some of them are retained showing spherical shape with size ranging between 5 to 30 μm . (Fig. 8)

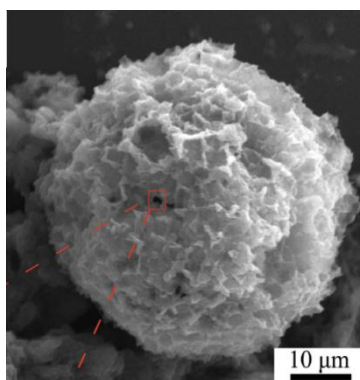


Fig 8 SEM images of dried hollow colloidosomes obtained from o/w emulsion stabilized by 0.25 wt% LDH modified with 10 mM. Reproduced with permission from ref (Li, Zhao et al. 2013). Copyright 2013 Elsevier.

4-3 Towards nanocomposite colloids

Stable MgAl-CO₃-LDH-armoured latexes were produced by Pickering emulsion polymerization. (Pearson, Pavlovic et al. 2018, Qiao, Dugas et al. 2020) In a control experiment using styrene as the sole monomer, the TEM images clearly show a mixture of bare polymer latex particles around 330 nm in diameter and free LDH evidencing no affinity between the two populations of particles. In these conditions, the LDH platelets are too hydrophilic for the polystyryl radicals formed in water to irreversibly adhere to their surface and lead to armoured latexes through Pickering emulsion polymerization. The addition of hydrophilic comonomers such as γ 2-hydroxyethyl methacrylate (HEMA) or methyl methacrylate (MMA) is key to promoting adhesion of the LDH nanoplatelets onto the polymer particle surface and latex stabilization. The addition of salt into the medium screened the positive charges between adjacent MgAl- sheets allowing closer packing of the LDH platelets onto the latex particle surface and the formation of larger the nanocomposite particles.

LDH based nanocomposite particles with armoured morphology was also produced using a monomer feed of MA/BA 80:20 (mass/mass) to facilitate subsequent nanocomposite film formation under ambient conditions. In this case, as a first step statistical copolymers of acrylic acid (AA) and n-butyl acrylate (BA) were adsorbed on the surface of the colloidal MgAl- LDH. (Pearson, Pavlovic et al. 2018) Sandwich and encapsulated morphology were obtained using a reversible addition fragmentation chain transfer (RAFT)-mediated emulsion polymerization while the use of A RAFT-free analogue produced armoured latexes,

highlighting the importance of the RAFT function for promoting growth of the polymer shell from the nanoparticle in avoiding the Pickering emulsion polymerisation way.

The microstructure and mechanical properties of nanocomposite films made from the different latex morphologies have been studied in detail (Dalmas, Pearson et al. 2018) showing improved properties for LDH based nanocomposites films compared to native polymer matrices, especially in the case of LDH armoured latex morphology. (Fig X)

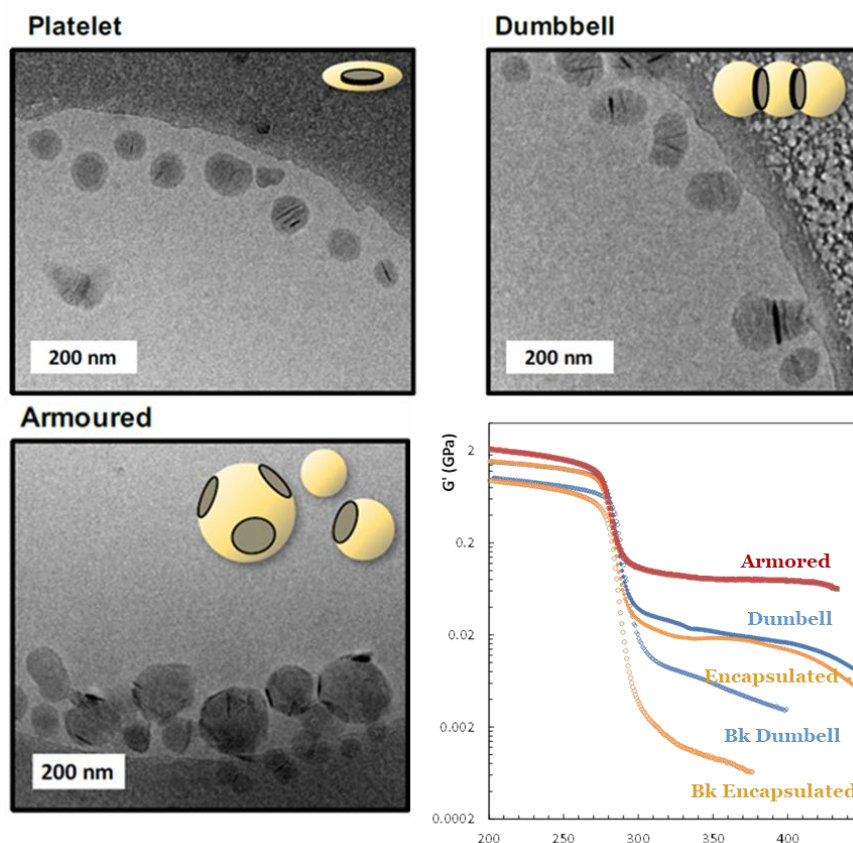


Fig. X CryoTEM images of the nanocomposite particles displaying the platelet, dumbbell and armoured morphology, and the evolution of G' as a function of temperature for the LDH-filled nanocomposites with different morphologies and the corresponding blank material. Adapter from ref. with permission from (Dalmas, Pearson et al. 2018, Pearson, Pavlovic et al. 2018) The Royal Society of Chemistry and the American Chemical Society. Copyright 2018 American Chemical Society.

5- Conclusions

The few reported papers on Pickering emulsions stabilized by Layered double hydroxides have demonstrated that these 2D materials are suitable candidates for emulsion preparation. Indeed, LDH

display easy tunable physico-chemical properties in term of charge density, surface functionalization, particle size and shape, wettability and hydrophilic lipophilic balance that may adapt to the thermodynamic control of the liquid-liquid interface. Already LDH modify by salts, amphiphilic molecules and polyelectrolytes have demonstrated efficient stabilization of different water in oil emulsion systems. The important knowledge that has been acquired on the preparation of a large variety of LDH, hybrid LDH and polymer based LDH nanocomposites is a great asset to open new opportunities for the stabilization of new water in oil emulsion systems not only for applications in the fields of pharmaceuticals, cosmetics or food but also for the design of novel systems of confinement or encapsulation interesting catalysis, photocatalysis, biocatalysis or nanomedicine. More investigations are needed however to overcome the difficulties to stabilize water in water emulsions of great interest for the development of green and sustainable chemistry.

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