

Fluorescent microparticles fabricated through chemical coating of O/W emulsion droplets with a thin metallic film†

Cite this: *RSC Adv.*, 2014, 4, 11564Received 29th November 2013
Accepted 23rd December 2013

DOI: 10.1039/c3ra47063f

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We have developed a simple fabrication process for fluorescent silver-coated liquid particles. The synthesis involves the encapsulation of quasi-monodisperse micronic soybean oil-in-water emulsion droplets in a polydopamine shell followed by an electroless silver plating of the surface. Due to the presence of the thin silver layer, the droplets exhibit a broad range fluorescence that shows no photobleaching upon illumination. The method shows that multimodal colloidal microparticles can be produced *via* a high-yield method from sustainable, off-the-shelf products with mild synthesis routes in aqueous conditions.

Introduction

Colloidal particles in the micron range with carefully designed surface and volume properties have been subjected to intense research effort in recent decades,¹ pushed by the potential industrial and fundamental developments in the domains of *e.g.* photonic crystals fabrication² or soft-matter physics.³ If historically synthetic colloidal particles were spherical and chemically homogeneous,⁴ they can now be fabricated with anisotropic shapes^{5,6} or core-shell structures^{6–8} that broaden their range of applications. Colloidal particles encapsulated in a thin metal layer are already available on the market as seeding particles for hydrodynamic studies.⁹ They show interesting developments in the domain of catalysis,¹⁰ owing to their large surface-to-volume ratio, and photonics.¹¹ Whereas continuous shells and films made from an assembly of nanoparticles have both their respective advantages in terms of optical properties,¹²

most of the fabrication processes of metallodielectric objects have been focused on the deposition or growth of nanoparticles on the surface of the colloidal particles^{8,11,13–19} and not on the deposition of continuous layers.

Several recent advances in the domain of sophisticated micronic colloidal particles are based on the usage of liquid emulsion droplets^{20,21} as they can encapsulate various materials and can be fabricated in a scalable manner.²² However, there has been no attempt so far to use oil-in-water emulsions as templates for the fabrication of core-shell metal-coated colloidal particles, despite the facility for droplets to be fabricated with a large range of core properties. Indeed, besides the sole choice of the materials, dealing with liquid particles can be quite difficult as they are prone to irreversible destabilization by phenomena such as ripening, coalescence and aggregation.²² These latter phenomena are especially encountered with fabrication processes that modify the surface of the droplets and change the nature of the particle-particle interactions. Several solutions have been proposed so far to overcome this issue: they involve either the use of new materials such high molecular weight polyelectrolytes,²³ solid phases^{6,24} or fluorinated oils²⁵ that increase the emulsion stability at the cost of a limitation of the formulation range, or the use of new fabrication technologies such as microfluidics²⁶ that are still limited in terms of production quantities.

Herein we describe a simple method to fabricate liquid droplets encapsulated in a thin continuous metal layer in bulk quantities. The method, shown in Fig. 1, is based on the deposition of a polydopamine layer at the interface of micronic droplets followed by the electroless deposition of metallic silver onto it. The process keeps the size distribution of the emulsion unchanged and maintains the colloidal stability of the suspension. Due to the presence of a thin silver layer, the droplets exhibit a broad range fluorescence that shows no photobleaching upon illumination.

Results and discussion

Synthetic melanins can be synthesized by the oxidation and polymerization of catecholamine molecules, such as dopamine,

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3ra47063f

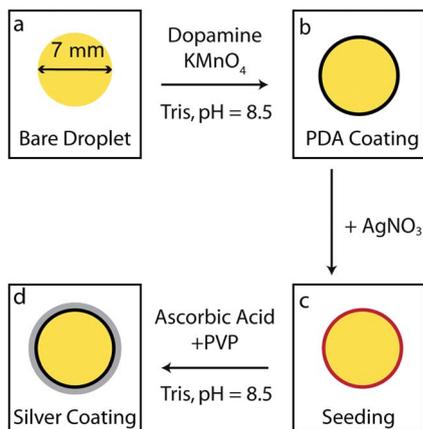


Fig. 1 Schematic representation of the fabrication of metal-coated emulsion droplets. The naked soybean oil droplets (a) are dispersed in an oxidative and alkaline aqueous solution of dopamine. The dopamine polymerizes at the surface of the droplets (b). After the addition of silver nitrate, the silver ions are adsorbed on the polydopamine layer (c). The addition of ascorbic acid, a reducing agent, and PVP, a stabilizing polymer, leads to silver-coated emulsion droplets.

in mild-alkaline aqueous solutions.²⁷ In the presence of a solid substrate²⁷ or specific emulsion formulations,^{28,29} the polycatecholamine macromolecules are able to form a thin-film layer that adheres strongly to the surfaces^{15,30–35} and can further be functionalized.^{15,16,30,36} To coat the surface of the droplets with polydopamine, we dispersed the soybean oil emulsion (see the Experimental section for the fabrication details) at a 20% w/w oil fraction in a Tris buffer (pH = 8.5, 20 mM) containing dopamine hydrochloride (2 mg mL⁻¹, 10 mM), potassium permanganate KMnO₄ (5 mM) and supplemented it with a surfactant (Tween 20, 0.2% w/w) to stabilize the droplets. After 2 hours of reaction at room temperature, the microtube and the droplets appear as shown in Fig. 2b. The samples that are used for further metallization are rinsed twice with the Tween 20-supplemented Tris buffer to remove the unreacted molecules

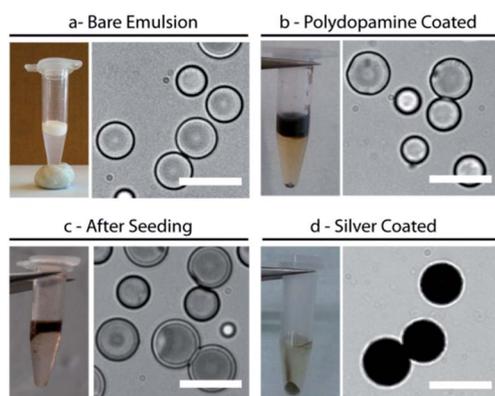


Fig. 2 Photographs of the reaction microtubes (left) and brightfield microscopy images of the droplets (right) during the silver-coating process. The oil is lighter than the aqueous buffer so the droplets tend to go upwards in the microtubes (a–c) except when the silver layer is present at the interface (d). Scale bar: 10 μm.

present in solution at the end of the reaction. The emulsion at the top of the microtube has a black color characteristic of polydopamine.³⁷ The droplets are slightly wrinkled, indicating that the droplet surface is coated by a thin polydopamine layer. The condensation takes place at the interface of the droplets solely, as demonstrated by the quasi-absence of a water-insoluble polydopamine black sediment at the bottom of the microtube after centrifugation. The resulting polydopamine-coated droplets show a strong negative surface potential (*ca.* –60 mV) as reported in Fig. S1.† By contrast with the existing literature on the polydopamine-coating of emulsion droplets^{28,29} taking place at the surface of specific surfactant-free emulsion formulations, Fig. 2b shows that simple and natural soybean oil-in-water emulsions, stabilized by a non-ionic surfactant, are able to withstand the deposition of a melanin film at their interface from a dopamine solution without being destabilized.

Classically, the oxidizing agent is the dioxygen dissolved in the aqueous buffer, but the use of an exogenous oxidant such as potassium permanganate has been shown to increase³⁷ the polymerization kinetics. In our experiments, polydopamine oxidized by dioxygen solely is unable to allow the formation of spherical silver-coated spheres, whereas for a reaction taking place in a solution supplemented with potassium permanganate in limited quantities, we obtain the black, silver-coated droplets shown in Fig. 2d and S2b.†

To cover the surface of the polydopamine-coated droplets with a metal layer, we used an electroless plating process that consists of a seeding followed by a reduction of metal ions.^{15,16,30} We first dispersed the droplets in a Tris–Tween 20 buffer containing AgNO₃ (0.176 M) for 90 minutes at room temperature in the dark. During the seeding step, the negatively charged polydopamine layer promotes electrostatically-driven adsorption of the Ag⁺ cations on the emulsion surface, as demonstrated in Fig. S1† by the zeta potential increase after the seeding compared to the zeta potential of the polydopamine-coated emulsions. During the reaction, the suspension turns brown-red, and centrifugation shows that only the emulsion changed its color, leaving the reaction buffer totally clear, as shown in Fig. 2c. The cryo-SEM picture of Fig. S3c† supports the hypothesis that the brown color of the emulsion is a consequence of the presence of a small amount of silver nanoparticles at the surface of the droplets. The silver reduction of some of the adsorbed cations is made possible thanks to the intrinsic redox behavior of polydopamine layers.³⁰

To complete the formation of the silver shell, we added 1.5 eq. of a reducing agent and polyvinylpyrrolidone (PVP, 0.02% w/w), a stabilizing polymer commonly used for silver nanoparticle synthesis,³⁸ to the microtube containing the Ag⁺-adsorbed droplet solution. After a short reaction time, *ca.* one minute, we rinsed the suspension with the Tris–Tween 20 buffer prior to the optical microscope observations. For the sake of comparison, we tried three different reducing agents: sodium borohydride, sodium citrate and ascorbic acid, among which only the latter gave excellent results as shown in the comparison in Fig. S2c and d.† In the absence of PVP, silver coats the inner walls of the microtubes and barely exists on the surface of the droplets. Fig. 2d shows that metallized droplets are perfectly

round and opaque to light in brightfield pictures. As their density is higher than the density of water, they settle at the bottom of the microtube instead of going upward under the effect of gravity. The silver-coated, freeze-dried droplets observed by cryo-SEM show a very regular and spherical shape, as demonstrated in the inset of Fig. 3a. On the sectioned droplet, we identified easily the frozen oil core and the silver shell, whose thickness can be estimated to be 50–100 nm, taking account of the observation angle. The process of silver deposition on the droplet surface is typical of the preparation of metallic nanoparticles, which could explain the presence of a small amount of silver nanoparticles attached to the continuous silver layer.

The Fig. 3b shows the comparison of the size distributions of the emulsion after each step of the silver-coating process to the original distribution of the naked droplets. The coating of the droplets first by polydopamine and then by a metal layer doesn't induce any change in the size distribution. Especially, we don't see any apparition of populations of larger particles, a

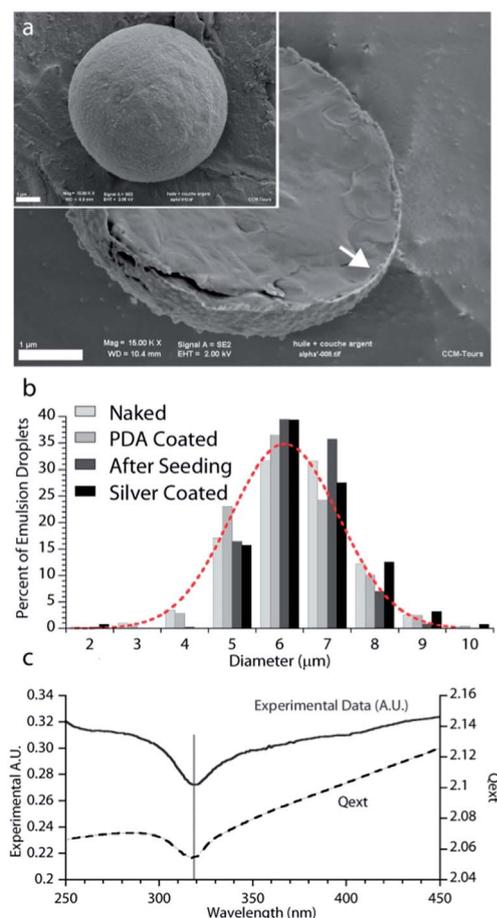


Fig. 3 (a) Cryo-SEM images of a full (inset) and sectioned silver coated droplet. The droplets are spherical and we see the continuous, ca. 50–100 nm thick, silver layer at the interface. Scale bar: 1 μm. (b) Size distribution histogram of the emulsion after each fabrication step. The red line corresponds to a gaussian fit of the size distribution of the naked droplets. (c) Comparison of the experimental absorption spectrum of the particles to the extinction efficiency Q_{ext} of silver-coated droplets with similar size parameters.

consequence of coalescence or irreversible aggregation of smaller droplets, usually observed when manipulating liquid colloids.²² The exceptional stability of the emulsion along the process has two different origins. First, the presence of the polydopamine layer provides a strong negative potential (ca. –60 mV) to the interface of the droplets that induces an electrostatic stabilization of the suspension and reduces the occurrence of coalescence.³⁹ Second, the polydopamine layer acts as a polymer skin at the surface of the droplets that is more difficult to disrupt than a sole oil/water interface stabilized by a surfactant monolayer.

Silver is a material prone to oxidation in alkali conditions, leading to the formation of a silver oxide with optical properties different from the metal.^{40,41} The UV-visible extinction spectrum of the silver-coated particles dispersed in water shown in Fig. 3c reports the existence of an extinction minimum at 320 nm and a barely flat profile on the whole spectrum. Fig. 3c also shows the results of the Mie calculation of the average extinction efficiency⁴² of a collection of particles with a normally distributed diameter of $6.8 \pm 1.3 \mu\text{m}$ and a constant silver thickness of 100 nm. As the exact concentration of droplets in the aqueous solution is not known, we are not able to scale the experimental data to the calculation. The extinction minimum is a consequence of the sudden drop of the real part of the silver refractive index and the existence of a minimum of the imaginary part of the refractive index at 320 nm. This behavior has already been reported for silver nanoparticles suspended in water.⁴³ The experimental data and the calculation are in good accordance and indicate that the shell is made from non-oxidized metallic silver.

Observed by epifluorescence microscopy, the metallized droplets show a strong and broad fluorescence range observable with the DAPI, GFP and DsRED filter sets, as shown in Fig. 4a. By diluting the ascorbic acid solution while keeping the droplet concentration equal after the seeding step, we are able to obtain an uneven metallization among the droplets of the sample that can be quantitatively characterized. The analysis shows that the degree of metallization, assessed by measuring the grey level of the droplets in Fig. 4b, correlates positively with the fluorescence intensity of the droplets, as reported in Fig. 4c. Fig. S4† reports the existence of fluorescence blinking of the silver-coated droplets, characteristic of the emission properties of single nanoparticles in general and silver nanoparticles in particular.^{43–46} Moreover, Fig. 4d shows the evolution of the normalized fluorescence of the metallized droplets under continuous light illumination at the full lamp power. In all cases, the fluorescence of the droplets shows no photobleaching after 10 minutes illumination period on the contrary to what we observe with molecular fluorophores.⁴⁷ No matter the illumination wavelength, the normalized curves share the same dynamics of the fluorescence increase with time. Despite our lack of understanding of its microscopic basis, this phenomenon resembles the photoactivation of fluorescence reported for individual silver nanoclusters under strong blue illumination.⁴⁸ These four arguments are in favor of an intrinsic fluorescence originating from the presence of the silver layer.

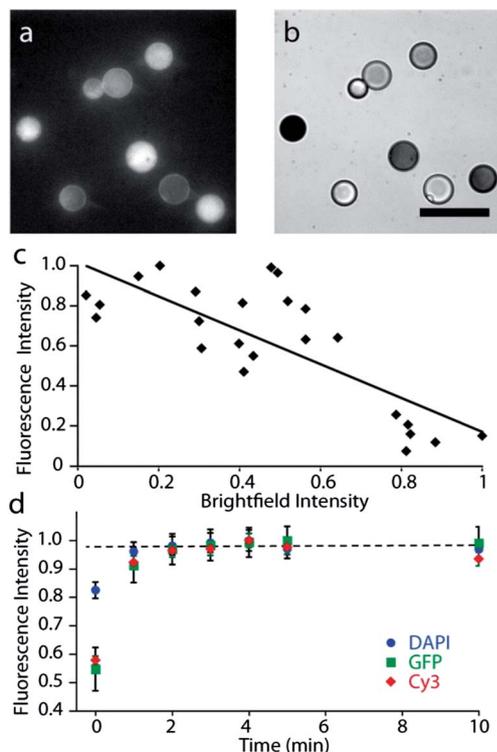


Fig. 4 Fluorescence (a) and brightfield (b) microscopy images of droplets coated with different silver thicknesses. Scale bar: 20 μm . (c) The fluorescence of the silver-coated droplets correlates positively with the degree of metallization. (d) Evolution of the fluorescence of the droplets under a continuous illumination at 365, 488 and 560 nm and measured with the corresponding filter sets. The fluorescence intensity shows no photobleaching.

Conclusion

In conclusion, the encapsulation of soybean oil-in-water emulsion droplets and the deposition of a silver layer on them enable the fabrication of fluorescent particles. The presence of the polydopamine layer greatly increases the stability of the suspension, despite the liquid nature of its core, and allows the size distribution and the shape of the droplets to remain unchanged until the end of the metallization process. The dark, silver-coated, emulsion droplets show a long lasting, broad fluorescence range that is a consequence of the intrinsic fluorescence of the thin silver layer.^{43–46}

The synthesis of metal-coated microparticles generally involves the electroless deposition of a metal shell on a solid core made from silica or a polymer.^{11,13–15,17–19} The fabrication of the central part of the particles is often done by nucleation/growth techniques, such as Stöber condensation⁴ or emulsion polymerization.⁴⁹ These manufacturing routes necessitate a significant amount of organic substances derived from petrochemicals and appear in contradiction with the increasingly stringent context of sustainable chemistry⁵⁰ that demands the development of environment-friendly processes. On the contrary to what has been achieved so far, the process described here is the first proof of principle that multimodal colloidal microparticles can

be produced *via* a high-yield method from sustainable, off-the-shelf products with mild synthesis routes in aqueous solvent.

Experimental

Materials

All the chemicals were purchased from Sigma-Aldrich. The Poloxamer 188 block-polymeric surfactant ($\text{HO}(\text{C}_2\text{H}_4\text{O})_{79}-(\text{C}_3\text{H}_6\text{O})_{28}-(\text{C}_2\text{H}_4\text{O})_{79}\text{H}$) was kindly provided by Croda France SAS. Ultrapure water (Millipore, 18.2 $\text{M}\Omega\text{ cm}$) was used for all experiments.

Emulsion fabrication

We first manually disperse the soybean oil (74% w/w) in an aqueous phase containing a Poloxamer 188 block-polymeric surfactant (15% w/w) and a thickening agent (sodium alginate, 2% w/w) by gentle stirring. This crude, polydisperse emulsion is further sheared and rendered quasi-monodisperse in a Couette cell apparatus under a controlled shear rate (5000 s^{-1}), following the method developed by Mason and Bibette.⁵¹ After fragmentation, the droplet population has a final diameter, measured by microscopy, equal to $6.8 \pm 1.3\ \mu\text{m}$, as shown by the size distribution in Fig. 2a.

Optical microscopy

Observations are carried out with a Zeiss Axio Observer Z1 inverted microscope linked to a Clara E interline CCD camera (Andor Technology). Pictures are acquired and analyzed with the image acquisition software $\mu\text{Manager}$.⁵² The epi-illumination is done with a HBO mercury arc-lamp and three filter sets (Semrock) corresponding to DAPI (Exc.: 360 nm, Em.: 461 nm), GFP (Exc.: 488 nm, Em.: 515 nm) and Cy3 fluorophores (Exc.: 560 nm, Em.: 620 nm). All images are taken with a $100\times$ oil immersion objective (NA: 1.25).

UV-Vis spectroscopy and simulation of the extinction efficiencies

The UV-Vis extinction spectra are carried out with a Peltier-cooled Varian Cary 500 spectrometer and Hellma QS quartz cuvettes. The computation of the extinction efficiency of the droplets is made according to the Mie theory of light scattering,⁴² using the code developed by C. Mätzler⁵³ for Matlab. The size parameters determined from light microscopy and cryo-SEM are taken as input parameters (core diameter: $6.8 \pm 1.3\ \mu\text{m}$, silver thickness: 100 nm). The experimental dielectric constants of silver by Johnson and Christy⁴¹ are used to model the silver shell, with no adjustable parameters. The soybean oil core and the aqueous surrounding medium are modeled with a refractive index of 1.48 and 1.33 respectively, and the polydopamine layer is neglected.

Electronic microscopy

A cryo-scanning electron microscope is used to study the uniformity and the roughness of the silver shell. The suspensions are suspended in DI water, freeze-dried at $-140\ ^\circ\text{C}$,

metalized and observed on a Zeiss Ultra Plus SEM (2 kV acc.) equipped with a Gatan Alto 2500 cryotransfer module.

Acknowledgements

We thank Ludovic Jullien, Thomas Le Saux and the Pôle Chimie-Biophysique of the Chemistry Department of the ENS for the discussions and the access to the UV-Vis spectrophotometer. We also acknowledge Jong Seto (Chemistry Department, ENS, Paris), Sébastien Bidault (Institut Langevin, ESPCI, Paris) and Marta Bally (Chalmers, Sweden) for the discussions about this work.

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