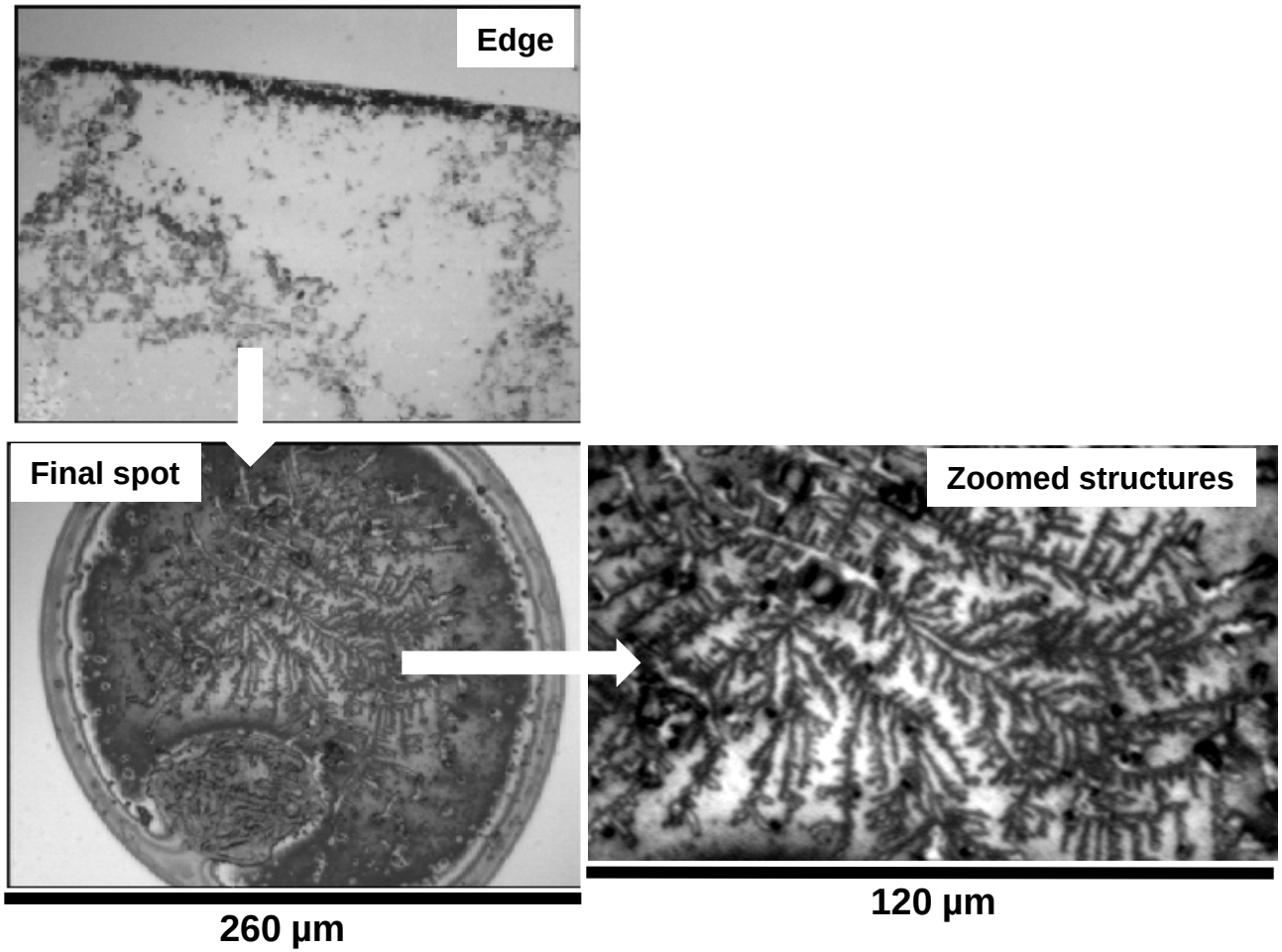
Electronic Supplementary Material (ESI) for Soft Matter

Supplementary Information 1a

Typical structures resulting from the drying of a *dialyzed* NH_3-stabilized NPs drop, the amount of NPs in which was increased by successive additions of a volume increment of 5 µL to the drying drop, at constant contact diameter, i.e. before it starts to recede. This way, the concentration of the final (dialyzed) drying drop was virtually increased 100 times to compensate for the loss of NPs during the dialysis process. This provides a way to discriminate between the role of the NPs concentration and of the influence of the synthesis salts which are also missing in that dialyzed solution. The dendrite aggregates which usually form on the entire drying area or along the outer-region of the drop here appear exclusively within a tiny final spot. Indeed, it is there that the residual salt traces have been dragged and concentrated over the large drying time to achieve the required (salt/NPs) compositional conditions for the genesis of those complex aggregation structures.



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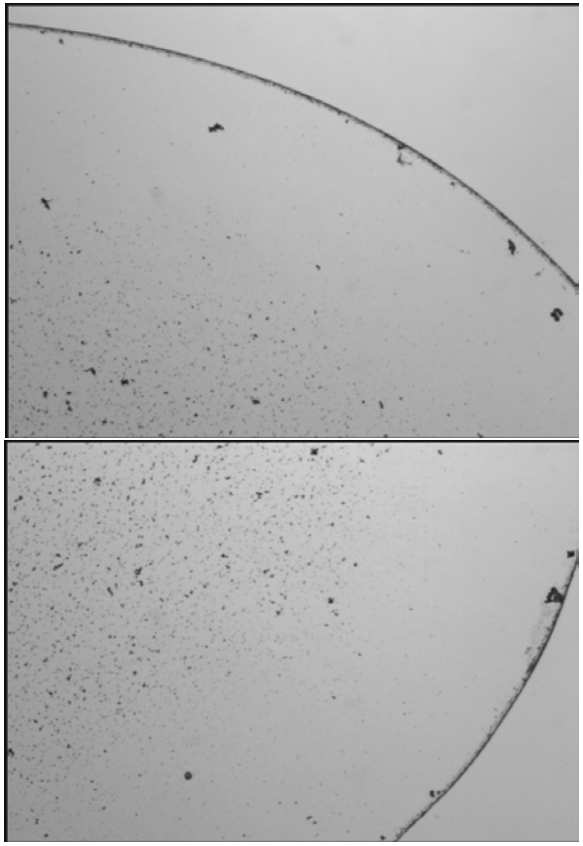
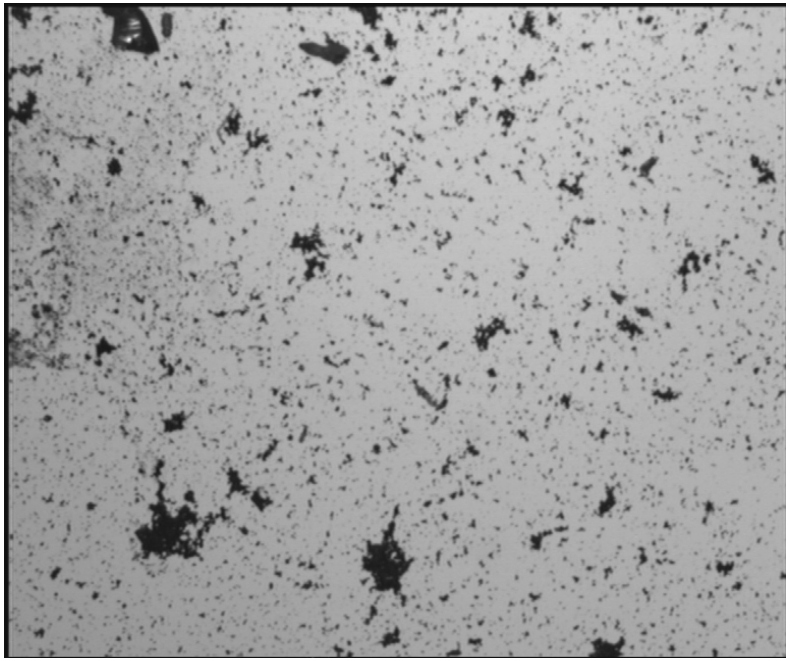
Supplementary Information 1b

Typical structures resulting from the drying of a *dialyzed* NPs solution drop concentrated by centrifugation at a nominal concentration equal to that of the "as-prepared" solution. 5 µL of this concentrated *dialyzed* solution was used in a single step drying experiment, i.e. in drying conditions comparable to those used for the "*as-prepared*" solution. The drying areas in this case have never led to any complex aggregation structures or patterns, displaying essentially a random distribution of featureless and discrete particles aggregates



Optical microscopy images of the border of the drying area at two different locations, showing small particles agregates

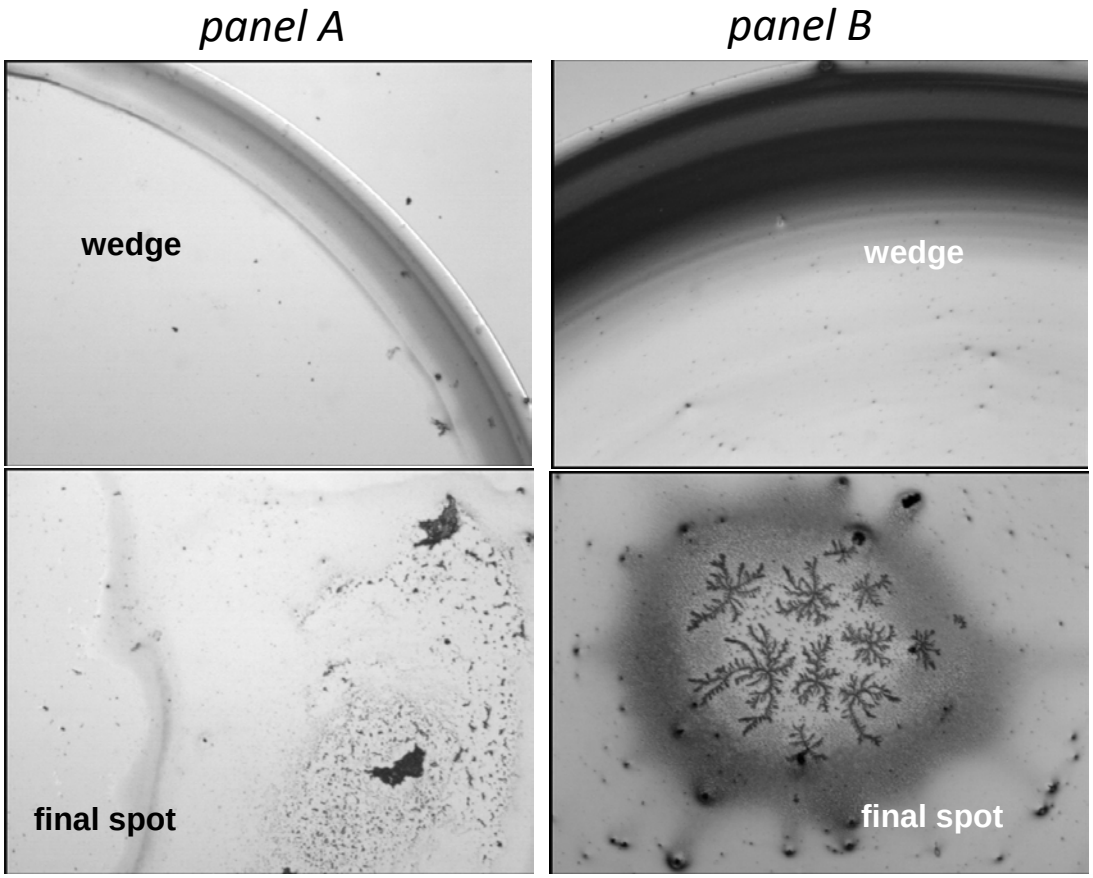


Optical microscopy image of the center of the drying area showing large and featureless aggregate deposits

Supplementary Information 2

Drying of the mixed (*SA*/*Dialysed*-NPs) solution drops, characterized by either the absence of structure (*SA* concentration of 10^{-7} M /*panel A*), or at best by the formation of a few small dendrite aggregates in the final spot as shown in *panel B* which is representative of both *SA* concentrations of 10^{-6} M and 10^{-5} M.

Nothing that resembles the patterns appearing in the mixed (*SA*/*as-prepared* -NPs) solution drops!



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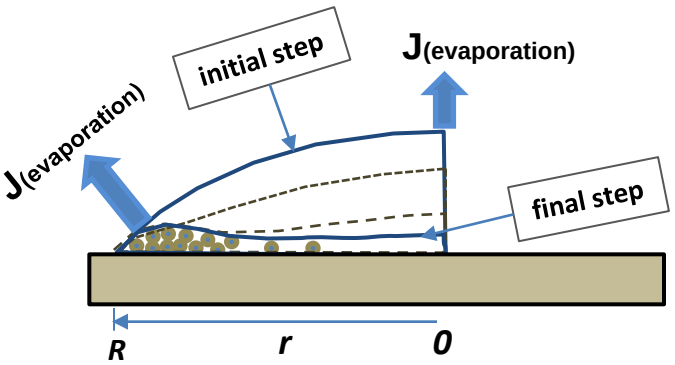
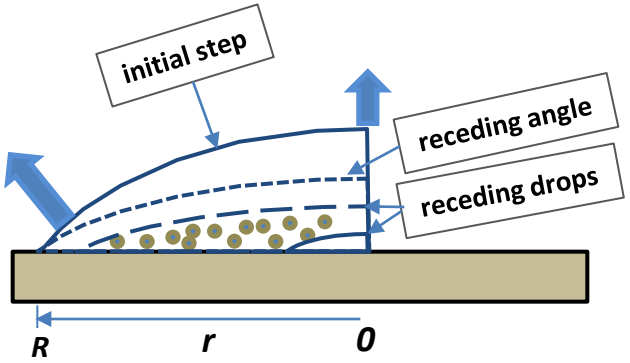
Supplementary Information 3

Sketch of the two extreme "evaporation/drying" regimes of sessile suspension droplets, and their associated localizations of the drying structures under partial wetting conditions.





Pinning-dominated evaporation/drying regime

Here, the drying results in an accumulation of solutes along the the drop border, either due to a complete pinning or a pinning for a finite but sufficient time for evaporation-gradient to drive the outward particle transport. In the final stage, the residual fluid may either detach from the peripheral accumulated particles and recede, or dry homogeneously in its depleted central part, or dewet through heterogeneous nucleation (most probable).

Depinning/receding-dominated evaporation/drying regime

Here, the evaporation leads to the 'early' depinning and receding of the drop, which now collects during its inward motion (shear-drainage) all the solutes that are loosely attached to the substrate. These solutes are then accumulated inside the final drying spot where the structures (when they form) appear essentially.

Supplementary Information 4

Surface tension-driven Rayleigh instability of cylindrical-shaped liquid segment, leading to its fragmentation and the formation of isolated droplets.