Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

Supplementary Information

Preparation of Ag Electroless Plating Baths

Electroless Ag plating solutions were prepared according to the composition given in Table S1 as developed in our laboratories [1]. All components are added to a small volume of distilled water (~10 ml) in the order listed, ensuring full dissolution with each addition. The completed solution was made up to volume with doubly deionised water and purged with N_2 for 20 min to deoxygenate. The pH of the solution was 11.5 and PIED was carried out at 298 K. Electroless plating solutions were freshly made immediately before use for optimum performance. As silver nitrate is light sensitive Ag solutions are prepared and stored in amber coloured flasks in the darkness before use.

Solution Component / Condition	Component Role	Component Concentration / Condition Value
Silver Nitrate	Metal precursor	1.496 g / dm^3 (8.8 mmol / dm^3)
Ethylenediamine	Complexant	3.245 g / dm^3 (54 mmol / dm^3)
3,5-diiodotyrosine	Stabiliser	0.017 g / dm^3 (39.2 µmol / dm^3)
Potassium Sodium Tartrate	Reducing agent / scavenger	0.7356 g / dm^3 (26 mmol / dm^3)
pH	-	11 - 12
Temp	-	298 K

Table S1 Composition of Ag electroless plating solution

Preparation of Pd Electroless Plating Baths

Electroless Pd solutions, also developed in these laboratories [1], were prepared to the composition given in Table S2. Palladium chloride, di-sodium EDTA and ammonium hydroxide (28% NH_3 in water) were added and, to ensure formation of the Pd-amine complex, stirred with gentle heating until the solution cleared. The solution was cooled and hydrazine reducing agent added. The solution was then made up to volume with doubly deionised water and purged with N_2 for 20 min. Electroless plating solutions were made immediately before use for optimum performance.

Solution Component / Condition	Component Role	Component Concentration / Condition Value
Palladium Chloride	Metal precursor	5.0 g / dm^3 (28 mmol / dm^3)
Ammonium Hydroxide (28%)	Complexant	100 ml / dm^3 (1.5 mol / dm^3 as NH_3)
Di-sodium EDTA	Stabiliser	20 g / dm^3 (53.8 mmol / dm^3)
Thiourea	Stabiliser	1.2 mg / dm^3 (15.8 µmol / dm^3)
Hydrazine (65%)	Reducing agent / scavenger	0.3 g / dm^3 (6 mmol / dm^3)
pH	-	11 - 12
Temp	-	303 K

Table S2 Composition of Pd electroless plating solution

Contact Angle Hysteresis

This repeated transition between bands of heavy sphere deposition and very little sphere deposition can be explained by considering the contact angle hysteresis of water droplets during evaporation [2]. In the case of a normal droplet, a stable contact area and angle are formed according to the surface chemistry and topography of the substrate. As evaporation occurs and the volume of liquid decreases and the contact angle drops as shown in Fig. S1 by the transition from state 1 to state 2. This occurs until surface tension causes the liquid front to slip on the substrate surface, receding to a smaller contact area and returning to its original contact angle and stable state, shown in Fig. S1 by the transition from state 2 to state 3.

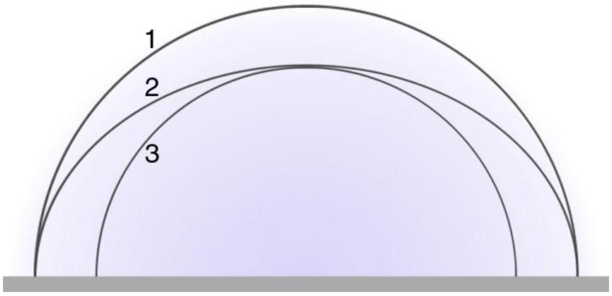

Fig. S1 Water droplet receding through evaporation

With continued evaporation this process repeats in a cycle of static contact area with reducing contact angle and rapidly receding contact area and constant contact angle. The length of each stage is largely determined by the rate of evaporation but also the properties of the substrate. Rougher and more hydrophobic surfaces lead to a greater decrease in contact angle before the drop slips while smoother, more hydrophilic surfaces allow the slip to occur more easily and hence with a less marked step between each stage.

This effect is directly translated into the deposition of particles suspended in the liquid. Particle deposition occurs at the shallowest point, in the case of a water droplet this is outer liquid boundary. As the droplet remains on a constant contact area with decreasing angle this deposition zone remains stationary on the substrate surface and hence an accumulation of particles occurs there. At the point when the liquid slips, the outer boundary moves quickly over the substrate resulting in little or no particle deposition in the area which has been travelled over. The droplet again stabilises and the suspended particles are once more deposited around the outer boundary as the front remains static.

In the microsphere deposition method described above, the liquid is formed into a concave meniscus by the tapered PTFE ring rather than forming a convex dome droplet. Here the shallowest region is not found at the outer edge but rather at the centre with a circular front retreating outwardly towards the PTFE ring as evaporation continues. Despite this difference, the process of the liquid front recession over the substrate surface follows the same principles as described above for water droplets. As the untreated glass is hydrophobic, the liquid cannot retreat smoothly and instead moves in marked steps. As microsphere deposition occurs at the shallowest region of liquid, thick microsphere deposits form at the liquid front during static periods while very few microspheres are deposited as the liquid slips. This leads to the formation of the concentric rings.

Geometric Determination of Metal Deposit Thickness

The thickness of the deposited porous metal layer can be determined by considering the geometry of the microspheres and resulting metal pores, Fig. S2. When considered in cross section, it can be seen that the deposited metal forms an arc around the lower portion of each microsphere, the sagitta (s) of this arc corresponding to the depth of the metal deposit. The size of s can be calculated using equation (1) where r = sphere radius and l = ½ chord length, the latter corresponding to the measured radius of the upper opening of the pore / hemispherical void, as determined by scanning electron microscopy.

$$s = r - \sqrt{r^2 - l^2} \tag{1}$$

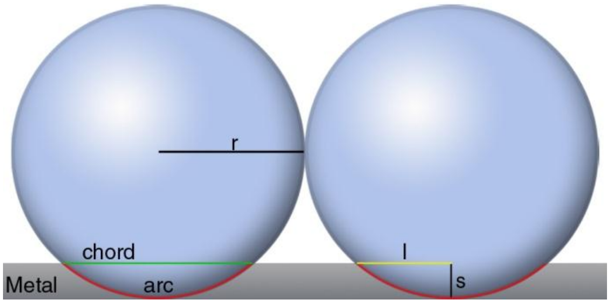

Fig. S2 Microsphere template and templated metal pore geometry for determination of metal film thickness

This equation calculates a metal depth which is only applicable to a deposit formed around a single microsphere layer. Where the metal thickness covers multiple microsphere layers, the overall thickness must include the depth of each fully covered lower microsphere layers as well as the partial coverage of the uppermost layer. The nature of hexagonal close packing dictates that the horizontal pitch, the distance between neighbouring sphere centres, is equal to twice the sphere radius, 2r. However, the vertical pitch is a smaller distance as spheres on the upper layer sit within the hollows formed between neighbouring spheres on the layer beneath. This vertical pitch distance can be calculated using equation (2).

$$\left(\sqrt{6} \times \frac{2r}{3}\right) \tag{2}$$

The horizontal and vertical pitch in hexagonally close packed spheres is shown in Fig. S3. While the vertical pitch is described as the centre-to-centre distance between vertically stacked spheres, it can also be interpreted as the distance between the basal points of these spheres. Given that equation (1) provides the distance from the base of the uppermost microsphere to the upper surface of the deposited metal, and that equation (2) provides the distance from the substrate surface to the base of the uppermost microsphere, the two distances can be combined to provide a complete metal layer thickness.

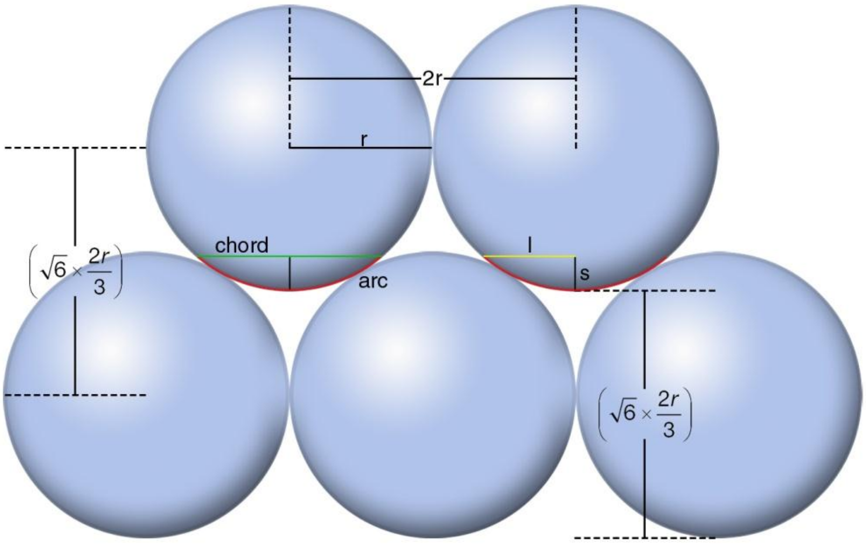

Fig. S3 Horizontal and vertical pitch of hexagonally close packed microspheres

Taking into account the number of lower microsphere layers, n, which have been covered by metal deposition, the following equation for the calculation of the total metal thickness across a multi-layer microsphere template by upper pore diameter measurement is derived:

$$\left(\sqrt{6}\times\frac{2r}{3}\right)_n+\left(r-\sqrt{r^2-l^2}\right) \tag{3}$$

1. M. A. Bromley, C. Boxall, S. Galea, P. S. Goodall and S. Woodbury, *Journal of Photochemistry and Photobiology A: Chemistry*, 2010, **216**, 228-237.
2. L. Gao and T. J. McCarthy, *Langmuir*, 2006, **22**, 6234-6237.