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A Two-step Synthesis for Preparing Metal Microcapsules with a Biodegradable Polymer Substrate

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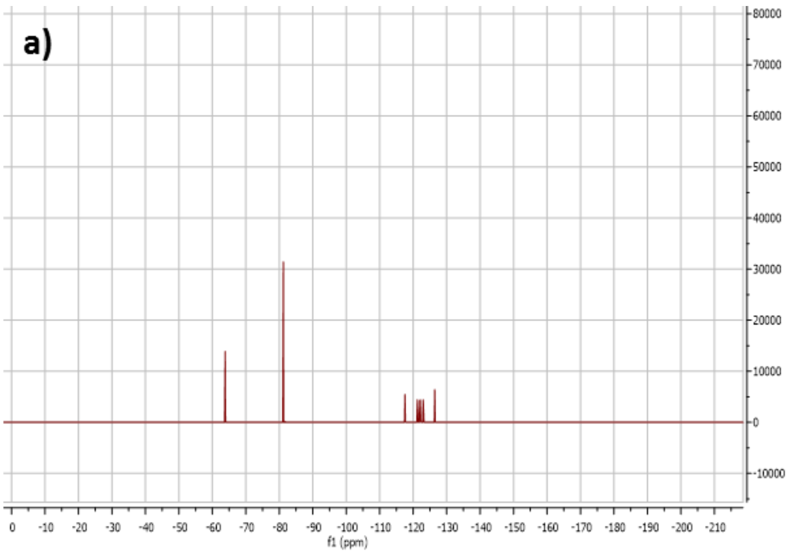
Supplementary Information



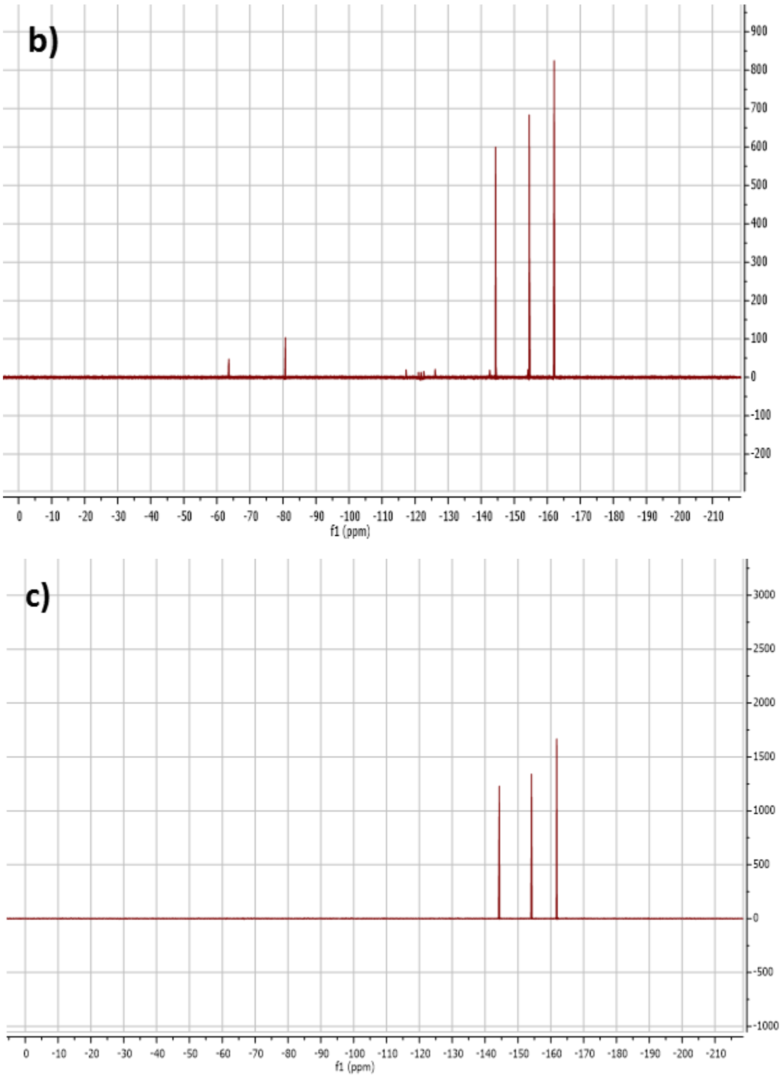


Figure S1 – ^{19}F NMR spectra showing a) PFOB alone, b) release of PFOB from PLGA capsules, with pentafluorobenzyl alcohol internal standard c) release of PFOB from gold capsules with 53 nm gold shell, with pentafluorobenzyl alcohol internal standard. Release into deuterated chloroform over 7 days at ambient temperature.

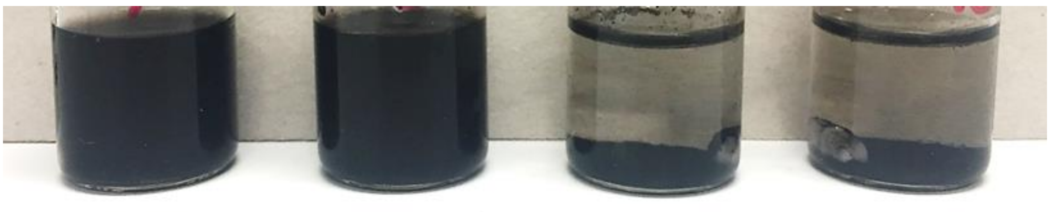


Figure S2 – Digital image showing increasing aggregation and destabilisation of PVP-Pt nanoparticles when platinum salt concentration of 4.44 mM reduced with a) 0.4 mL, b) 0.8 mL, c) 1.2 mL and d) 1.6 mL of $NaBH_4$ (0.5M).

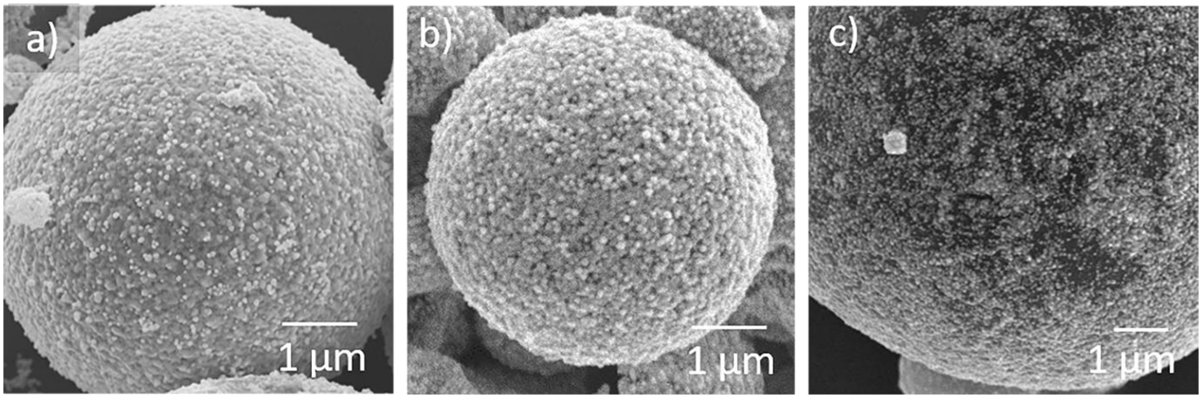


Figure S3 - Scanning electron micrographs showing the resulting gold shell when a) 4.0 nm b) 3.5 nm and c) 2.8 nm diameter nanoparticles were used to stabilise PLGA microcapsules. Insets show magnified images to demonstrate shell quality for each sample.

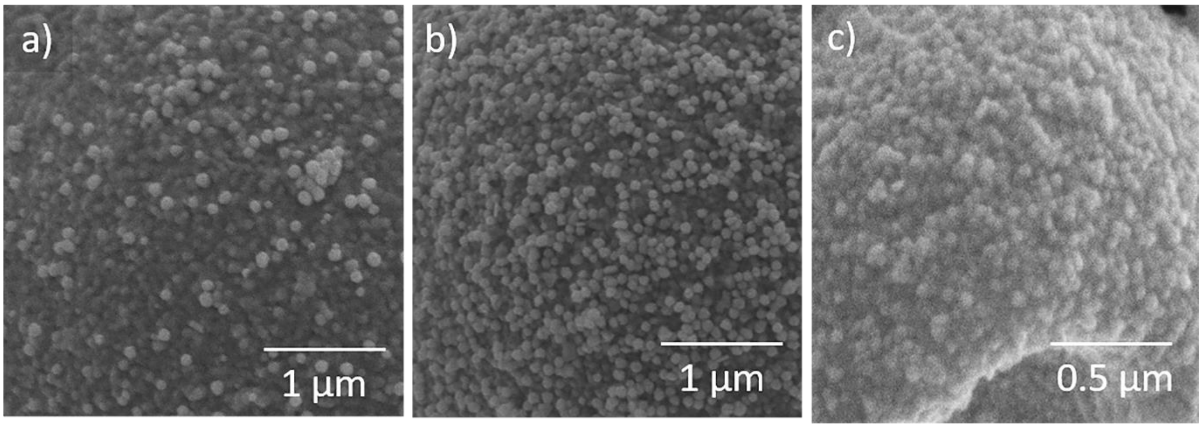


Figure S4 - Scanning electron micrographs showing gold shell microcapsule surfaces becoming increasingly rough as the amount of gold salt, and thus shell thickness increases, a) 5 mM, b) 10 mM and c) 40 mM $HAuCl_4$ used for electroless deposition.

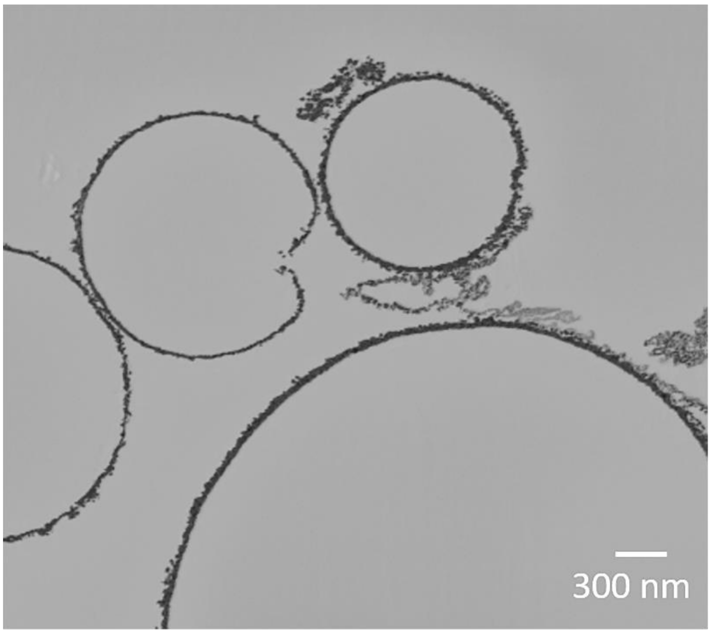


Figure S5 – Image taken from microcapsule reconstruction movie to show shell thickness of 58 nm at the equator of a microcapsule formed using reduction of 10 mM gold salt solution.

Table S1 – Interfacial tensions between each of the three phases involved in capsule formation and the calculated spreading coefficients showing predicted core-shell behaviour of PVP stabilised PLGA microcapsules and combined PVP-Pt and PVP stabilised PLGA microcapsules. For core-shell morphologies S3 should be positive with S1 and S2 negative.[1]

Stabiliser	$\gamma_{1,2}$	$\gamma_{2,3}$	$\gamma_{1,3}$	s1	s2	s3	prediction	observed
PVP	4.7	8.8	2.1	-6.2	-11.4	2.0	core shell	core shell
PVP-Pt	3.3	5.5	2.1	-4.3	-6.7	0.1	core shell	core shell

Matlab script used to measure metal shell thickness:

```
%% Read images into one variable

size_files = size(files);

for a = 1:2:size_files(1);
    filename = files(a).name;
    image = importdata(filename);

    %Uncomment this line if there is a lot of noise in the image.
    %image = image(1:4000,500:3500);

    minval = min(image(:));

    %This is the threshold value, uncomment the one that works!
    %mask = image<(minval+(minval/10));
    mask = image<(minval+(minval*4));

    imagesc(mask)
```

```
    drawn_mask = roipoly;

    object_mask = mask.*drawn_mask;

    dist_mask = imcomplement(object_mask);
    dist = bwdist(dist_mask);
    RegionMax = imregionalmax(dist);

    [x, y] = find(RegionMax ~= 0);
    size_x = size(x);
    list = zeros(size_x(1),1);
    for i = 1:size(x)
        list(i,1)=dist(x(i),y(i));
    end

    thickness(a,1) = ((mean(list))*2)*10;
end
```


1. A. L. Tasker, J. P. Hitchcock, L. He, E. A. Baxter, S. Biggs and O. J. Cayre, *J Colloid Interface Sci*, 2016, **484**, 10-16.