Catalysis by multifunctional polyelectrolyte capsules

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Supporting Information

I) Characterization of gold nanoparticles

II) Characterization of gold and iron oxide nanoparticle modified capsules

III) Remarks about the catalysis with polyelectrolyte capsules

I) Characterization of gold nanoparticles

Figure S1 shows the UV-Vis spectra of AuNP1 before and after ligand exchange with bis(psulfonatophenyl)phenylphosphine. The spectra demonstrate that there was no agglomeration of the AuNPs during this step. Similarly, no agglomeration was observed for 14.9 nm AuNPs during the ligand exchange. Figure S2 shows transmission electron microscopy images of AuNP1 and AuNP2 and their corresponding size distribution.



Figure S1. UV-Vis spectra of 4.3 nm citrate capped AuNPs before ligand exchange (black line) and after exchanged with bis(*p*-sulfonatophenyl)phenylphosphine (red line).



Figure S2. Transmission electron microscopy images of AuNP1 and AuNP2 (on the left) and their corresponding size distribution (on the right).

II) Characterization of gold and iron oxide nanoparticle modified capsules

For the encapsulation of AuNPs the first step is to coprecipitate the nanoparticles within the CaCO₃ particles. In this case, the AuNPs should be well stabilized with a ligand that avoids the agglomeration of the nanoparticles at the high pH and high ionic strength of the precursor solutions of Na₂CO₃ and CaCl₂. Citrate-stabilized gold nanoparticles are for example not suitable for this CaCO₃ loading because they strongly agglomerate when they are mixed with the 0.33M solutions of Na_2CO_3 or $CaCl_2$ and the solution become immediately black. Bis(*p*sulfonatophenyl)phenylphosphine is an appropriated ligand to stabilize the nanoparticles in such rush conditions. However, once the capsule was formed and the CaCO3 was dissolved in EDTA, the plasmon band of the encapsulated AuNPs shifted to higher wavelengths due to the interaction between the AuNPs within the hollow shell. The maximum of the plasmon band for the 4.3 nm AuNP was shifted from 516 to 542 nm. For 14.9 nm AuNPs the shift was between 520 nm for free AuNPs to 558 nm for the encapsulated AuNPs. There is partial agglomeration of the AuNPs as it can be seen in the TEM images. Nevertheless, the size of the AuNPs did not change after the encapsulation as it was measured from the TEM images shown in the main manuscript. We verified that the encapsulation of AuNPs did not degrade or reshape the nanocrystals.

Figure S3 shows confocal images of the PEM capsules used for catalysis and their corresponding size distribution.



Figure S3. Confocal images (on the left) and size distribution of all capsules used for the catalysis of the reduction of hexacyanoferrate(III) by borohydride

III) Remarks about the catalysis with polyelectrolyte capsules

PEM capsules with only magnetic nanoparticles in the shell were produced following the same protocol than the described in the main manuscript but using cores of CaCO3 which did contain AuNPs. Figure S4 shows TEM images of such capsules after EDTA dissolution of the core.



Figure S4. TEM images of magnetic capsules at two different magnifications used to check the catalytic activity of the magnetic nanoparticles in the reduction of hexacyanoferrate(III) by borohydride.

These magnetic capsules were used to check that the catalysis performed by MCAP1 and MCAP2 was due to the presence of AuNPs. The presence of MNPs did not affect the catalytic activity of such capsules in the conditions used for the study of the reduction of hexacyanoferrate(III) by borohydride.

Figure S5 shows the spectra of CAP1 and CAP2 before and after the catalysis. The plasmon band of the AuNPs in both cases did not suffer any considerable modification which indicates that the AuNPs did not degrade during the catalysis.



Figure S5. UV-Vis spectra of (A) CAP1 and (B) CAP2 before the being used as catalysts (black line), after addition of hexacyanoferrate(III) to the reaction solution (red line) and finally, after the reaction was finished and all Fe(III) was reduced to Fe(II) (blue line)