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Supporting Information

Fabrication of hollow nanoporous gold nanoshells with high structural tunability based on the plasma etching of polymer colloid templates

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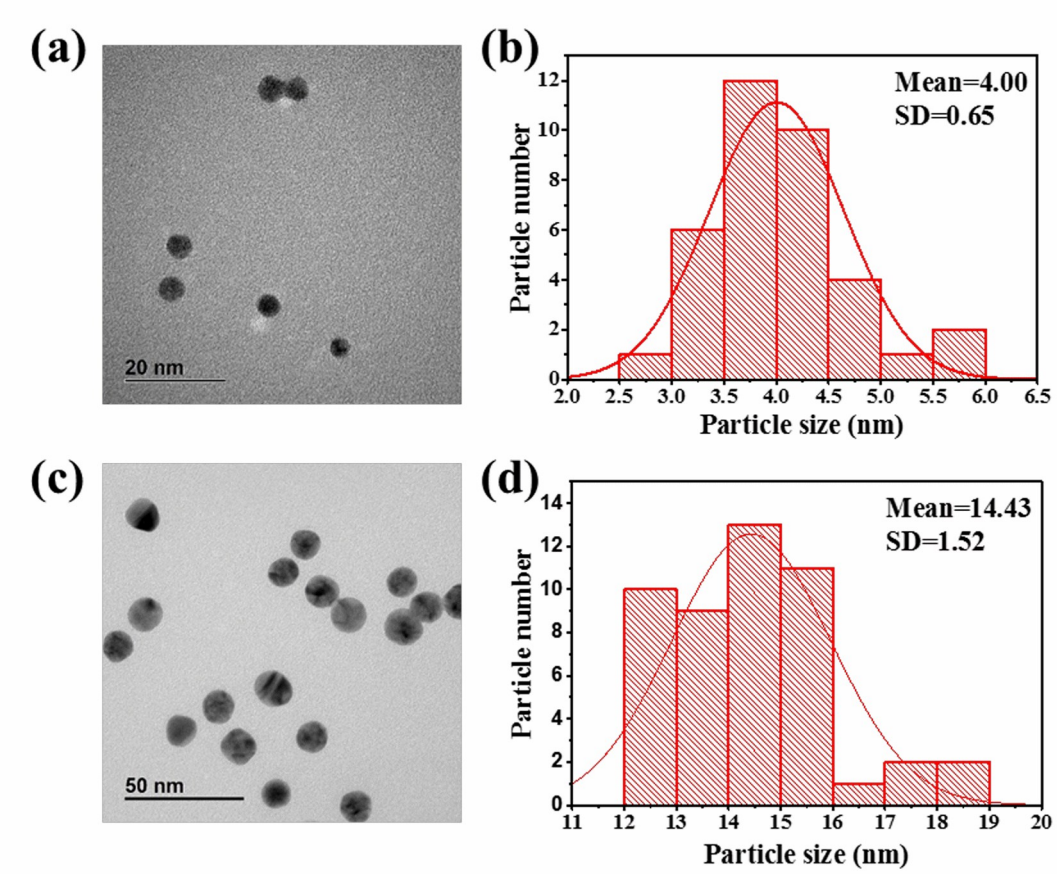

Figure S1. HR-TEM images of spherical AuNPs of (a) 4.00 nm ± 0.65 nm and (c) 14.43 nm ± 1.52 nm chemically synthesized by us; and (b, d) their size distribution calculated from the size measurement of AuNPs in TEM images

Number ratio of AuNPs and PS colloid particles in the mixing solution:

Number ratio of AuNPs and PS colloid particles in the mixing solution are as follows.

PS size (nm)	AuNP size (nm)	Number ratio of AuNP/PS	Reference surface coverage*	Real surface coverage#
500	4	20000	0.32	N/A
1000	4	81320	0.33	N/A
500	14	560	0.11	0.09
1000	14	1900	0.09	0.08
2600	14	12660	0.09	0.06
1000	40	280	0.11	N/A
1000	AuNR (length 103 nm, aspect ratio 5.6)	110	0.07	0.05

The number ratio of AuNPs and PS particles was adjusted to keep the reference surface coverage* of AuNPs on the PS to be about 11% for the case of AuNPs of 14 nm or 40 nm sizes, whereas about 32% for the case of AuNPs of 4 nm size. The higher number ratio of AuNPs and PS particles were used for 4 nm AuNPs because of relatively weak adsorption of 4 nm AuNPs to the surface of PS colloid particles, which may be attributed to the different surface charge density of AuNPs of small size. It is to be noted that the real surface coverage# measured by SEM is slightly smaller than the reference surface coverage, which indicates that not all of mixed AuNPs adsorb on the PS surface.

By increasing the initial number ratio of AuNP (or AuNR) per PS, the surface coverage of AuNP on PS can be increased more. However, as the number ratio becomes higher, the difference between “reference surface coverage” and “real surface coverage” will become larger, which means that more AuNPs can exist in the water without adsorbing on the PS surface due to the saturation of surface coverage or the electrostatic repulsion between adsorbed AuNPs. Therefore, it is not economic to increase the initial number ratio very much if considering the loss of AuNPs.

*The reference surface coverage is defined as the area ratio of AuNPs and PS that can be obtained under the assumption of perfect adsorption:

$$\frac{\pi \times (radius\ of\ AuNP)^2 \times (number\ ratio\ of\ AuNP/PS)}{4\pi \times (radius\ of\ PS)^2}$$

[#]The real surface coverage was estimated by directly counting the number of AuNPs on the PS surface in the SEM image. The real surface coverages for 4 nm AuNPs are not available because 4 nm AuNPs are too small to be identified in our SEM image. In the case of 40 nm AuNPs, the deviation of surface density of AuNPs on the PS surface was relatively large due to their large size.

Robustness of NPGNS:

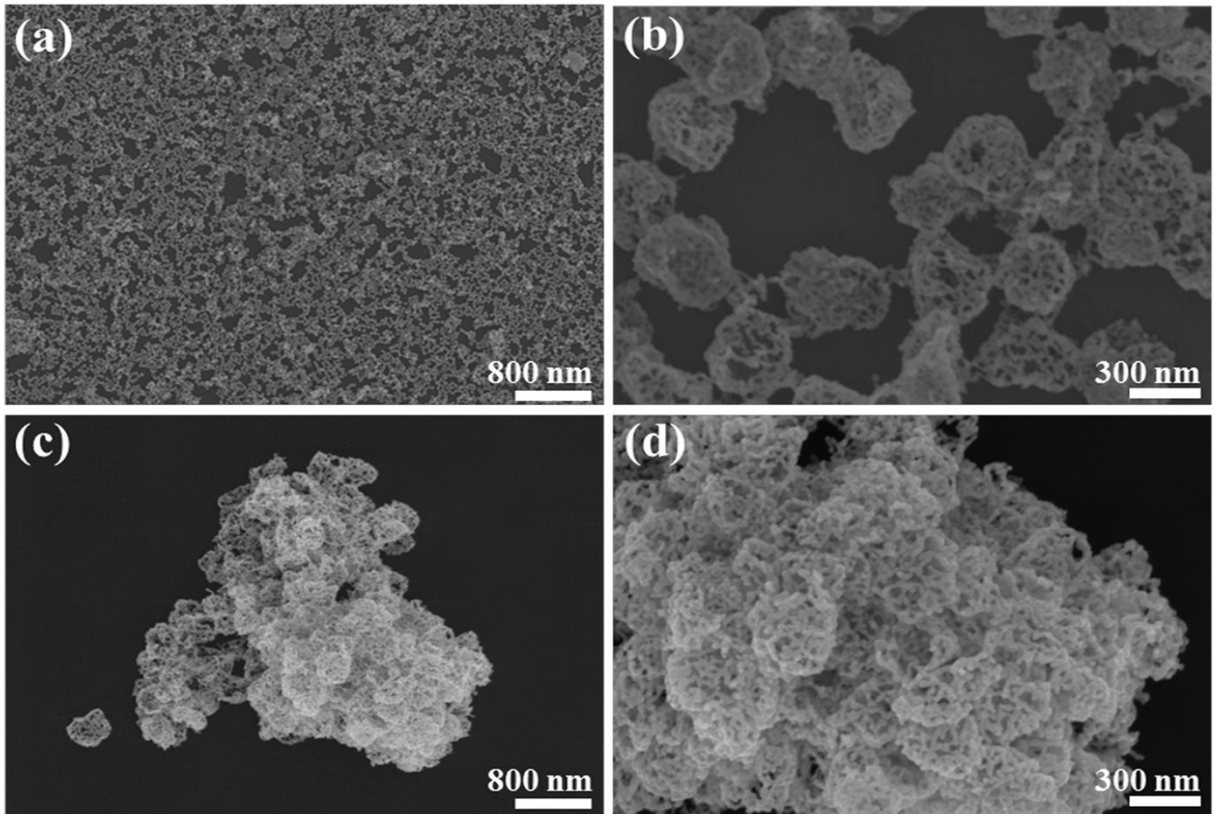

Figure S2. Robustness of NPGNS. FE-SEM images of concentrated NPGNSs (a), (b) after detached from the initial substrate by sonication and (c), (d) by mechanical scrubbing using a blade.

The robustness of fabricated NPGNS structures was confirmed against sonication and mechanical scrubbing using a blade. For the sonication, the plasma etched NPGNS structures on the glass substrate were immersed in the ethanol and sonicated. The detached NPGNS in the ethanol was then spread on the air/water interface to make a dense monolayer of NPGNS, which was transferred to another glass substrate for the SEM imaging (Figure S2a-b). For the mechanical blading, the fabricated NPGNS on the glass substrate was scrubbed using a blade to collect powder of NPGNS, which was dispersed in the ethanol and then dropped on the another substrate for the SEM imaging (Figure S2c-d).

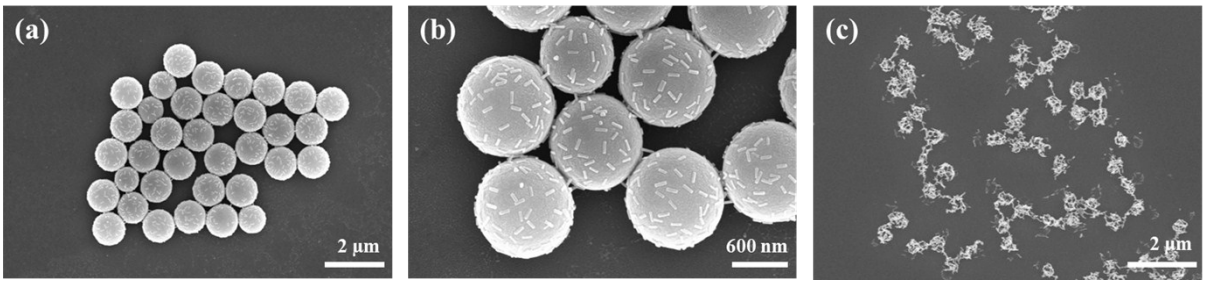

Figure S3. Large area FE-SEM images of PS colloid particles with attached AuNRs with an aspect ratio of 5.6 (a, b) before and (c) after plasma treatment.

Figure	PS (nm)	AuNPs (nm)	Plasma Treatment time (min)	Ligament (nm)	Pore (nm)	Diameter (nm)
3 a	1000	4	25	20.8 ± 6.8	12.1 ± 4.0	267.2 ± 20.4
3 b	1000	14	25	16.1 ± 2.6	29.6 ± 14.2	372.0 ± 23.4
3 c	1000	40	35	35.3 ± 7.7	99.0 ± 59.9	553.4 ± 33.9
3 d	500	4	20	N/A	N/A	152.6 ± 12.3
3 e	500	14	20	30.3 ± 10.9	20.3 ± 6.1	214.8 ± 10.2

Table S1. Plasma treatment conditions to obtain NPGNS in Figure 3a-e for different size combinations of PS and AuNPs, and their size parameters obtained by a statistical analysis of FE-SEM images.

Plasma treatment time in Table S1 represents the time required to obtain final NPGNSs with a complete removal of PS colloid templates.

Due to the irregular shapes of pores, the standard deviation of pore size is very large. In the case of pores with asymmetrical shape, both a long axis size and a short axis size are included in the statistical analysis of pore size.

In the case of 3d (PS of 500 nm & AuNPs of 4 nm), a statistical analysis of ligament and pore sizes from FE-SEM images was difficult because they were very small.