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## Journal of Materials Chemistry A

## **Electronic Supplementary Information**

## Synthesis and Characterization of Novel Stellate Sea-Urchin-Like Silver Particles with Extremely Low Density and Superhydrophobicity

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#### Model estimation of relative density and specific surface area for a stellate silver particle

Consider a stellate silver particle having *n* rays. Let the radius of the particle core is *r*, and the maximal distance between the ends of oppositely directed rays is  $L_{\text{max}}$ . Find the surface area *S* and volume *V* of such particle. For the calculation in the first approximation we assume that the core surface is completely covered (without clear space) by the ray bases, all rays having equal shape and length (height)  $h = (L_{\text{max}}/2 - r)$ . The lateral area of all rays of a stellate particle is equal to the surface area of this particle.

The surface area of the core is equal to  $s_{\text{core}} = 4\pi r^2$ , that is why the base area of one ray is  $s_{\text{base}} = s_{\text{core}}/n = 4\pi r^2/n$ .

The lateral surface area is minimal for cone-shaped rays and maximal for the rays in the form of a trihedral pyramid, all other factors being equal.

The base radius of a cone-shaped ray is equal to  $r_{\rm con} = (s_{\rm base}/\pi)^{1/2} = (4\pi r^2/\pi n)^{1/2} = 2r/n^{1/2}$ , and the lateral surface area of one cone-shaped ray is  $s_{\rm con} = \pi r_{\rm con} l = \pi r_{\rm con} (r_{\rm con}^2 + h^2)^{1/2} = 2\pi r (4r^2/n^2 + h^2/n)^{1/2}$ . The lateral surface area of all *n* cone-shaped rays of a stellate particle (or the whole surface area of this particle) is equal to  $S_{\rm con} = s_{\rm con} n = 2\pi r (4r^2 + nh^2)^{1/2}$ .

The lateral surface area of a trihedral pyramidal ray is  $s_{3-\text{piram}} = 6r(\pi/\sqrt{3})^{1/2}(4\sqrt{3}\pi r^2/9n^2 + h^2/n)^{1/2}$ . The lateral surface area of all trihedral pyramidal rays of a stellate particle is  $S_{3-\text{piram}} = s_{3-\text{piram}}n = 6r(\pi/\sqrt{3})^{1/2}(4\sqrt{3}\pi r^2/9 + nh^2)^{1/2}$ .

The volume of a ray of any shape (conical or pyramidal) is equal to the product of the ray base area  $s_{\text{base}} = s_{\text{core}}/n = 4\pi r^2/n$  by one third of its height *h*, i.e.  $v = s_{\text{base}}h/3 = 4\pi r^2h/3n$ . The total volume of all *n* rays of a stellate particle is  $V = vn = (4\pi/3)r^2h$ . The total volume  $V_{\text{part}}$  of a stellate particle is equal to the sum of volumes of its core and rays, i.e.  $V_{\text{part}} = V_{\text{core}} + V = (4\pi/3)r^3 + vn = (4\pi/3)r^3 + (4\pi/3)r^2h = (4\pi/3)r^2(r+h)$ . It is easily seen that the volume of a stellate particle depends only on the core size *r* and the rays' length (height) *h*, but it does not depend on the quantity and shape of the rays.

Indeed, the volume of a cone-shaped ray is  $v_{con} = (\pi/3) r_{con}^2 h$ ,  $r_{con} = (s_{base}/\pi)^{1/2} = (4\pi/2/\pi n)^{1/2}$ =  $2r/n^{1/2}$ , whence  $r_{con}^2 = 4r^2/n$  and  $v_{con} = (4\pi/3)r^2h/n$ . The volume of all cone-shaped rays is equal to  $V_{con} = v_{con}n = (4\pi/3)r^2h$ .

The volume of a trihedral pyramidal ray is  $v_{3-\text{piram}} = s_{\text{base}}h/3 = 4\pi r^2 h/3n$ . The volume of all pyramidal rays is  $V_{3-\text{piram}} = v_{3-\text{piram}}n = (4\pi r^2 h/3n) \times n = (4\pi/3)r^2 h$ .

Since the volume  $V_{\text{part}}$  of a stellate particle depends only on the core size and the rays's length (height), but does not depend on the quantity and shape of the rays, the mass *m* of a stellate silver particle also depends only on its size and is equal to  $m = V_{\text{part}}\rho_{\text{Ag}}$ , where  $\rho_{\text{Ag}} = 10.5$  g cm<sup>-3</sup> is the density of silver.

The volume of space occupied by a stellate particle in the assumption of partial nonwettability of its rays is the volume of a sphere with a diameter equal to the maximal distance  $L_{\text{max}}$  between the ends of oppositely directed rays reduced by the coefficient k, i.e.  $V_{\text{non-wet}} = (4\pi/3)(kL_{\text{max}}/2)^3 = (4\pi/3)[k(r+h)]^3$ . For complete nonwettability of rays k = 1, and for partial nonwettability k < 1.

According to the SEM data, the distance between the ends of neighboring rays of a stellate Ag particle is from 20 to 40  $\mu$ m for particles with  $L_{\text{max}} \approx 70 \,\mu$ m. In this case, partial nonwettability of rays with the solution is likely to be realized, and the coefficient *k* can be taken equal to 0.8.

The relative density  $\rho_{\text{stell}}$  of a stellate silver particle with allowance for its nonwettability is equal to  $\rho_{\text{stell}} = (V_{\text{part}}/V_{\text{nonwet}})\rho_{\text{Ag}} = \rho_{\text{Ag}}r^2(r+h)/[k(r+h)]^3 = r^2\rho_{\text{Ag}}/[k^3(r+h)^2]$ . The relative density of a stellate Ag particle calculated as a function of core size *r* and the rays's height *h* at *k* = 0.8 is given in Table S1.

The specific surface area of a stellate silver particle is equal to the total surface area *S* of particle per particle mass *m*, i.e.  $S_{sp} = S/m$ . The specific surface area  $S_{sp}$  of a stellate Ag particle with conical or pyramidal rays is given in Table S2.

## SI Tables

## Table S1.

The relative density  $\rho_{\text{stell}}$  of a stellate Ag particle with different core radius r and ray's length (height) h

<i>r</i> (µm)	$L_{\max}$ (µm)	$h = L_{\text{max}}/2 - r (\mu m)$	п	$V_{\rm part}$ ( $\mu m^3$ )	<i>m</i> (mg)	$V_{\rm nonwet}~(\mu m^3)$	$\rho_{\text{stell}} (g \cdot \text{cm}^{-3})$
3	20	7	32	377	0.396·10 <sup>-5</sup>	2145	1.846
3	27	10.5	32	509	0.534.10-5	5277	1.013
3	30	12	32	565	$0.594 \cdot 10^{-5}$	7238	0.820
3	60	27	32	1131	$1.188 \cdot 10^{-5}$	57910	0.205
3	70	32	32	1319	1.385·10 <sup>-5</sup>	91950	0.151
3	80	37	32	1508	$1.583 \cdot 10^{-5}$	137260	0.115
3	90	42	32	1696	$1.781 \cdot 10^{-5}$	195430	0.091
4	20	6	32	670	$0.704 \cdot 10^{-5}$	2145	3.281
4	27	9.5	32	905	0.950 ·10 <sup>-5</sup>	5277	1.800
4	30	11	32	1005	$1.056 \cdot 10^{-5}$	7238	1.458
4	60	26	32	2011	$2.111 \cdot 10^{-5}$	57910	0.365
4	70	31	32	2346	$2.463 \cdot 10^{-5}$	91950	0.268
4	80	36	32	2681	$2.815 \cdot 10^{-5}$	137260	0.205
4	90	41	32	3016	3.167·10 <sup>-5</sup>	195430	0.162
3	20	7	56	377	0.396.10-5	2145	1.846
3	27	10.5	56	509	0.534.10-5	5277	1.013
3	30	12	56	565	$0.594 \cdot 10^{-5}$	7238	0.820
3	60	27	56	1131	$1.188 \cdot 10^{-5}$	57910	0.205
3	70	32	56	1319	$1.385 \cdot 10^{-5}$	91950	0.151
3	80	37	56	1508	$1.583 \cdot 10^{-5}$	137260	0.115
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4	60	26	56	2011	2.111.10-5	57910	0.365
4	70	31	56	2346	2.463.10-5	91950	0.268
4	80	36	56	2681	2.815.10-5	137260	0.205
4	90	41	56	3016	3.167.10-5	195430	0.162

<i>r</i> (µm)	L <sub>max</sub> (µm)	$h=L_{\text{max}}/2$ - $r(\mu m)$	п	Ray's form <sup>*</sup>	$V_{\text{part}}$ ( $\mu m^3$ )	<i>m</i> (mg)	$S(\mu m^2)$	$S_{\rm sp}$ (m <sup>2</sup> ·g <sup>-1</sup> )
3	30	12	32	conical	565	0.594·10 <sup>-5</sup>	1285	0.216
3	60	27	32	conical	1131	$1.188 \cdot 10^{-5}$	2881	0.243
3	70	32	32	conical	1319	1.385.10-5	3414	0.246
3	80	37	32	conical	1508	1.583.10-5	3947	0.249
3	90	42	32	conical	1696	1.781.10-5	4480	0.252
4	30	11	32	conical	1005	1.0556e-5	1577	0.149
4	60	26	32	conical	2011	2.111.10-5	3702	0.175
4	70	31	32	conical	2346	2.4630e-5	4412	0.179
4	80	36	32	conical	2681	2.8149e-5	5122	0.182
4	90	41	32	conical	3016	3.1667e-5	5833	0.184
3	30	12	56	conical	565	0.594.10-5	1696	0.286
3	60	27	56	conical	1131	$1.188 \cdot 10^{-5}$	3810	0.321
3	70	32	56	conical	1319	1.385·10 <sup>-5</sup>	4515	0.326
3	80	37	56	conical	1508	1.583.10-5	5220	0.330
3	90	42	56	conical	1696	1.781.10-5	5925	0.333
4	30	11	56	conical	1005	1.056.10-5	2079	0.197
4	60	26	56	conical	2011	$2.111 \cdot 10^{-5}$	4984	0.232
4	70	31	56	conical	2346	2.463.10-5	5834	0.237
4	80	36	56	conical	2681	2.815.10-5	6774	0.241
4	90	41	56	conical	3016	3.167·10 <sup>-5</sup>	7714	0.244
3	30	12	32	pyramidal	565	0.594.10-5	1649	0.278
3	60	27	32	pyramidal	1131	1.188.10-5	3702	0.312
3	70	32	32	pyramidal	1319	1.385.10-5	4390	0.317
3	80	37	32	pyramidal	1508	1.583.10-5	5075	0.321
3	90	42	32	pyramidal	1696	$1.781 \cdot 10^{-5}$	5761	0.323
4	30	11	32	pyramidal	1005	1.0556e-5	2021	0.192
4	60	26	32	pyramidal	2011	$2.111 \cdot 10^{-5}$	4758	0.225
4	70	31	32	pyramidal	2346	2.4630e-5	5672	0.230
4	80	36	32	pyramidal	2681	2.8149e-5	6585	0.234
4	90	41	32	pyramidal	3016	3.1667e-5	7499	0.237
3	30	12	56	pyramidal	565	$0.594 \cdot 10^{-5}$	2180	0.367
3	60	27	56	pyramidal	1131	$1.188 \cdot 10^{-5}$	4899	0.413
3	70	32	56	pyramidal	1319	1.385·10 <sup>-5</sup>	5806	0.419
3	80	37	56	pyramidal	1508	$1.583 \cdot 10^{-5}$	6713	0.424
3	90	42	56	pyramidal	1696	1.781.10-5	7620	0.428
4	30	11	56	pyramidal	1005	1.056.10-5	2668	0.253
4	60	26	56	pyramidal	2011	$2.111 \cdot 10^{-5}$	6292	0.298
4	70	31	56	pyramidal	2346	2.463.10-5	7501	0.305
4	80	36	56	pyramidal	2681	$2.815 \cdot 10^{-5}$	8710	0.309
4	90	41	56	pyramidal	3016	3.167·10 <sup>-5</sup>	9919	0.313

# **Table S2.**The specific surface area $S_{sp}$ of a stellate Ag particle with conical or pyramidal rays

\* conical (cone-shaped rays), pyramidal (rays in the form of a trihedral pyramid)

### **SI Figures**



**Figure S1.** Dependence of the specific surface area  $S_{sp}$  of stellate Ag particles with core size  $r = 3 \mu m$  on the number *n* and length (heigth) *h* of the rays. Surface I corresponds to the particles with trihedral pyramidal rays, and surface II corresponds to the particles with cone-shaped rays. Specific surface area of synthesized stellate Ag particles is an average between the minimal (for stellate particles with cone-shaped rays) and the maximal (for stellate particles with trihedral pyramidal rays) specific surface area.