Appendix (Ⅰ)

The characteristic parameters of NPs shown in Fig. 8 in the manuscript are presented here in Tables 1.1–1.5. R_{max} is maximum radius which refers to the maximum distance from the center point to the core or shell interface. For example, R_{max} of b.1, (4.00, 5.50) represent R_{max}= 4.00 nm for core and 5.50 nm for shell. R_{min} is minimum radius which refers to the minimum distance from the center point to the core or shell interface. R_{ave} is average radius, which is the average length of the distances between center point and mesh points of interface. $\mathrm{RMS} = 100\times\sqrt{\frac{\left(R_i - R_{\mathrm{equ}}\right)^2}{n}}\%, \quad (i = 1, 2, \cdots, n)$, where n is the number of points on the interface. RMS describes level the shape deviates from the sphere. Larger RMS indicating a larger deformation relative to the sphere. R_{equ} and T_{equ} are equivalent radius and equivalent thickness separately. We first calculate the volume of the space enclosed by the interface, where R_{equ} is the radius of a sphere of the same volume. T_{equ} is the difference between R_{equ} of shell and R_{equ} of core.

Table 1.1 Characteristic parameters of egg-shaped core–shell NPs.

egg	b.1	b.2	b.3	b.4	b.5	b.6
R_{max} (nm)	(4.00,5.50)	(4.00,6.50)	(4.00,7.50)	(4.00,8.50)	(4.00,9.50)	(4.00,10.50)
R_{min} (nm)	(4.00,5.00)	(4.00,5.00)	(4.00,5.00)	(4.00,5.00)	(4.00,5.00)	(4.00,5.00)
R_{ave} (nm)	(4.00,5.09)	(4.00,5.27)	(4.00,5.46)	(4.00,5.66)	(4.00,5.86)	(4.00,6.07)
R_{equ} (nm)	(4.00,5.06)	(4.00,5.21)	(4.00,5.36)	(4.00,5.50)	(4.00,5.63)	(4.00,5.76)
T_{equ} (nm)	1.06	1.21	1.36	1.50	1.63	1.76
RMS (%)	(0.00,2.68)	(0.00,7.90)	(0.00,12.91)	(0.00,17.66)	(0.00,22.14)	(0.00,26.37)

R_{max}: maximum radius; R_{min}: minimum radius; R_{ave}: average radius

R_{equ}: volume equivalent radius; T_{equ}: equivalent thickness

RMS: radius deviation

Table 1.2 Characteristic parameters of ellipsoid-shaped core–shell NPs.

ellipsoid	c.1	c.2	c.3	c.4	c.5	c.6
R_{max} (nm)	(4.00,5.50)	(4.00,6.00)	(4.00,6.50)	(4.00,7.00)	(4.00,7.50)	(4.00,8.00)
R_{min} (nm)	(4.00,5.00)	(4.00,5.00)	(4.00,5.00)	(4.00,5.00)	(4.00,5.00)	(4.00,5.00)
R_{ave} (nm)	(4.00,5.17)	(4.00,5.35)	(4.00,5.53)	(4.00,5.71)	(4.00,5.91)	(4.00,6.10)
R_{equ} (nm)	(4.00,5.13)	(4.00,5.29)	(4.00,5.43)	(4.00,5.56)	(4.00,5.69)	(4.00,5.82)
T_{equ} (nm)	1.13	1.29	1.43	1.56	1.69	1.82
RMS (%)	(0.00,2.90)	(0.00,5.64)	(0.00,8.22)	(0.00,10.65)	(0.00,12.92)	(0.00,15.05)

R_{max}: maximum radius; R_{min}: minimum radius; R_{ave}: average radius

R_{equ}: volume equivalent radius; T_{equ}: equivalent thickness

RMS: radius deviation

Table 1.3 Characteristic parameters of rod-shaped core–shell NPs.

rod	d.1	d.2	d.3	d.4	d.5	d.6
R_{max} (nm)	(1.75,2.75)	(3.00,4.00)	(4.50,5.50)	(6.50,7.50)	(8.50,9.50)	(10.50,11.50)
R_{min} (nm)	(1.50,2.50)	(1.50,2.50)	(1.50,2.50)	(1.50,2.50)	(1.50,2.50)	(1.50,2.50)
R_{ave} (nm)	(1.62,2.61)	(2.16,3.12)	(2.77,3.83)	(3.69,4.67)	(4.85,5.64)	(5.96,6.71)
R_{equ} (nm)	(0.75,1.21)	(0.83,1.26)	(0.87,1.29)	(0.89,1.31)	(0.90,1.31)	(0.90,1.32)
T_{equ} (nm)	0.4642	0.4336	0.4224	0.4148	0.4145	0.4544
RMS (%)	(4.79,2.96)	(22.34,15.46)	(34.21,24.86)	(42.55,34.18)	(46.21,39.19)	(46.92,42.22)

R_{max}: maximum radius; R_{min}: minimum radius; R_{ave}: average radius

R_{equ}: volume equivalent radius; T_{equ}: equivalent thickness

RMS: radius deviation

Table 1.4 Characteristic parameters of rough-surface core–shell NPs.

rough	e.1	e.2	e.3	e.4	e.5	e.6
R_{max} (nm)	(5.00,6.00)	(5.00,6.50)	(5.00,7.00)	(5.00,7.50)	(5.00,8.00)	(5.00,8.50)
R_{min} (nm)	(5.00,5.50)	(5.00,5.50)	(5.00,5.50)	(5.00,5.50)	(5.00,5.50)	(5.00,5.50)
R_{ave} (nm)	(5.00,5.75)	(5.00,6.00)	(5.00,6.25)	(5.00,6.50)	(5.00,6.75)	(5.00,7.00)
R_{equ} (nm)	(5.00,5.72)	(5.00,5.97)	(5.00,6.22)	(5.00,6.47)	(5.00,6.72)	(5.00,6.97)
T_{equ} (nm)	0.72	0.97	1.22	1.47	1.72	1.97
RMS (%)	(0.00,2.52)	(0.00,4.84)	(0.00,6.96)	(0.00,8.92)	(0.00,10.74)	(0.00,12.43)

R_{max}: maximum radius; R_{min}: minimum radius; R_{ave}: average radius

R_{equ}: volume equivalent radius; T_{equ}: equivalent thickness

RMS: radius deviation

Table 1.5 Characteristic parameters of star-shaped core–shell NPs.

star	f.1	f.2	f.3	f.4	f.5	f.6
R_{max} (nm)	(2.50,5.00)	(2.50,6.75)	(2.50,8.63)	(2.50,9.49)	(2.50,10.29)	(2.50,12.00)
R_{min} (nm)	(2.50,3.00)	(2.50,3.00)	(2.50,3.00)	(2.50,3.00)	(2.50,3.00)	(2.50,3.00)
R_{ave} (nm)	(2.50,3.61)	(2.50,4.39)	(2.50,4.95)	(2.50,5.49)	(2.50,6.00)	(2.50,6.35)
R_{equ} (nm)	(2.50,3.37)	(2.50,3.48)	(2.50,3.54)	(2.50,3.43)	(2.50,3.28)	(2.50,3.44)
T_{equ} (nm)	0.87	0.98	1.04	0.93	0.78	0.94
RMS (%)	(0.00,18.78)	(0.00,28.89)	(0.00,38.73)	(0.00,42.30)	(0.00,46.14)	(0.00,52.42)

R_{max}: maximum radius; R_{min}: minimum radius; R_{ave}: average radius

R_{equ}: volume equivalent radius; T_{equ}: equivalent thickness

RMS: radius deviation

Appendix (Ⅱ)

Here CTMC method is applied on spherical core-shell NPs. We consider Cu $2p_{3/2}$ photoelectrons traveling in Cu-core/Cu-shell NPs, which is not only convenient for calculations, but also to compare with the results of Powell et al. in simulations with SESSA.[1] From predictive formulas[2] $L_{1,a}$=0.80 nm; $A=I_1/I_2$ and $B = C = 1$ for Cu-core/Cu-shell NPs .

For the spherical case, we use the same size and geometry as in Powell et al.[1] The diameter D of the core is 1, 2, 5, and 10 nm. The thickness T is from 0.25-3.75 nm, with a step length of 0.25 nm. Elastic scattering effect is included in our simulations. The angle between the X-rays and detector is 55° and the collection range of the detector is less than 5°.

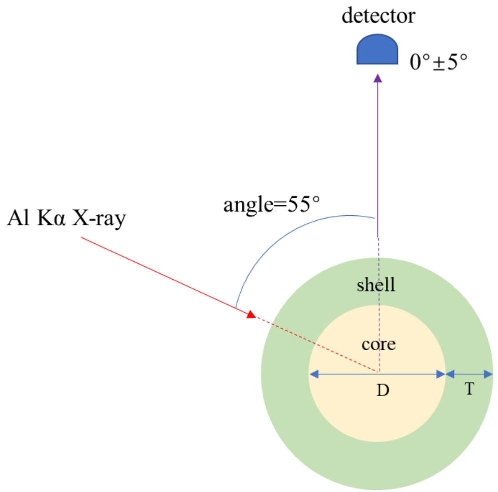
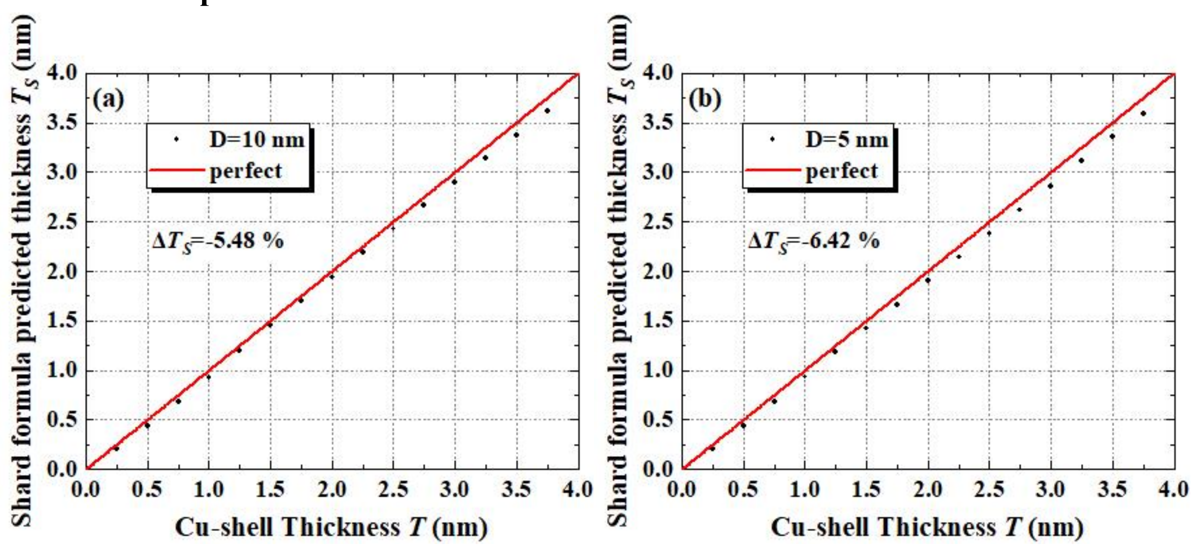


Figure 1. Geometric conditions of XPS. The X-rays is incident at an angle of 55° with respect to the axis of the detector, and the collection range of the detector is less than 5°.

Evaluation of Spherical Core-Shell NPs



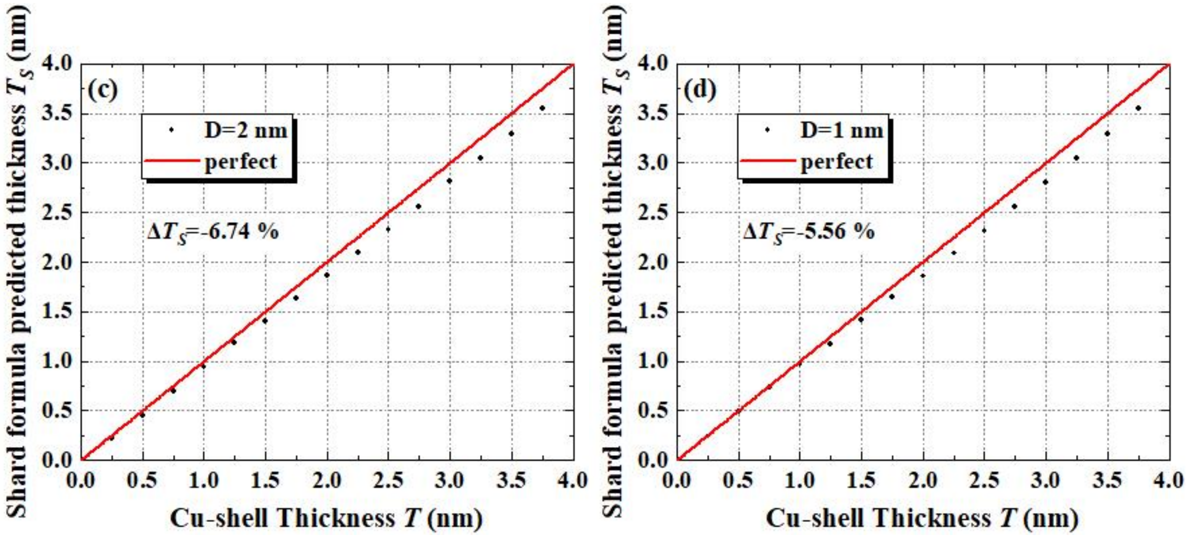


Figure 2. Comparisons of shell thickness, T_S, derived from Shard formula (Eq. (7) in main text) by CTMC simulations of the Cu 2$p_{3/2}$ photoelectrons emitted from the Cu core and Cu shell, and the Cu shell thickness. The red line corresponds to a perfect correlation between T_S and the real shell thickness. D represents the core diameter: (a) 10 nm; (b) 5 nm; (c) 2 nm; (d) 1 nm.

In **Fig. 2**, the abscissa represents the real shell thickness of the core–shell NPs, and the ordinate represents the predicted thickness obtained by Shard formula (Eq. (7) in main text). The red line indicates that in perfect conditions without error, the horizontal and vertical coordinates are equal. ΔT_S is the relative error between the predicted shell thickness and the real thickness: defined as eq. (16) in main text. The relative errors ΔT_S of the SESSA simulation results were within 5%, whereas the relative errors ΔT_S of the CTMC simulation results ranged from 5% to 7%.[1] The CTMC result is similar to SESSA simulation which indicate that the Shard formula produces accurate results for the shell thickness of ideal core–shell NPs with a spherical core and shell. Our method and those of Powell and Shard complement verify each other, although the error of the shell thickness simulated by the Monte Carlo method (ca. 7%) is slightly larger than the error of SESSA (less than 5%).

References:

1. C. J. Powell, W. Werner, A. Shard and D. G. Castner, *The Journal of Physical Chemistry C*, 2016, **120**, 22730-22738.
2. A. Jablonski and C. Powell, *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 2009, **27**, 253-261.