Preserving the Shape of Silver Nanocubes under Corrosive Environment by Covering Their Edges and Corners with Iridium

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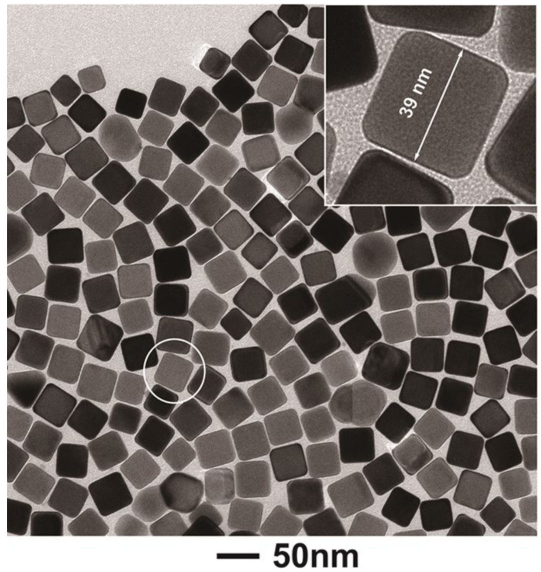

Fig. S1 TEM image of the Ag nanocubes with an average edge length of 38.7 ± 2.6 nm.

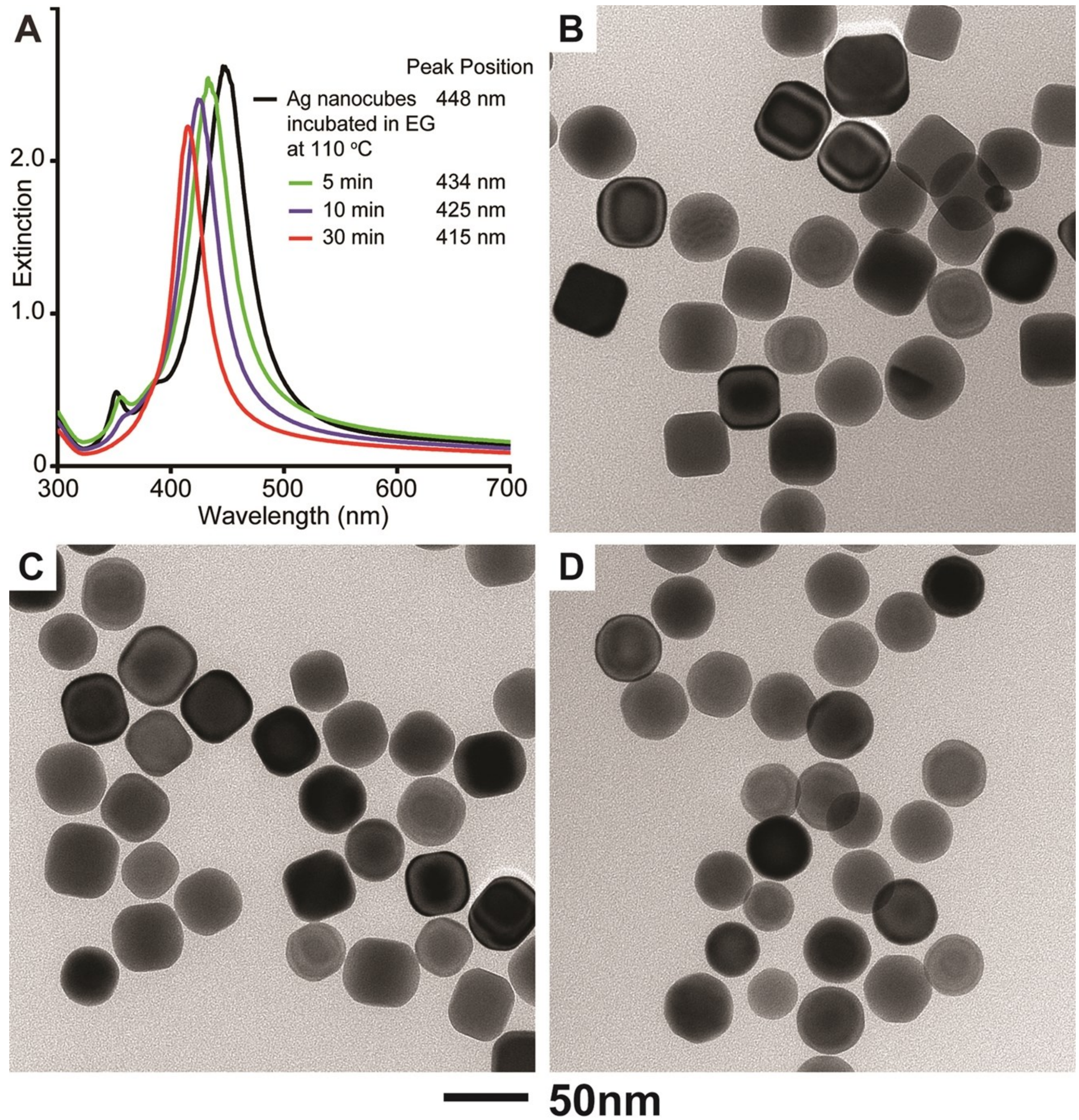

Fig. S2 (A) UV−vis spectra recorded from suspensions of the Ag nanocubes before and after they had been treated in a PVP/EG solution at 110 ^{o}C for different periods of time. (B-D) TEM images of the resultant nanoparticles after the thermal treatment at (B) 5, (C) 10, and (D) 30 min, respectively.

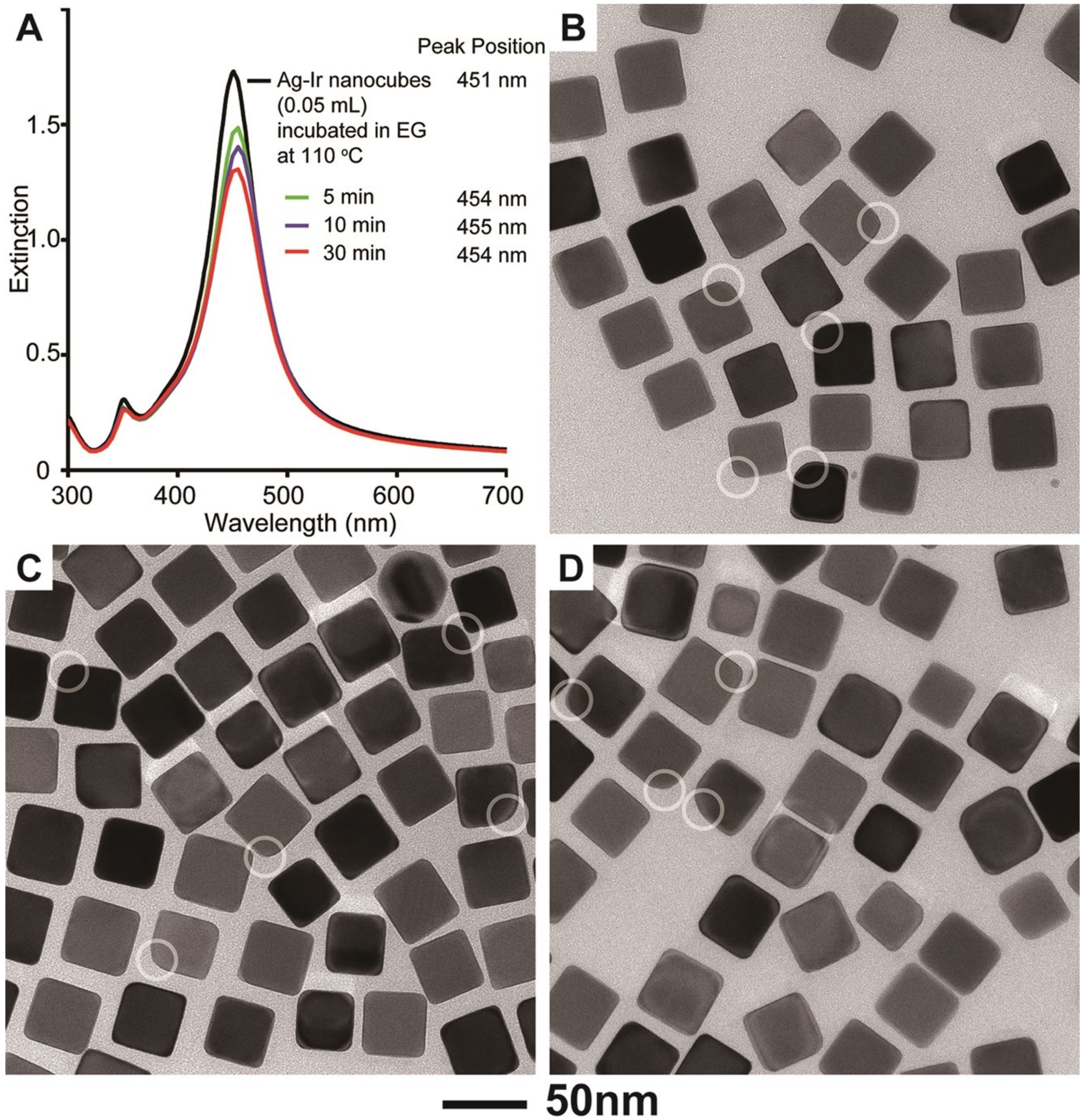

Fig. S3 (A) UV−vis spectra recorded from suspensions of the Ag-Ir nanocubes before and after they had been incubated in a PVP/EG solution at 110 ºC for different periods of time. These Ag-Ir nanocubes were prepared by reacting the Ag nanocubes with 0.05 mL of the Na_3IrCl_6 solution. (C-D) TEM images of the resultant nanoparticles after the thermal treatment for (B) 5, (C) 10, and (D) 30 min, respectively.

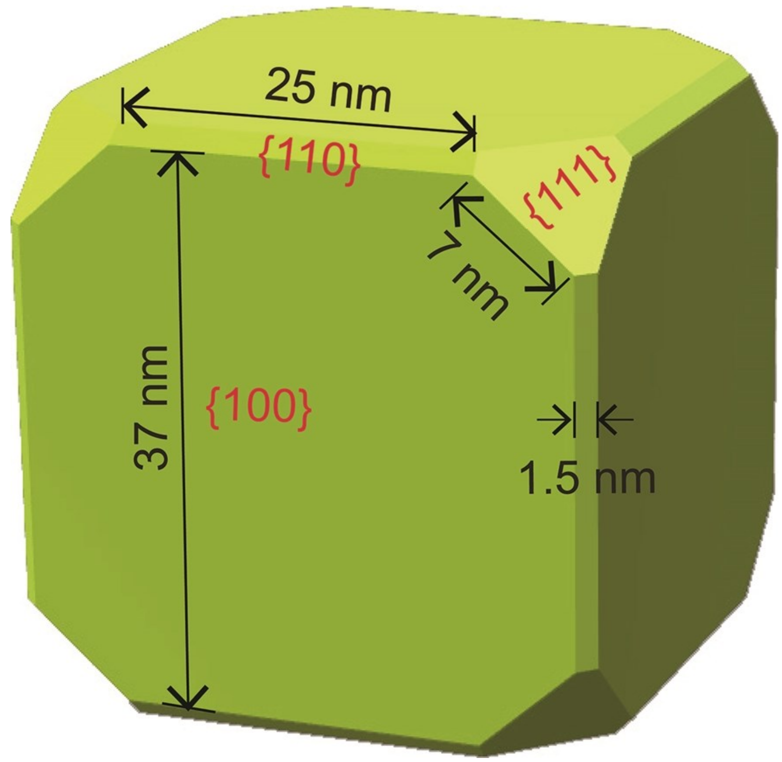

Fig. S4 Schematic illustration of a Ag nanocube, with all the dimensions labeled, used for calculating the Ir coverage on the edges and corners of a Ag nanocube.

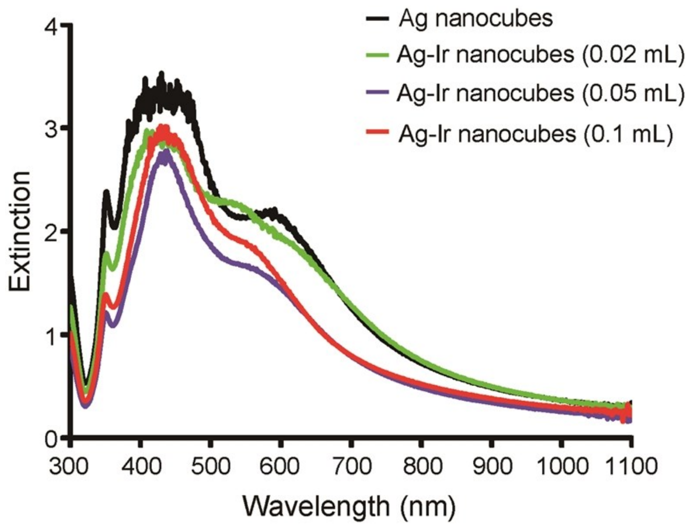

Fig. S5 UV-vis spectra recorded from the aqueous suspension of 2,6-DMPI (10^{-4} M) functionalized Ag nanoubes and Ag-Ir nanocubes prepared at different titration volume of Na_3IrCl_6.

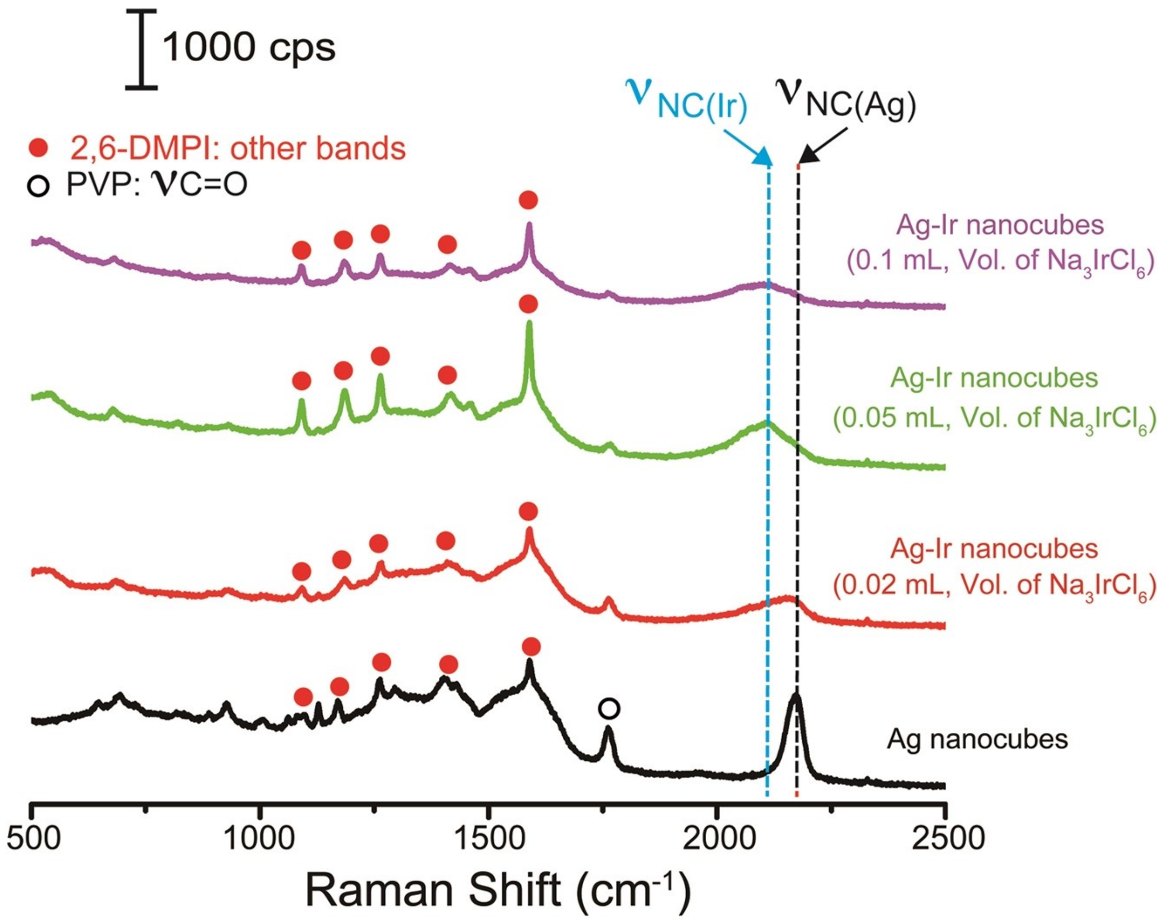

Fig. S6 SERS spectra recorded from an aqueous suspension of the 2,6-DMPI-functionalized Ag-Ir nanocubes with laser excitation at 532 nm. The Ag-Ir nanocubes were prepared by reacting the Ag nanocubes with different volumes of Na_3IrCl_6 solution, as marked on each spectrum.

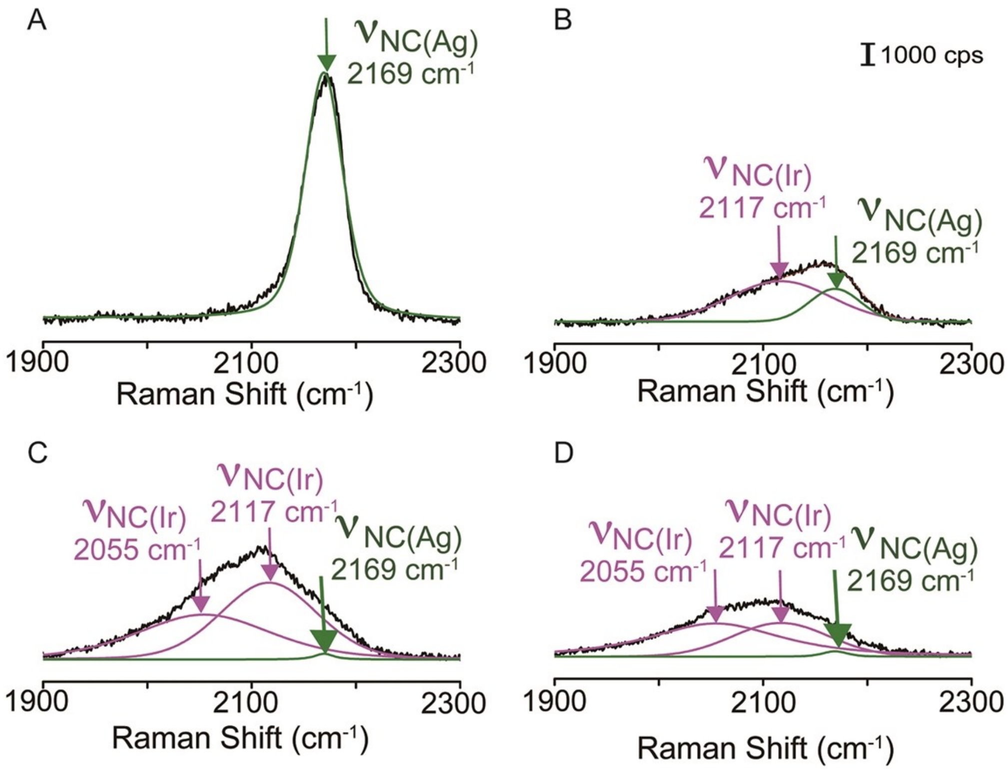

Fig. S7 SERS spectra recorded from an aqueous suspension of the 2,6-DMPI-functionalized Ag-Ir nanocubes after background substraction and the corresponding curve fitting results. The Ag-Ir nanocubes were prepared by reacting the Ag nanocubes with different volumes of the Na_3IrCl_6 solution: (A) 0, (B) 0.02, (C) 0.05, and (D) 0.1 mL, respectively.

Table S1 The Ag and Ir contents in the solid products determined using ICP-MS analyses.

Samples	Ag content (μg)		Ir content (μg)		Ir to Ag atomic ratio	
	Measured	Average	Measured	Average	Calculated	Average
Sample 1 (0.02 mL Na_3IrCl_6)	170.49	179.74±16.85	0.81	0.73±0.06	1:375	1:444
	165.35		0.72		1:409	
	203.39		0.66		1:549	
Sample 2 (0.05 mL Na_3IrCl_6)	182.74	184.96±6.53	1.42	1.37±0.06	1:229	1:241
	178.31		1.41		1:225	
	193.84		1.28		1:270	
Sample 3 (0.1 mL Na_3IrCl_6)	198.72	194.94±15.22	2.07	2.10±0.16	1:171	1:165
	174.70		1.93		1:161	
	211.41		2.31		1:163	
Sample 4 (0.2 mL Na_3IrCl_6)	195.95	191.79±6.38	3.91	3.68±0.19	1:89	1:93
	182.77		3.69		1:88	
	196.64		3.44		1:102	
Sample 5 (0.4 mL Na_3IrCl_6)	171.33	144.41±19.42	9.93	8.84±0.16	1:31	1:29
	135.64		9.37		1:26	
	126.25		7.23		1:31	

Appendix 1: Calculation of the number of Ag nanocubes in the reaction

Because the Ag-Ir nanocubes prepared by 0.1 mL of Na_3IrCl_3 solution show shape stability in EG and PVP, we used the average Ag mass in solid listed in Table S1, 194.94±15.22 μg, to calculate the number of Ag nanocubes in the reaction solution. Based on our TEM results that give the average edge length of Ag nanocubes is 38.7±2.6 nm, we developed a model of Ag nanocube with dimension labelled in Fig. S3 to complete the following steps:

1. Calculation of the average number of Ag atoms, n_1(Ag), in the reaction solution:

n_1(Ag) = [(0.19494 mg)/(107.86×10^3mg/mol)]×6.022×10^{23} atoms/mol

= 1.09×10^{18} atoms

2. Calculation of the volume of a Ag nanocube, V(Ag nanocube).

V(Ag nanocube) = $(39\ \text{nm})^3 - 1/2 \times (1.5 \times \sqrt{2}/2\ \text{nm})^2 \times 25\ \text{nm} \times 12 - 1/3 \times 1/2 \times [\sqrt{2}/2\ (7 + 2 \times 1.5\ \text{nm})]^3 \times 8 = 58679\ \text{nm}^3$

3. Calculation of the number of Ag atoms in a Ag nanocube, n_2(Ag), with an edge length of 39 nm using unit cell approach with the lattice constant of Ag at 0.408 nm:

n_2(Ag) = V(Ag nanocube)/the volume of a unit cell × 4 = $58679\ \text{nm}^3/(0.408\ \text{nm})^3 \times 4 = 3.46\times10^6$ atoms

4. Calculation of number of Ag nanocubes, n_3(nanocube) in the reaction solution:

n_3(nanocube) = (1.09×10^{18} atoms) / (3.46×10^6 atoms) = 3.15×10^{11} Ag nanocubes

Appendix 2: Calculation of Ir atoms deposited onto a Ag nanocube

Based on the ICP-MS results from Table S1, the average mass of Ir in the solid sample 3 prepared from 0.1 mL Na_3IrCl_6 was 2.10±0.16 μg. We calculated the number of Ir atoms deposited on a Ag nanocube with an edge length of 39 nm as follows:

1. Calculation of the number of Ir atoms, n_1(Ir), on Ag-Ir nanocubes:

n_1(Ir, 0.1 mL) = [2.10 $\times 10^{-6}$ g/ (192.21 g/mol)] × 6.022$\times 10^{23}$ atoms/mol = 6.58$\times 10^{15}$ atoms

2. Calculation of the number of Ir atoms, n_2(Ir), deposited to one Ag nanocube:

n_2(Ir, 0.1 mL) = (6.58$\times 10^{15}$ atoms / 3.15$\times 10^{11}$ cubes) = 20889 atoms/cube

3. By using the same number of Ag nanocubes, 3.15$\times 10^{11}$ in the reaction solution (see Appendix 1) and the average mass of Ir in the solid sample, 2 and 3, prepared by 0.02 and 0.05 mL Na_3IrCl_6 (see Table S1), we repeated Step 1-2 to calculate n_2(Ir) for these two samples:

n_1(Ir, 0.02 mL) = [0.73 $\times 10^{-6}$ g/ (192.21 g/mol)] × 6.022$\times 10^{23}$ atoms/mol = 2.29$\times 10^{15}$ atoms

n_2(Ir, 0.02 mL) = (2.29$\times 10^{15}$ atoms / 3.15$\times 10^{11}$ cubes) = 7261 atoms/cube

n_1(Ir, 0.05 mL) = [1.37 $\times 10^{-6}$ g/ (192.21 g/mol)] × 6.022$\times 10^{23}$ atoms/mol = 4.29$\times 10^{15}$ atoms

n_2(Ir, 0.05 mL) = (4.29$\times 10^{15}$ atoms / 3.15$\times 10^{11}$ cubes) = 13628 atoms/cube

Appendix 3. Calculation of the surface coverage of Ir atoms on the edges and corners of a Ag nanocube

1. Calculation of the surface area of 12 edges and 8 corners of a Ag nanocube:
Based on the dimension of a Ag nanocube as shown in Fig. S4, we calculated the surface area of edges (Ag(110) surfaces), S_{edge}, and corners (Ag(111) surfaces), S_{corner}, of one Ag nanocube as follows:
S_{edge} = 25 nm × 1.5 nm × 12 = 450 nm^2
S_{corner} = [1/2 × (7 + 2 ×1.5 nm) × $\sqrt{3}$/2 (7 + 2 ×1.5 nm) - 1/2 × 1.5 nm × ($\sqrt{3}$/2 × 1.5 nm) × 3] × 8 = 323 nm^2

2. Assuming that Ir atoms would form one atomic layer on all edges and corners of Ag nanocube, we argue that the thickness of the layer is equivalent to the lattice constant of Ir at 0.3839 nm. As such, we calculated the total volume of Ir atoms needed to form one atomic layer on the edges and corners of one nanocube, V(Ir), as follows:
V(Ir, edges) = 450 nm^2 × 0.3839 nm = 172.75 nm^3
V(Ir, edges and corners) = 450 nm^2 × 0.3839 nm + 323 nm^2 × 0.3839 nm = 296.75 nm^3

3. We calculated the number of Ir atoms needed to form one atomic layer of Ir on edges only and both edges and corners of one Ag nanocube, n_3(Ir), using the unit cell approach as follows:
n_3(Ir, edges) = [172.75 nm^3/ (0.3839 $nm)^3$/unit cell] × 4 atoms/unit cell = 12213 atoms/cube
n_3(Ir, edges and corners) = [296.75 nm^3/ (0.3839 $nm)^3$/unit cell] × 4 atoms/unit cell = 20980 atoms/cube

4. Based on the Ir atoms deposited on one Ag nanocube, n_2(Ir, 0.02, 0.05, and 0.1 mL) (see Appendix 2), we calculate the surface coverage of Ir atoms, N(Ir), on all edges of a Ag nanocube as follows:

N(Ir, 0.02 mL, edges) = n_2(Ir, 0.02 mL)/n_3(Ir) = 7261 atoms/ 12213 atoms = 59.4%
N(Ir, 0.05 mL, edges) = n_2(Ir, 0.05 mL)/n_3(Ir) = 13628 atoms/ 12213 atoms = 111.6%
N(Ir, 0.1 mL, edges) = n_2(Ir, 0.1 mL)/n_3(Ir) = 20889 atoms/ 12213 atoms = 170.0%

5. Based on the Ir atoms deposited on one Ag nanocube, n_2(Ir, 0.02, 0.05, and 0.1 mL) (see Appendix 2), we calculate the surface coverage of Ir atoms, N(Ir), on all edges and corners of a Ag nanocube as follows:

N(Ir, 0.02 mL, edges and corners) = n_2(Ir, 0.02 mL)/n_3(Ir) = 7261 atoms/ 20980 atoms = 34.6%
N(Ir, 0.05 mL, edges and corners) = n_2(Ir, 0.05 mL)/n_3(Ir) = 13628 atoms/ 20980 atoms = 64.9%
N(Ir, 0.1 mL, edges and corners) = n_2(Ir, 0.1 mL)/n_3(Ir) = 20889 atoms/ 20980 atoms = 99.5%