Electronic Supplementary Information

for

Synthesis of Fullerene@Gold Core-Shell Nanostructure

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Experimental Details

Materials: C_{60} was obtained from BuckyUSA (TX, USA) and other reagents were purchased from Sinopharm (Shanghai, China).

Sample preparation: The nano C_{60} in water suspension was prepared following previously reported method with some modification.[1, 2] In brief, C_{60}/toluene solution (2 mg/ml, 1 ml) was injected into water (50 ml). The solution was sonicated to produce toluene/water emulsion. The solution was then poured into a glass petri dish and put on water bath to evaporate the toluene. The solution was further evaporated to 20 ml to obtain the nano C_{60} suspension.

To synthesize fullerene@gold nano structure, $AuCl_3$ (10 mM) was mixed with 4 volumes of K_2CO_3 solution (2.5 mg/ml) and incubated at room temperature for 30 min. Then to 1 ml of the nano C_{60} suspension, formaldehyde solution (30%, 50 μl) was added, followed by slow dropping in of the $AuCl_3$-K_2CO_3 solution. The dropping rate was kept very low and up to 200 μl of $AuCl_3$-K_2CO_3 solution were dropped over 6 h. The samples were then centrifuged at 5,000 g to remove free nano C_{60} and the pellet was re-suspended in water. To remove the gold nanoshells from fullerene@gold, one volume of HCl-H_2O_2 (1:1 v/v) was added in and shaked. Then sample was centrifuged under 30,000 *g* followed by re-suspension in fresh H_2O.

Characterization: Morphology of the samples was observed using a JEOL 2010 TEM while size distribution was analyzed using a 380 ZLS particle sizer (NICOMP, CA, USA). The SPR of samples was analyzed using a Varian Cary 300 UV-vis spectroscope. Mie calculation was conducted with a free Mie calculator program provided by Southern Methodist University, supposing the inner and outer diameter of gold nanoshells were 100 nm and 150 nm as measured by zeta sizer. To study the effect of medium refractive index on the SPR, the sample was suspended in DMSO-water solution (50%). A DXR Raman microscope (Thermo Scientific, WI, USA) with 1 mW exciting energy at 532 nm was used to measure the spectrum of samples, previously dried on glass slides.[3] The accumulation time was set as 3 s or 15 s.

Experiment with $Mo(CO)_6$ to prove the formation of C_{60}@Au nanoshells

0.05 mmol of C_{60} and $Mo(CO)_6$ was dissolved in 5 ml of toluene under inert atmosphere. Then the reaction mixture was stirred under sunlight for 6 hours. The reddish-purple color of the solution was changed to brownish black. The solvent was reduced to induce precipitation and the mixture was filtered to give the desired product. This is in agreement with the reaction proposed by José E. Cortés-Figueroa. [4]

$$Mo(CO)_6 + C_{60} \xrightarrow[\text{6 hr}]{\text{sunlight}} (n^2\text{-}C_{60})Mo(CO)_5$$

On the other hand, in case of the sample of C_{60}@Au nanoshell, 0.05 mmol of $Mo(CO)_6$ was dissolved in 5 ml of MeOH under inert atmosphere and the water suspension of C_{60} @Au nanoshell was added to the reaction mixture drop wise. Then the mixture was stirred under sunlight for 6 hours. The violet color of the solution was not changed after 6 hr. Then the solution was dried under vacuum. The TLC showed that the spot of $Mo(CO)_6$ was identical with the product spot and no new spot was generated.

$$Mo(CO)_6 + C_{60}\text{@Au nanoshell} \xrightarrow[\text{6 hr}]{\text{sunlight}} \text{No reaction}$$

The result of this reaction clearly indicated that, while pure C_{60} easily reacted with metal carbonyl, C_{60}@Au nanoshell did not react with $Mo(CO)_6$ as it was coated with Au.

Supplementary Figures and Tables

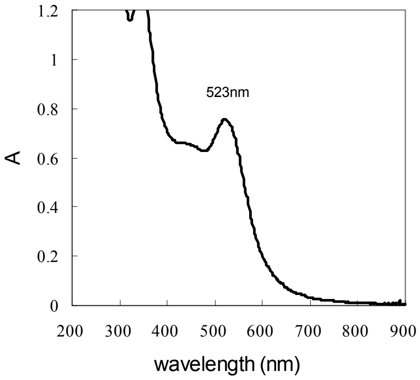

Fig. S1 Quick pouring in of $AuCl_3$- K_2CO_3 resulted in a sample with λ_{max} around 523 nm, suggesting formation of Au nanoparticles [5] rather than Au nanoshells.

Energy Dispersive X-ray Spectroscopy (EDX):

Different C_{60} samples were prepared on 200 mesh copper grids coated with formvar and subjected to transmission electron microscopy (TEM) and Energy Dispersive X-ray Spectroscopy (EDX) using JEOL JEM 3010F HRTEM equipped with EDX instrument (300 kV LaB6).

This was used for quantitative elemental analysis of different samples. The collection and quantification of spectra was computer controlled with integrated software.

The data reported in the table below show that

- In case of C_{60} alone or with $AuCl_3$ and K_2CO_3 (but without formaldehyde as reducing agent), as expected mainly C (due to C_{60}) and Cu (due to the TEM grids) were present, while no Au was detected.
- With nanoshells obtained by reacting C_{60} with $AuCl_3$ and K_2CO_3 in the presence of formaldehyde as reducing agent, additional peaks corresponding to Au were detected, thus suggesting the successful incorporation of Au only in these samples.

Mass %	**C_{60}**	**C_{60}+Aucl$_3$ (without HCHO)**	**C_{60}@Au nanoshell**
C	63.07	61.82	59.41
O	11.44	11.03	2.16
Si	0.86	-	-
P	1.15	-	-
Cu	19.49	19.57	28.6
Au	-	-	**9.83**
Cl	4.00	7.58	-

Table 1: Element composition mapping of samples (1a), (1b) and (1c) in Fig. 1 *via* EDX analysis.

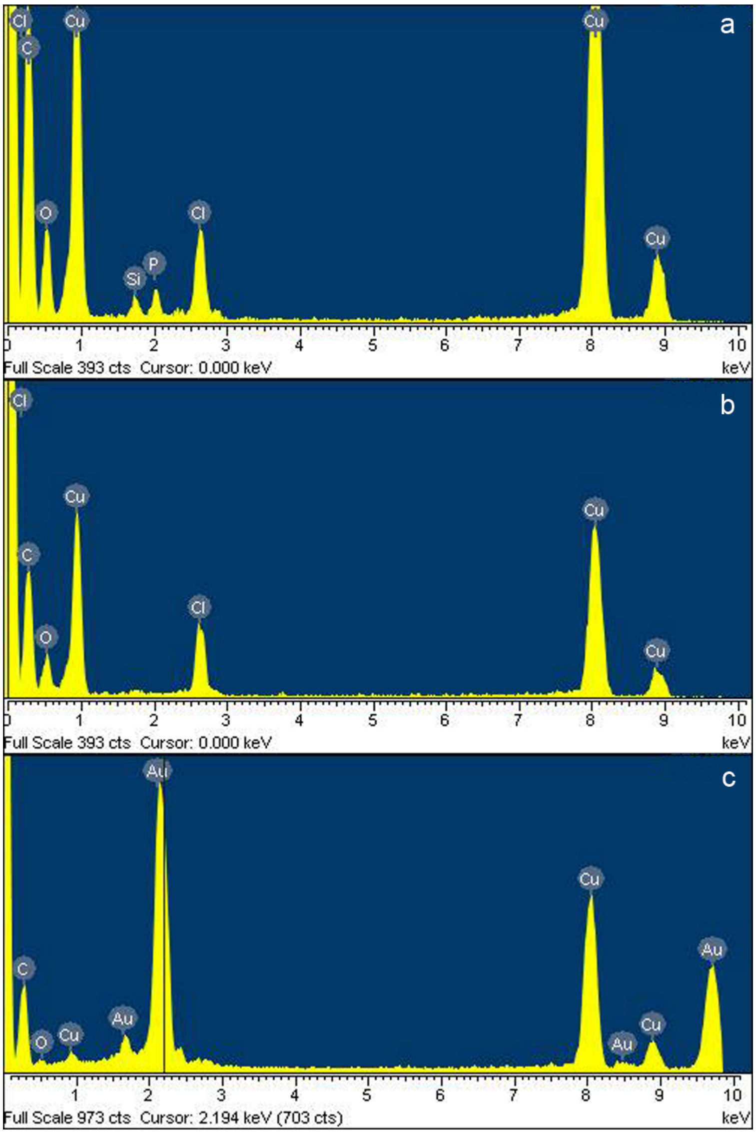

Fig. S2 Element composition mapping of samples (1a), (1b) and (1c) in Fig. 1 of the main text *via* EDX analysis. Horizontal axis: Energy (in keV); Vertical axis: Counts (arbitrary unit).

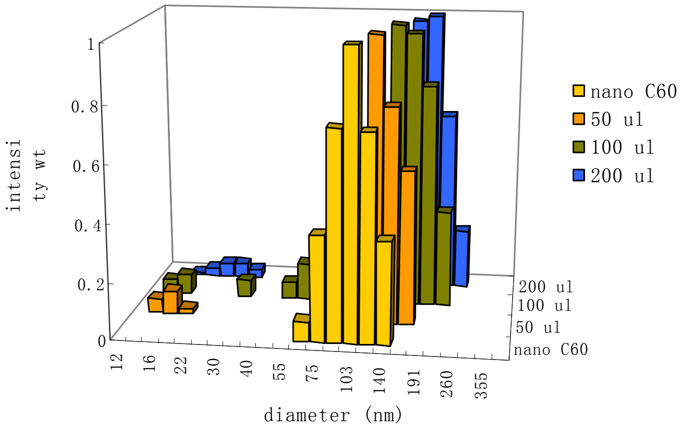

Fig. S3 Zeta-size distribution of nano C_{60} was 100 nm while samples prepared using 50 µl, 100 µl and 200 µl $AuCl_3$-K_2CO_3 solutions were around 120 nm, 150 nm and 150 nm, respectively.

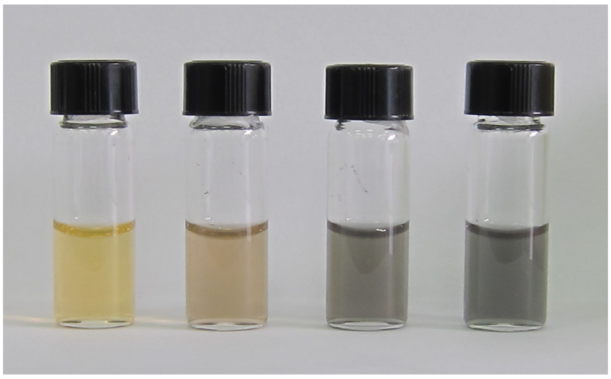

Fig. S4 From left to right are digital photos of nano C_{60} solution, C_{60}@Au solutions prepared using 50 µl, 100 µl and 200 µl $AuCl_3$-K_2CO_3 solutions.

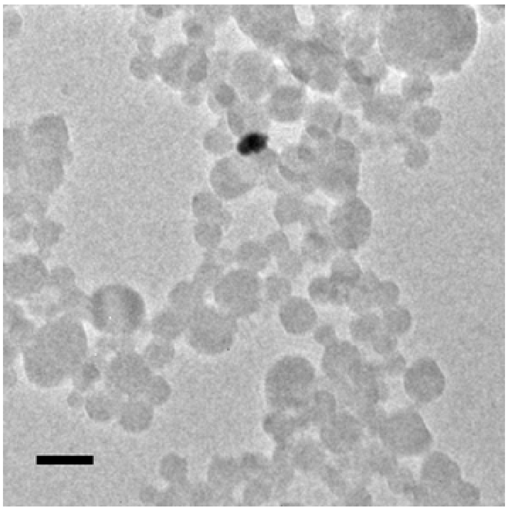

Fig. S5 TEM of C_{60}@Au nanoshells' core after removal of the Au nanoshells using H_2O_2-HCl. Scale bar: 100 nm.

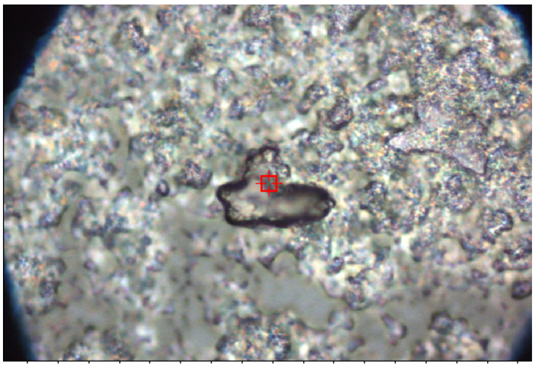

Fig. S6 Digital photo obtained by optical microscope equiped with the Raman spectroscope. Sample near the red corss was irradiated under 1mW for 15 sec and it was intensively burnt.

Acknowledgements

The authors G.P. and W.H. A. acknowledge support by A*STAR SERC TSRP-Integrated Nano-Photo-Bio Interface grant (Project Number: 102 152 0016).

References

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