

RSC Advances

Supporting Information:

A highly efficient ligand exchange reaction on gold nanoparticles: preserving their size, shape and colloidal stability.

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1. Experimental section

1.1 Synthesis of spherical gold (Au) nanoparticles

Materials. The following chemicals were purchased and used as received without further purification. Gold (III) chloride trihydrate > 99% ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), sodium borohydrate 98% (NaBH_4), cetylmethylammonium chloride 25 wt.% in water (CTAC) and cetylmethylammonium bromide >99% (CTAB), 3-mercaptopropionic acid (3-MPA) and dichloromethane (DCM) were purchased from Sigma Aldrich. Ascorbic acid 99% (AA) was purchased from Chem-Watch.

Synthesis and purification of colloidal Au NPs.

Gold nanoparticles synthesis consists of two consecutive stages including the preparation of the gold seeds and the preparation of Au NPs.

- a. Preparation of CTAB capped Au seeds.

The Au seeds were prepared by mixing the aqueous solution of 10mL of 0.25 mM

HAuCl₄ with 100 mM CTAB thoroughly. Into the mixture, 6mL of 10 mM aqueous NaBH₄ was rapidly introduced. Immediately after the addition of the NaBH₄, the mixture changed its color into a light brown solution. The solution was then stirred at RT for 3 hours.

b. Synthesis of spherical Au NPs.

Following the order, the aqueous solution of CTAC (200mM, 2mL), AA (100mM, 1.5 mL) and 100 μL of the seeds solution from the previous synthesis were thoroughly mixed and into the solution, 2mL of 0.5mM HAuCl₄ solution was rapidly injected. The reaction was then allowed to stir for about 15 minutes at RT. The final product was washed by water and centrifuged at 15000rpm for 30 minutes. At the end, the precipitate was dissolved in water.

Gold (Au) MNPs ligand exchange. The as-synthesised Au NPs dispersion is mixed with dichloromethane (DCM) solvent in 1:1 volume ratio. The mixture was then gently shaken and stirred for approximately 5 minutes until cloudy pink mixture is observed. This mixture was then centrifuge at 5000 rpm for 5 minutes and the red supernatant solution is extracted (two phases are occurred: top phase is AuNPs in water solution whereas bottom is CTAB/CTAC in DCM solution). Repeat the washing for 3 times to ensure the removal of CTAB/CTAC surfactant. The extracted AuNPs solution is then ready for the next surface treatment. Into the washed AuNPs, 0.19M, 3-mercaptopropionic (3-MPA) in water solution is added in approximately 1: 1 volume ratio (as-synthesised Au NPs: 3-MPA solution). The mixture was then sonicated for about 4-5 hours to ensure the complete exchange of the ligand molecules. The resulting mixture was then centrifuged at 26000rpm for 30mins for the first round and followed by washing the mixture 2x with

water (26000rpm, 10mins) to ensure the removal of the excess 3-MPA and the left over CTAB/CTAC surfactants. After centrifugation, the supernatant was discarded and the resulting precipitate was redispersed in water.

Transmission Electron Microscopy (TEM). TEM imaging was carried out by using a Philips CM200 operated at 200kV. TEM samples were prepared by placing a small drop of solutions on a holey carbon film on a 3 mm TEM copper grid supplied by Agar Scientific.

Dynamic Light Scattering (DLS). The particles size determination was carried out at 25 °C by using a Zetasizer-Nano instrument from Malvern, UK.

Ultraviolet-visible spectroscopy (UV-VIS). UV-Vis spectra were recorded with a Cary 300 UV-Vis spectrometer with UV-Vis quartz cuvette.

Fourier Transform Infrared Spectroscopy (FTIR). Infrared spectra analysis as-synthesised and treated AuNPs were carried out by using the transmission mode of VERTEX 70 FT-IR Spectrometer with HYPERION 3000 FT-IR Microscope from Bruker Optics. FTIR samples were prepared by placing a small drop of nanoparticle solution on a 2 cm x 2 cm reflective substrate (cut silicon wafer). The sample then dried in a vacuum desiccator to create a very thin layer on the silicon wafer prior to the measurement.

X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) was carried out to analyse surface ligands – especially (3-MPA) – of the Au NPs after ligand exchange. The results are shown in Figure S1 and Table S1. The results suggest that thiol

groups from 3-MPA have effectively exchanged the original ligands on the surface of AuNPs.

Table S1: Fitted binding energies for oxygen, carbon and sulphur.

Element	Binding energy [ev]	Fitted area	Total Area
O 1s	530.84	5485	55565.3
	533.36	19561.7	-
	532.14	30518.6	-
C 1s	286.79	4951.7	50409.7
	284.79	40461.5	-
	289.02	4996.5	-
S 2p	163.45	5051.3	7577
	164.68	2525.7	-

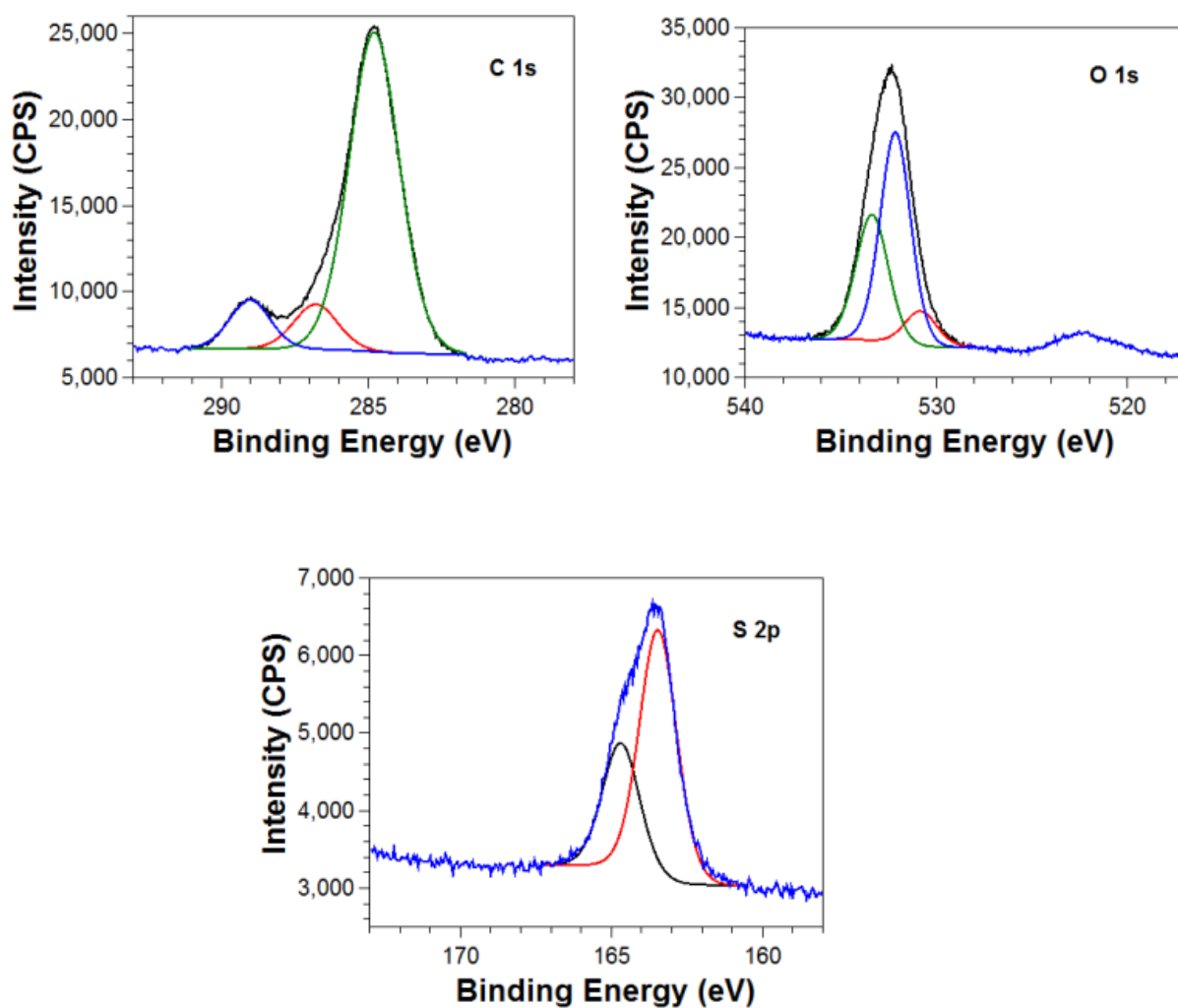


Figure S1: XPS spectra of thiol capped Au nanoparticles after ligand exchange.