# PROCEEDINGS OF SPIE

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**SPIE.**

# Functionalisation of 20 nm citrate-coated gold nanoparticles using perfluorodecanethiol

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## ABSTRACT

Colloidal synthesis of metal nanoparticles (NPs) requires the use of surfactants or other capping agents as stabilisers. These capping agents form monolayers on the NP surface and determine their functionalities. In most cases, the capping agent used for the synthesis does not provide the required properties for the desired applications and must be exchanged in a separate step. NP functionalisation through ligand exchange is a common strategy to alter their chemical and physical properties to expand their applications. Here, we show the functionalisation of 20 nm citrate-capped gold NPs (AuNPs) with perfluorodecanethiol (PFDT) to generate reversible interactions by exploiting the fluorous effect. Ultraviolet-visible (UV-vis) spectrophotometry and zeta potential (ZP) characterization was performed before and after functionalisation to confirm ligand exchange.

**Keywords:** Gold nanoparticles, ligand exchange, fluorous compounds

## 1. INTRODUCTION

The outstanding chemical robustness and biocompatibility of AuNPs compared to their silver or platinum counterparts have made gold the prefered material for many plasmonic applications. The most common strategy to synthesise AuNPs is to mix a capping agent, normally a surfactant, with an oxidised gold precursor and a reducing agent. For most applications, it is necessary to exchange these capping agents with different molecules (or biomolecules) in order to manipulate the NP's optical, catalytic, electronic or interfacial properties.[1]

The strong affinity of gold and sulphur makes thiols the most popular candidates to tailor the properties of AuNPs.[2] There are two main approaches to achieve self-assembled monolayers (SAMs) of thiolated molecules on the surface of AuNPs. The first is based on the Brust-Schiffrin method,[3] in which the ligand exchange takes place before the reduction of the colloidal gold. Although this method yields gold spheres capped with densely packed monolayers, it is not suitable for the synthesis of colloids larger than 5 nm in diameter. For applications requiring larger sizes or different morphologies, AuNPs must be synthesised in the presence of surfactants and the ligand exchange must be performed in a separate step. The aqueous synthesis of AuNPs in the presence of citrate was reported in 1951 by Turkevich and co-workers[4] and has become one of the most popular methods due to its simplicity and tuneability. Here, we report the functionalisation of commercial citrate capped AuNPs of 20 nm with PFDT.

Perfluorinated compounds are omniphobic; they favour interactions with each other over aqueous and organic phases. This property arises from the low polarizability of fluorine atoms, which yields very weak Van der Wall forces, and is commonly known as the fluorous effect.[5] The lack of intramolecular interactions between fluorous moieties and other species makes fluorous layers good anti-fouling platforms.[6] Furthermore, fluorous-fluorous interactions are non-covalent and highly specific, and can be employed as orthogonal recognition modes[7] or for reversible molecular patterning.[8] We aim to expand these functionalities to build new reversible systems.
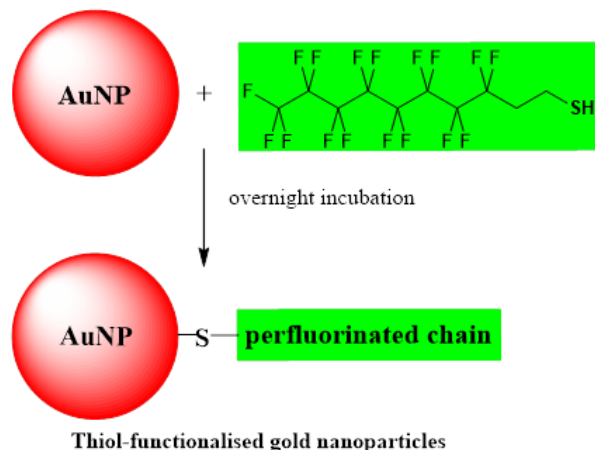
**Figure 1**. Schematic showing ligand exchange between a perfluorinated thiol and negatively charged AuNP

## 2. METHODS

### 2.1 Functionalisation of AuNPs

20 nm AuNPs were purchased from Sigma-Aldrich and used without further purification. 3 ml of AuNPs were dispensed in eppendorf tubes and centrifuged at 6000 r.p.m for 30 min. The supernatant was discarded and the precipitated NPs were re-dissolved in reversible osmosis (RO) water to yield a concentration of 0.05 mM. An appropriate volume of PFDT (Sigma-Aldrich) was added into the AuNP solution and stirred overnight. Excess PFDT was removed by the same centrifugation procedure while the resulting precipitate was diluted with RO water to form a 1.2 mM solution used for further analysis.

### 2.2 UV-vis characterization

A double beam UV-vis spectrophotometer (Ultrospec 9000) was used to monitor changes in the LSPR wavelength before and after each step of the functionalisation process. Spectra were recorded from 300-1000 nm using a 1 cm clear quartz cuvette.

### 2.3 DLS and ZP characterization

ZP analysis was performed on 700 µl samples, in triplicate, at an angle of 90 ° at 25 °C using a Zetasizer Nano Series 6.12 (Malvern).

## 3. RESULTS AND DISCUSSION

UV-vis spectra were recorded before and after functionalisation (Figure 2, Table 1) to monitor changes in the AuNPs resonance. AuNPs support localised surface plasmon resonances (LSPRs), which lie in the visible region and are extremely sensitive to changes in the local environment of the NPs, such as the formation of a new SAM. ZP characterisation was recorded to further confirm the presence of the PFDT monolayer (Figure 3). ZP measures the electrokinetic potential difference at the slipping plane, and thus provides useful information about immediate surroundings of the NP (such as whether a molecular mono layer has formed).
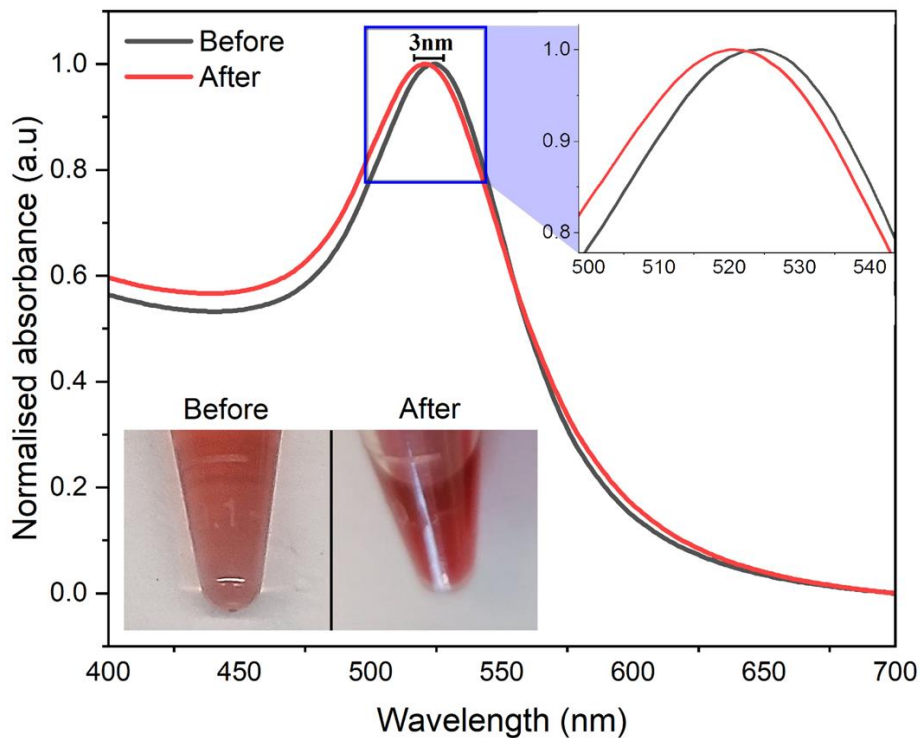
**Figure 2.** UV-vis spectra of 20 nm AuNPs showing a 3 nm blue-shifted plasmonic peak after functionalisation with PFDT. Inset are images of the colloidal solution before (left) and after functionalisation (right). The lack of colour change proves the stability of the system upon ligand exchange.
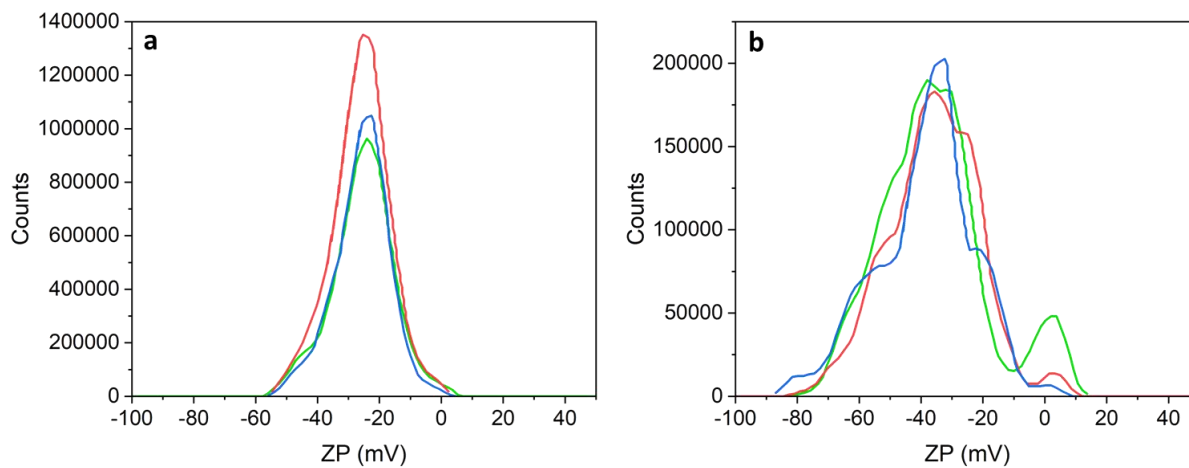


**Figure 3**. Average Zeta potential a) before functionalisation and b) after functionalisation. Each colour represents an individual measurement.

**Table 1**. UV-vis and Zeta potential characterisation before and after functionalisation. Zeta potential values represent the average of three independent measurements of each sample.

| LSPR wavelength before functionalisation (nm) | LSPR wavelength after functionalisation (nm) | Zeta potential before functionalisation (mV) | Zeta potential after functionalisation (mV) |
|---|---|---|---|
| 520.5 | 523.5 | -25.00±10.0 | -39.60±14.8 |

As shown in Figure 2, the LSPR peak experienced a 3 nm blue shift upon ligand exchange. Although in most cases the incorporation of thiols results in red shifts due to the increase in the local refractive index compared to citrate layers, the electron-withdrawing properties of perfluorinated compounds result in blue-shifted resonances.[11] A slight widening of the plasmonic peak is observed, which could indicate minor aggregation. However, no colour changes were observed (Figure 2b), and the solutions were stable over time, so we attribute this widening to transient fluorous-fluorous interactions between NPs as opposed to irreversible aggregation.

Finally, the ZP of the NPs also changed after the formation of the PFDT layer. The negative charges supported by the citrate groups yield a negative ZP of -25mV±10 mV, in agreement with the values found in the literature, whilst the functionalised NPs presented a more negative ZP (-39.60±14.8 mV), even though PFDT molecules have a net charge of zero (Figure 3). This effect has been observed before[12] and is attributed to the high hydrophobicity of perfluorinated SAMs. The lack of intramolecular interactions with the solvent, in this case water, causes an increase in slip length which brings the ZP to more negative values.

## 4. CONCLUSIONS

In this work we employ a simple, efficient, water-based ligand exchange method that can be used to tune the surface properties of citrate-coated AuNPs. In this case, citrate molecules were exchange by a perlfuorinated chain supporting a thiol group. UV/vis and ZP characterization obtained before and after functionalisation was compared with literature values and it was concluded that this method was successful to create a PFDT layer.

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