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Electronic Supplementary Information

One-pot synthesis of gold nanodimers and their use as Surface-Enhanced Raman Scattering Tags

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Experimental

All chemicals were of analytical grade and were used without further purification. The water used in all experiments was milli-Q grade. Gold chloride trihydrate ($HAuCl_4$. $3H_2O$), sodium trisodium citrate dihydrate (Nacit) (99.0%, $Na_3C_6H_5O_7.2H_2O$), sodium hydroxide (>98.5%, NaOH), Bis(*p*-sulfonatophenyl)phenylphosphine dihydrate dipotassium salt (>97%, BSPP), 1-benzenethiol (>98.0%, BT), O-[2-(3-Mercaptopropionylamino)ethyl]-O′ methylpolyethylene glycol (PEG-SH, M_w=5000) were purchased from Sigma-Aldrich. Spherical GNPs of 40nm diameter were synthesized using the standard citrate method.[1] The synthesis of GDs was carried out by adapting a previously published protocol.[2] 4.2µL of a 0.88M NaOH aqueous solution were added under vigorous stirring during 10min into 10mL of a 40nm GNPs seed solution. Subsequently, 0.2mL of a 1.7mM Nacit aqueous solution were added under stirring at 39°C. Finally, 600µL of a 1.2mM $HAuCl_4$ aqueous solution were added, which resulted in a gold atomic ration between ions in solution and neutral gold atoms in the seeds (Au^{3+}:Au^0 ratio) being 0.36:1. The reaction proceeded without stirring for 90 minutes at 39°C. The GDs were purified by two cycles of centrifugation (5000 rpm, 4 minutes) / redispersion in 6mL of a 1.7mM Nacit aqueous solution. Regarding the growth of the silica shell, 0.5 mL of a freshly prepared aqueous solution of PEG-SH (40 µM) was added dropwise to 3 mL of as-prepared GDs diluted in H_2O (17.5mL) under vigorous magnetic stirring and the mixture reacted for 30 min, ensuring the replacement of the citrate molecules adsorbed onto the gold surface by PEG-SH. Subsequently, the suspension was centrifuged at

4500 rpm for 15 min (twice) in order to eliminate excess PEG-SH and the precipitate obtained (0.9mL) was redispersed in 1 mL of EtOH. Silica (SiO_2) coating was performed by following a previously reported method.[3] The concentrations of Au/TEOS/NH_3/H_2O were: 0.02 mM/0.8 mM/0.2 M/ 10.55 M. GDs@mPEG-SH NPs were added into 15.86 mL of EtOH, followed by the addition of 2 mL of H_2O, 253 µL of aq. NH_3 (30%) and 101 µL of a TEOS solution in EtOH (0.16 M). The reaction mixture was stirred for 14 h, and the resulting GD@SiO_2 core–shell NPs were purified by centrifugation at 4500 rpm for 10 min (twice) and redispersed in 2 mL of EtOH. For the surface modification of GDs, 10mL of a 2.8mM BSPP aqueous solution were added to 2mL of the purified dimers solution under stirring during 12h. Subsequently, the mixture was centrifuged at 5000rpm during 20min. The precipitate was redispersed in 6mL of a 1.7mM aqueous Nacit solution, centrifuged again at 2500rpm during 15 minutes and finally redispersed in 1mL of a 1.7mM aqueous Nacit solution. BT chemisorption on GDs for SERS investigations was achieved by mixing 100 µL of nanodimers (without SiO_2 shell) solution with 900 µL of a 5mM ethanolic solution of BT.

Optical characterization of nanoparticle suspensions was carried out by UV/Vis spectroscopy with a Varian Cary 100 Bio spectrophotometer. Transmission Electron Microscopy (TEM) images were obtained with a Hitachi H600 microscope operating at 75 kV. In order to avoid any unwanted aggregation of the nanoparticles onto the grid due to drying effects, we always prepared a highly diluted solution of dimers by adding 10µL of the original dimer solution into 500 µL milli-Q water. Sample preparation was performed by depositing one drop of the highly diluted dimer solution onto a copper grid coated with a carbon membrane and the excess of solution was blotted with filter paper. Colocalized SERS, AFM and DFRSM measurements were carried out using an instrument described in detail elsewhere,[4,5] which has been slightly upgraded (ESI, Fig.S6). SERS measurements were performed by means of a He-Ne laser (λ=632.8 nm). The power at the sample was limited to 45 µW to avoid undesired damages, and could be as low as 5 µW for particularly SERS efficient GDs. AFM phase images were realised in soft tapping mode by means of commercial silicon AFM cantilevers (Nanosensors, PPP-NCST, nominal resonance frequency 160 kHz, nominal force constant 7.4 N/m).

1 N. G. Bastús, J. Comenge and V. Puntes, *Langmuir*, 2011, **27**, 11098.
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3 C. Fernández-López, C. Mateo-Mateo, R.A. Álvarez-Puebla, J. Pérez-Juste, I. Pastoriza-Santos and L.M. Liz-Marzán *Langmuir*, 2009, **25**, 13894.
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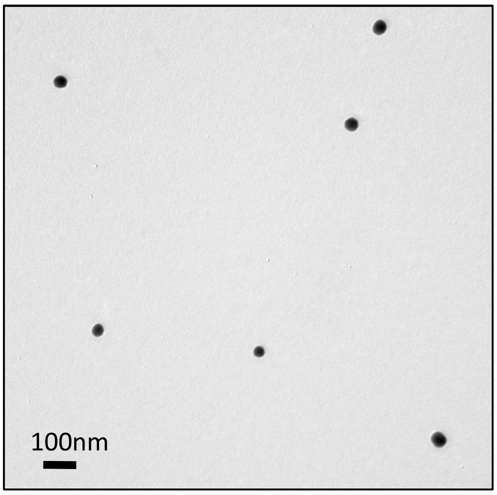

Fig.S1 TEM image of the 40 nm gold seeds.

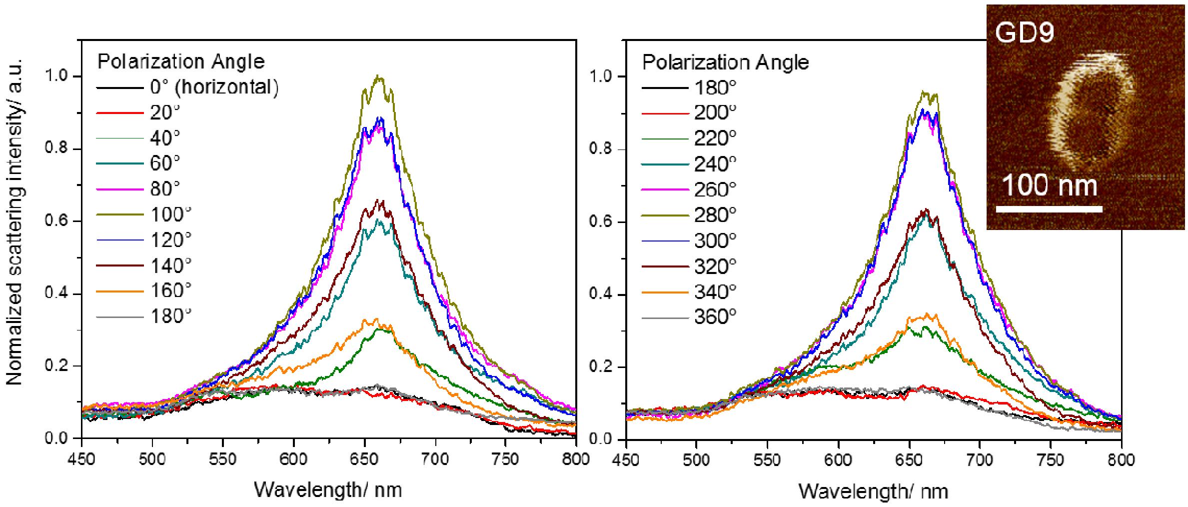

Fig.S2 Rayleigh scattering spectra associated with the gold dimer GD9 coated with a BT monolayer for different polarization of the incident white light. The inset shows the tapping-mode phase image of GD9. This figure indicates that the band centred at 660 nm is related to the longitudinal plasmon mode excited by light polarized along the dimer axis (for a ~ 100° polarization angle).

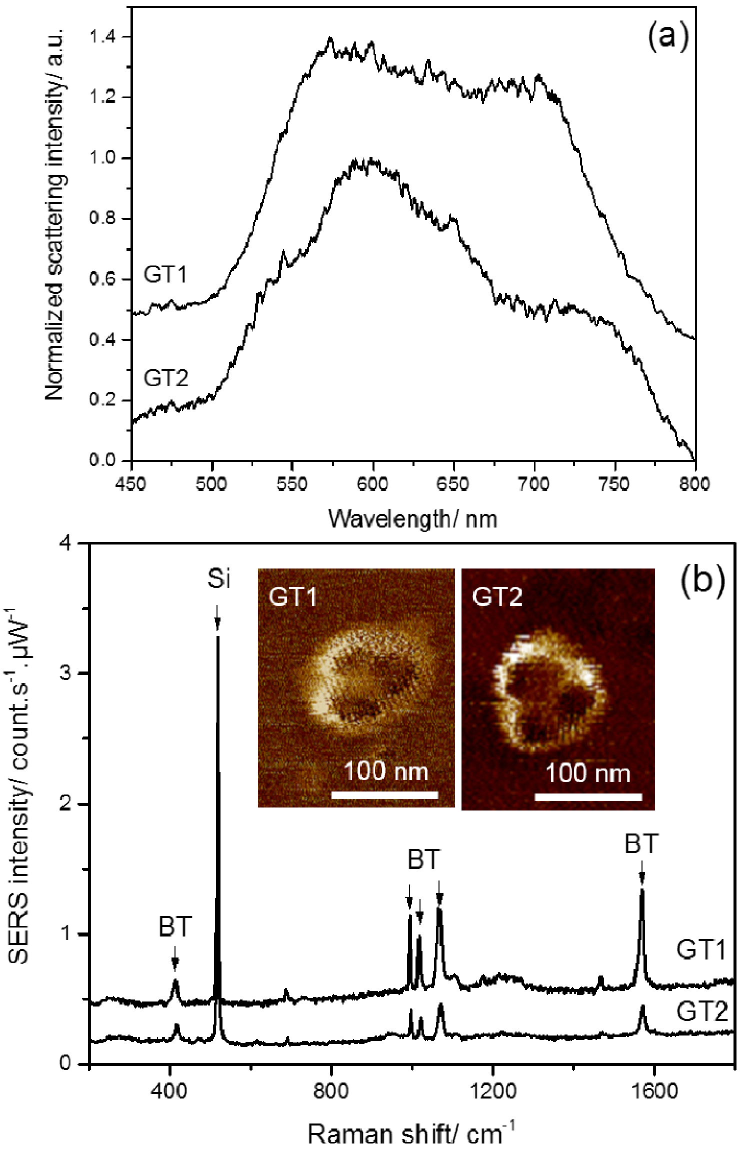

Fig.S3 (a) Rayleigh scattering spectra associated with two gold trimers (GT1 and GT2) coated with a benzenethiol (BT) monolayer. (b) Corresponding SERS spectra under 632.8 nm excitation and a laser power of 45 μW. Insets show tapping-mode phase images of GT1 and GT2. Note that SERS intensities are similar to those reported in the body text for GDs (Fig.3), in good agreement with previous observations that the hot spot with the smallest interparticle gap dominates the overall enhancement [K.L. Wustholz et al., *J. Am. Chem. Soc.*, 2010, **132**, 10903]. In addition, even for similar interparticle gaps, it is important to mention that, if the laser polarization is optimized to excite resonantly the longitudinal plasmon mode of a couple of GNPs, the other two in GT1 and GT2 are not resonantly excited. In this scenario, the hot spot of a single couple of GNPs still dominates the SERS enhancement.

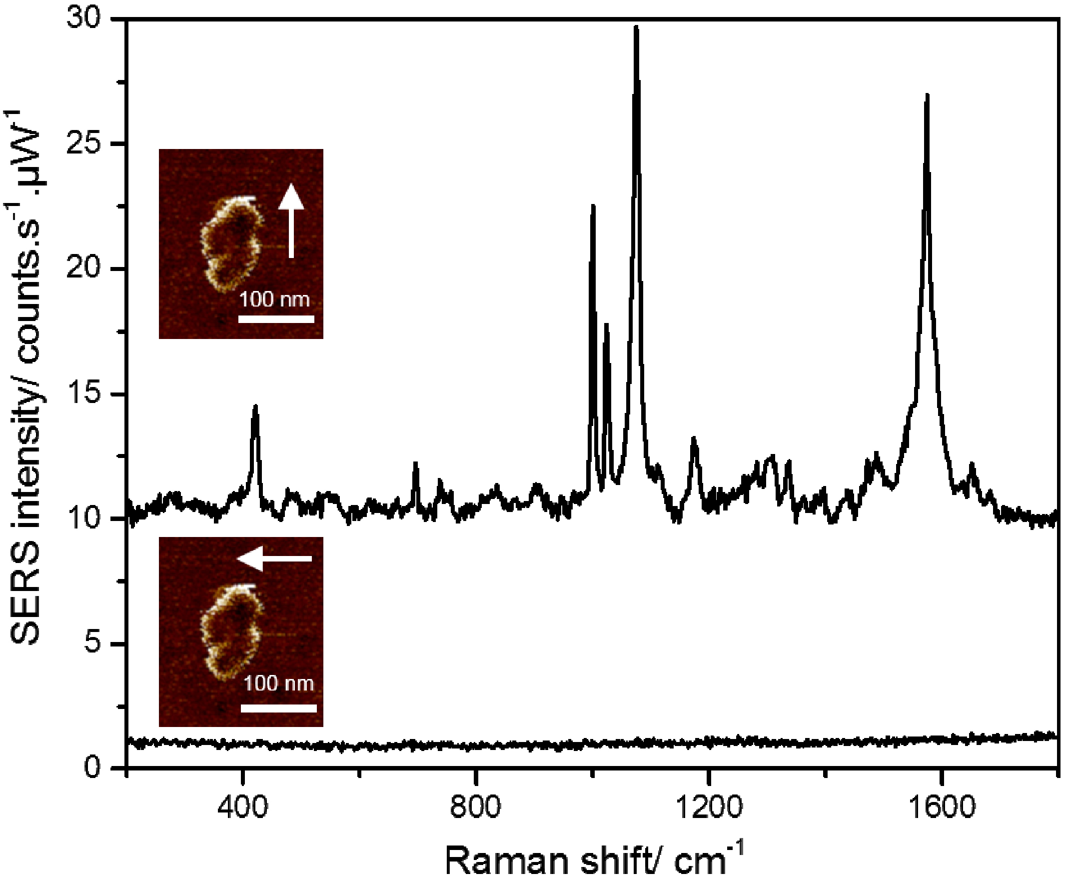

Fig.S4 SERS spectra associated with the gold dimer GD12 under 632.8 nm irradiation with horizontal (bottom spectrum) and vertical (top spectrum) light polarization. Insets show tapping-mode phase images of GD12 and indicate the direction of the incident electric field. The polarization dependence of several other GDs has been measured and the SERS signal was always much weaker for the transverse polarization than for the longitudinal one, although the transverse signal sometimes showed detectable SERS peaks.

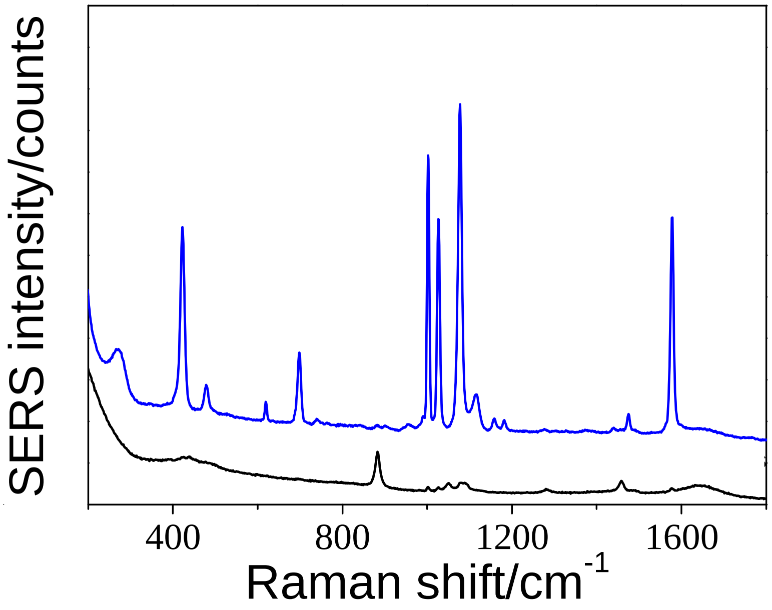

Fig.S5 Comparison of SERS spectra of a gold dimer (top) and of an individual gold nanoparticle (bottom). SERS spectra were obtained by exciting under red (785 nm) irradiation BT-coated 40 nm individual nanoparticles and corresponding nanodimers deposited onto a glass slide. The concentration of the BT solution into which particles were immersed to achieve the functionalization was 10^{-7} M.

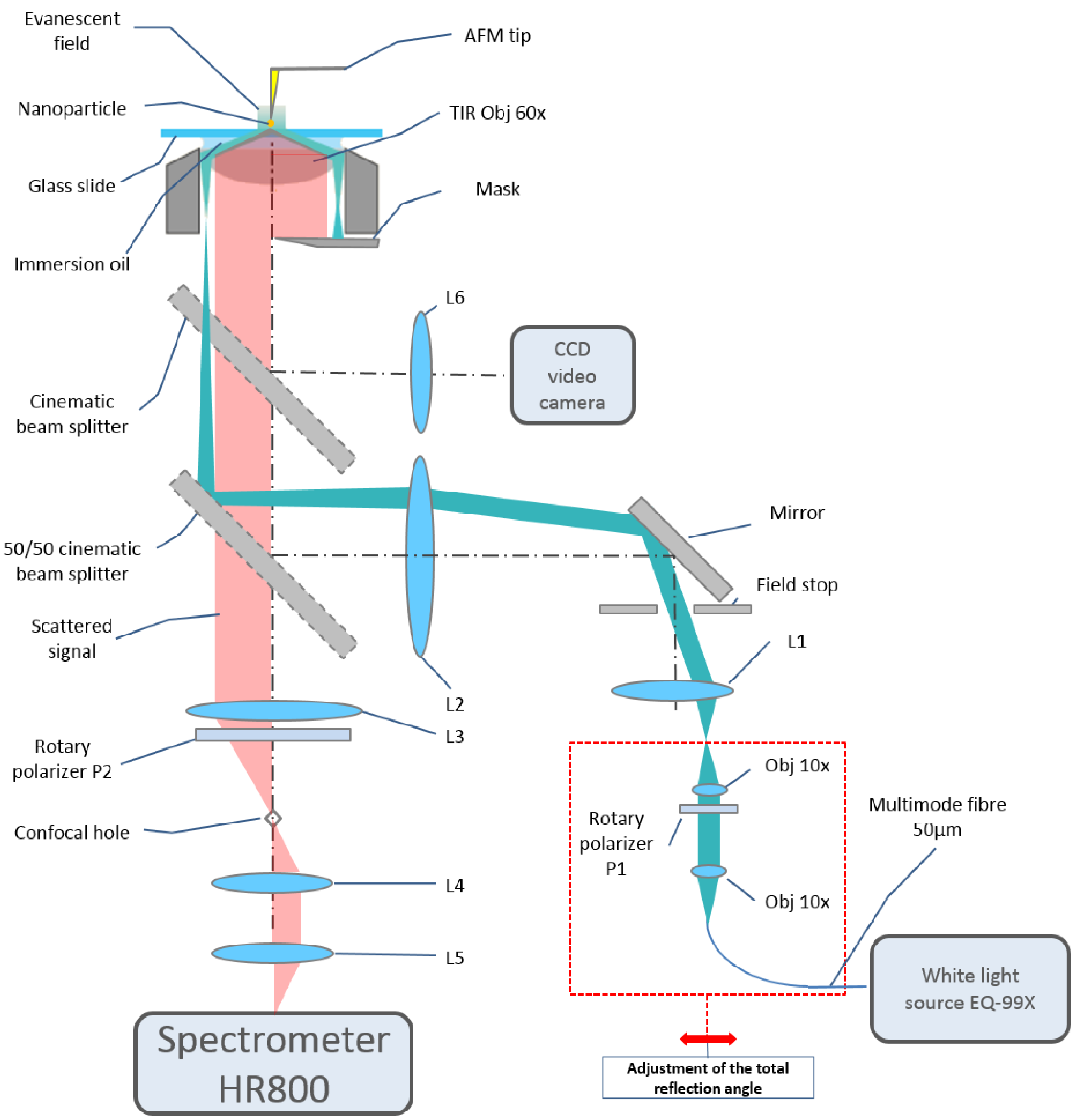

Fig.S6 Schematic view of the instrument combining AFM, Raman spectroscopy and dark-field scattering microscopy. This upgraded version includes two rotary polarizers P1 and P2 to adjust the polarization of the incoming and outgoing white light, and both the 200mm achromatic lens L6 and the CCD camera IDS UI-2250-C have been displaced in order to improve the video image quality.