Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Mediating Ordered Assembly of Gold Nanorods by Controlling Droplet Evaporation Modes for Surface Enhanced Raman Scattering

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Synthesis of gold nanorod stabilized by CTAB bilayer

Gold nanorods (GNRs) were synthesized by the seed mediated growth method reported by Murphy and coworkers with minor modification. In detail, the seed solution was prepared by addition of 250 μL of 10 mM solution of $HAuCl_4 \cdot 3H_2O$ to the 7.5 mL of 100 mM CTAB solution in a glass vial. The mixture was gently mixed by shaking. The color of mixture was bright brown-yellow. Then, 600 μL of 10 mM ice-cooled $NaBH_4$ solution was added to the mixture at once and the mixture was gently mixed by shaking for 2 min. After addition, the color of mixture changed to pale brown. The prepared seed solution was kept under room temperature for minimum 6 hours before use. The growing solution was prepared by addition of 2 mL of 10 mM solution of $HAuCl_4 \cdot 3H_2O$ and 300 μL of 10 mM $AgNO_3$ to 47.5 mL of 100 mM CTAB solution. The mixture was mixed by gentle shaking. The color of mixture was bright brown-yellow and 320 μL of 100 mM ascorbic acid solution was then added to the mixture. After addition, the color of mixture disappeared. Finally, the 100 μL of the seed solution was added to the prepared growing solution and the mixture was gently mixed by shaking for 10 sec and kept under room temperature overnight without disturbance. GNRs in the reaction mixture were purified by centrifugation at 12857 rcf and re-suspension into distilled water 2 times. The synthesized gold nanorods showed an average diameter, length and aspect ratio of 25 ± 2 nm, 50 ± 2 nm and 2.1 ± 0.2.

Preparation of differently functionalized Si substrates

Si substrates were immersed in piranha solution at 120 ^oC for 10 min, washed with water and ethanol and dired under a stream of nitrogen. This substrate was used as a piranha treated Si substrate. Then, other piranha treated Si substrates were respectivley used for subsequnt surface functionalization with 3-aminopropyltriethoxysilane (3-APTES) and octadecanetrimethoxysilane (ODTMS) by immsering into 10 mM toluene solutions of 3-APTES and ODTMS for 30 min at room temperature. Then, the Si substrates were washed with toluene, water and ethanol and dried under a stream of nitrogen.

Preparation of ordered assemblies of gold nanorods on differently functionalized Si substrates

A 10 μL of the colloidal suspension of GNRs was respectively applied on the differently functionalized Si substrates and evaporated at approximately 30% humidity and room temperature. After evaporation, the ordered assemblies of GNRs along the edges or whole area of droplets were observed on the substrates.

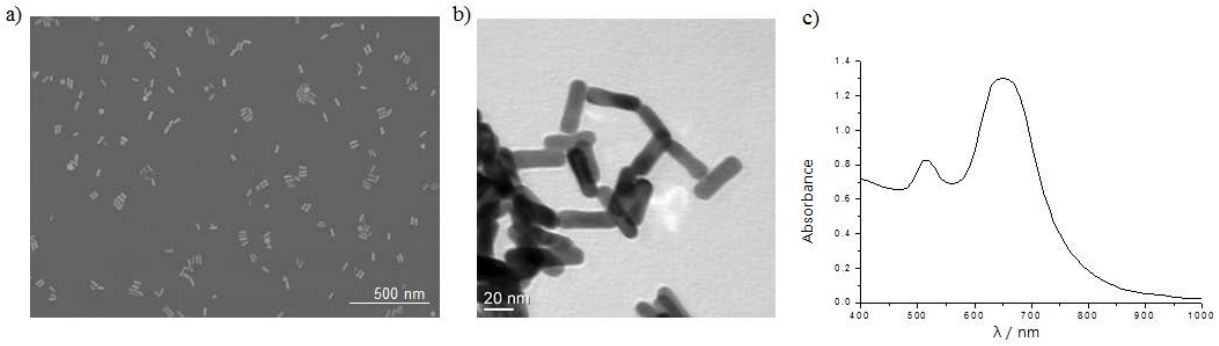

Figure S1. a) SEM and TEM (b) image. c) UV-vis absorption spectrum of the synthesized GNRs with an average diameter, length, aspect ratio of 25 ± 2 nm, 50 ± 2 nm and 2.1 ± 0.2 and two specific surface plasmon bands at around 520 and 650 nm corresponding to short and long axis of GNRs.

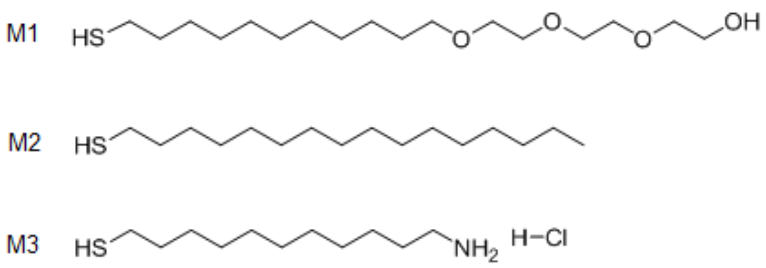

Figure S2. Chemical structures of thiol derivatives presenting tri(ethylene glycol) (EG_3, M1), methyl (HDT, M2) and primary amine (NH_2, M3) terminal groups used to form self-assembled monolayers (SAMs) on gold substrates.

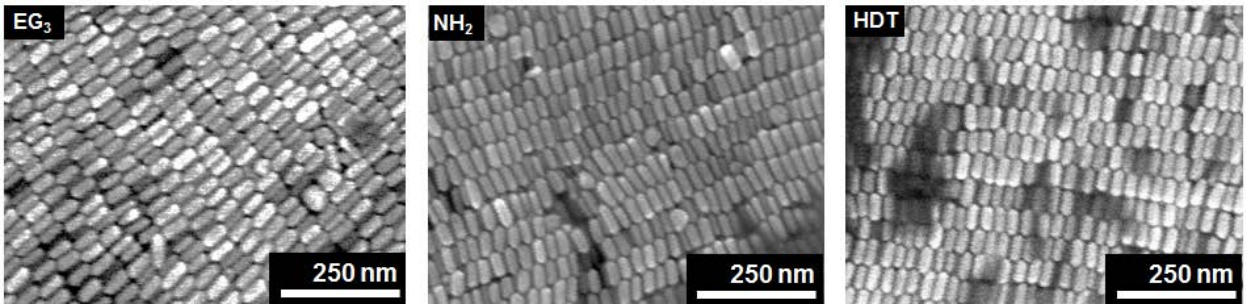

Figure S3. SEM images of ordered assemblies of gold nanorods on self-assembled monolayers (SAMs) presenting different functional groups such as EG_3, NH_2 and HDT.

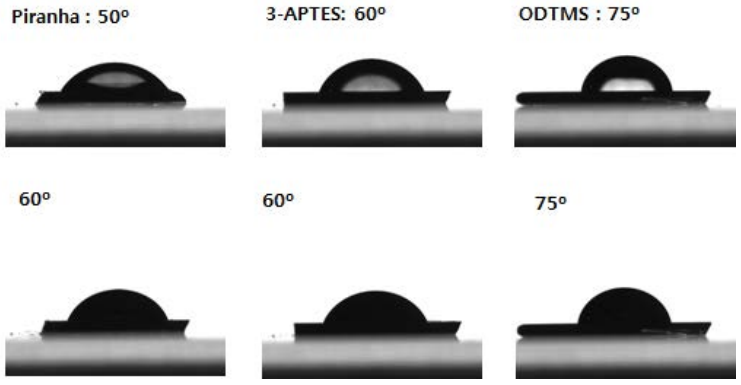

Figure S4. The contact angles of water (first row) and gold nanorod suspension (second row) on piranha, 3-APTES and ODTMS treated Si substrates. The difference of contact angle on the differently treated Si substrates was not high compared to differently functionalized gold substrates (Figure S6) to make the evaporation mode on their surfaces distinct. This difference could be attributed to different surface engineering efficiency of silane compounds for functionalization of Si substrates compared to that of thiols for functionalization of gold substrates.

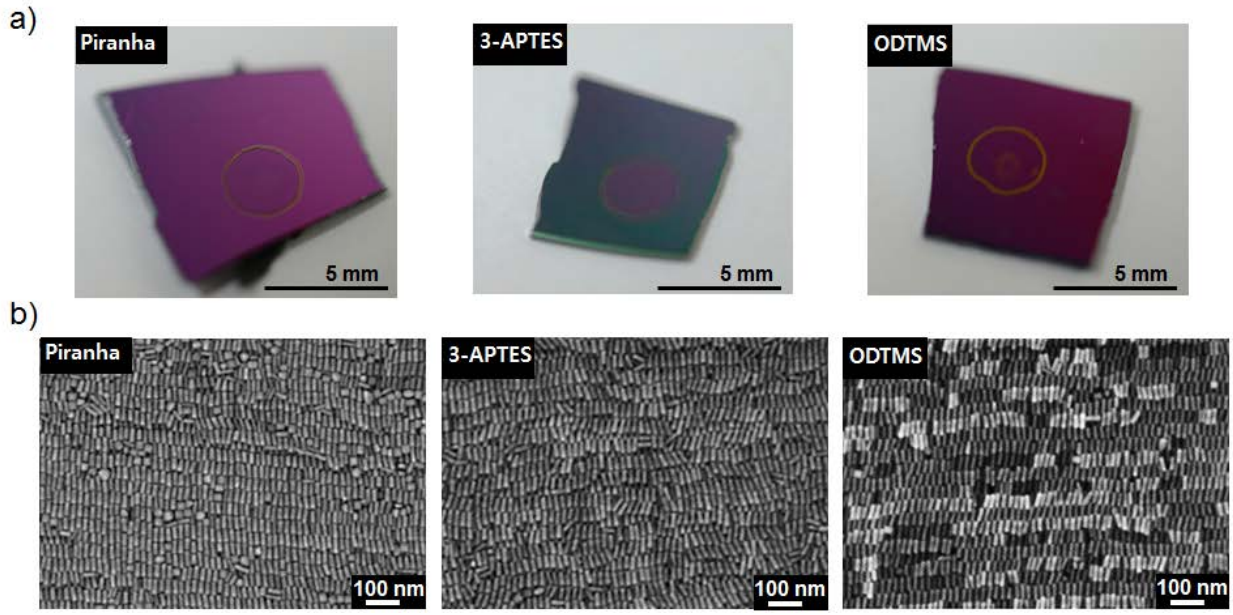

Figure S5. SEM images of ordered assemblies of GNRs formed on piranha, 3-APTES and ODTMS treated Si substrates. Generally, the inorganic crystals are supposed to assemble into ordered structures with the equally shaped crystals. When GNRs were assembled by droplet evaporation method in the presence of gold polyhedral, GNRs and gold polyhedral were assembled separately to form segregated assemblies each other.[1] In Figure S5b, the ordered assembly of GNRs on piranha was composed of GNRs and spherical gold nanoparticles (Au NPs), a side product of GNRs. Considering the tendency of gold nanocrystals to assemble with the equally shaped one, the droplet evaporation on the piranha treated substrate (CA: 50 ^{o}) might not provide enough evaporation time (110 min) to separately assemble GNRs and Au NPs each other and thus there were many Au NPs incorporated into ordered assemblies of GNRs. This tendency was weakened on 3-APTES (CA: 60) and ODTMS (CA: 75) treated Si substrate because of their relatively high contact angles of colloidal droplets of GNRs which make their evaporation mode close to the constant contact angle mode. Therefore, the evaporation of colloidal droplet of GNRs on 3-APTES and ODTMS treated Si substrates took 120 min and 150 min, respectively, and lead to assembly of GNRs without Au NPs based on their shape preference. As a result, there were a few Au NPs in ordered assemblies of GNRs formed on 3-APTES and ODTMS treated Si substrates compared to the piranha treated Si substrate. There was also slight difference in the degree of order between assemblies formed on 3-APTES and ODTMS treated Si substrates. Although most of GNRs in their assembled structures formed on 3-APTES treated Si substrates were aligned with the same direction, there was a small portion of GNRs aligned with different direction. On the other hand, the ordered assemblies of GNRs on ODTMS showed almost equal alignment like smectic phase liquid crystals. The results clearly showed that the degree of order in assembled GNRs increased in order of piranha, 3-APTES and ODTMS and this tendency was in agreement with assembled GNRs on SAMs treated gold substrates presenting different functional groups such as EG_3, NH_2 and CH_3.

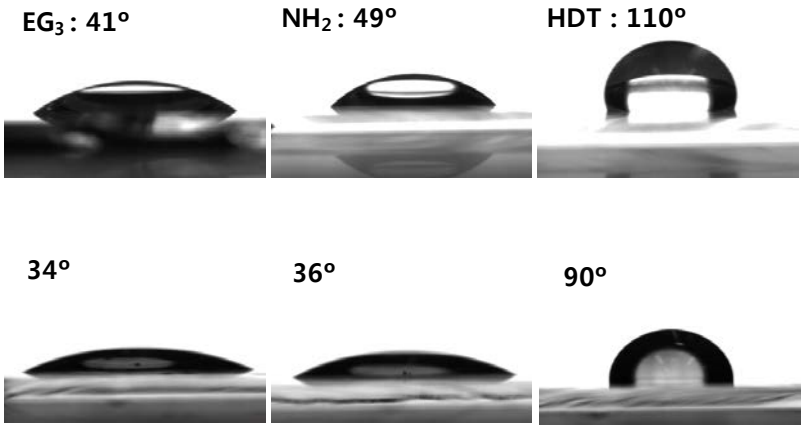

Figure S6. The contact angles of water (first row) and gold nanorod suspension (second row) on SAMs presenting different functional groups such as EG_3, NH_2 and HDT.

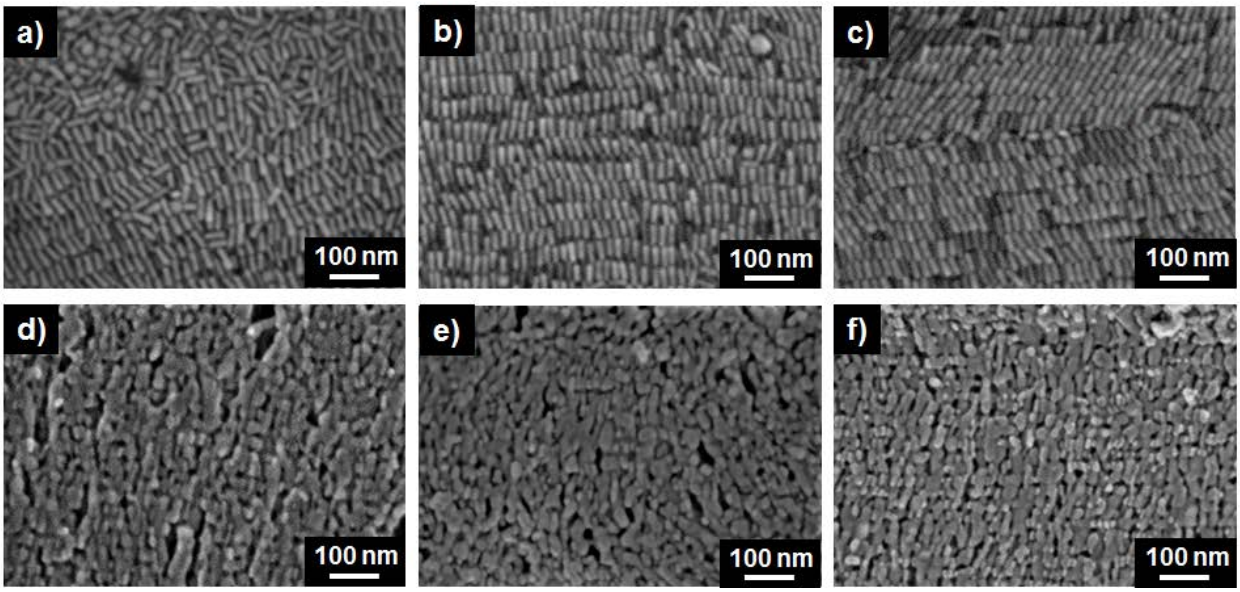

Figure S7. SEM images of ordered assemblies of GNRs on EG_3 (a), NH_2 (b) and HDT (c). SEM images of ordered assemblies of GNRs on EG_3 (d), NH_2 (e) and HDT (f) after 1 min piranha treatment.

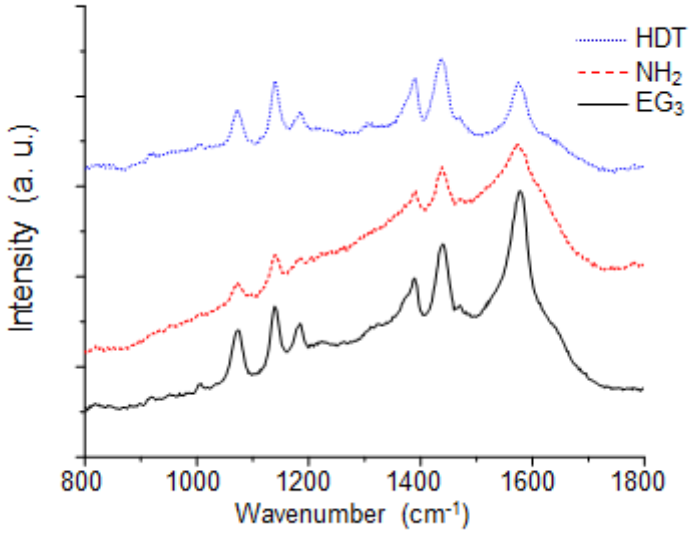

Figure S8. SERS spectra of 4-ATP from ordered assemblies of GNRs formed on SAMs presenting EG_3 (a), NH_2 (b) and HDT (c) without piranha treatment.

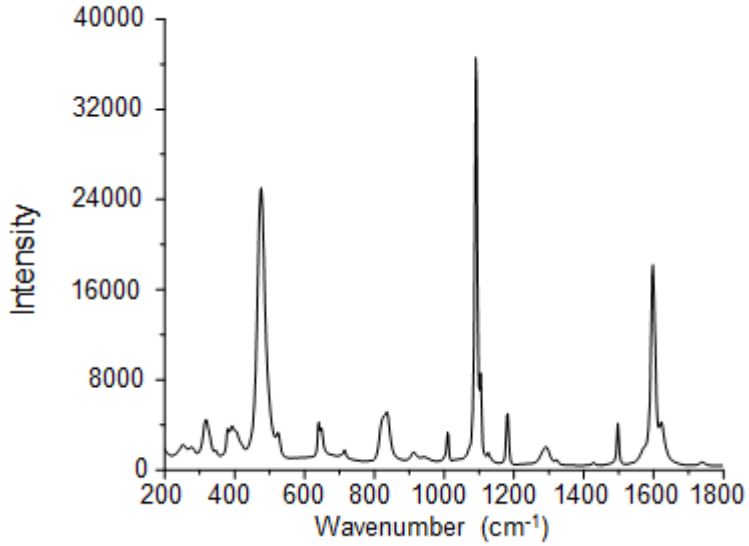

Figure S9. Raman spectrum of 4-ATP powder.

Terminal functional groups of SAMs	EF
EG_3	$1.1X10^3$
NH_2	$1.7X10^3$
HDT	$1.8X10^3$

Figure S10. Enhancement factor (EF) of ordered assemblies of GNRs on SAMs presenting EG_3, NH_2 and HDT. The N_{bulk} (8.9×10^9) was calculated by considering the laser spot size (1 μm), the penetration depth (2 μm), the molecular weight (125.19 g/mol) and the density of 4-ATP (1.18 g/cm^3). To simply estimate $N_{surface}$ on the ordered assemblies of GNRs, 1 cm^2 sized gold substrates were employed to fabricate ordered assemblies of GNRs and then 1 μL of 1 mM ethanolic solution 4-ATP was applied to each ordered assembly. Since ethanolic solution was well spread out and dried on the overall surface of substrates, $N_{surface}$ could be simply calculated as 1.9×10^6 by considering the number of 4-ATP distributed in the laser spot.

Reference

1. T. Ming, X. Kou, H. Chen, T. Wang, H. L. Tam, K. W. Cheah, J. Y. Chen, J. Wang, *Angew. Chem. Int. Ed.* 2008, **47**, 9685.