Graphene-based Plasmonic Composite Nanostructures for Surface Enhanced Raman Scattering-based Biosensing

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Surface Enhanced Raman Scattering (SERS) has been of growing interest to engineer highly sensitive biosensors based on optical detection. Especially, clustered metallic nanoparticles as SERS nanoprobes provide high sensitivity because of increased hot spot junctions. Although extensive research has been undertaken to develop highly sensitive SERS nanoprobes, there are some issues to be solved for the achievement of signal reproducibility and colloidal stability. In this study, we report a series of plasmonic composite nanostructures composed of two dimensional graphene-polymer hybrids and metallic nanoparticles for SERS-based biosensing applications. We hypothesized that different surface modifications of nanoscale graphene with various polymer architectures could be useful to have plasmonic organic-inorganic composite nanostructures as advanced SERS nanoprobes for biosensing. Nanoscale graphene (NG) with poly(ethylene glycol) conjugates induced metal nanoparticle (MNP) clustering and an effect of concentration of Raman reporter, graphene, graphene size on SERS intensity was studied with excellent control on clustered nanostructures. Furthermore, graphene with stimuli-responsive polymer brushes controlled the loading density and clustering degree of MNPs on the graphene, resulting in stimuli-triggered enhancement of SERS signal. As a proof of concept that graphene-based plasmonic composite nanostructures would be usefulness as SERS nanoprobes, we showed the formation of sandwich-type immunocomplexes, which were composed of antibody-conjugated SERS nanoprobes and magnetic beads (MBs) as magnetic field-based separation agent in the presence of biological moieties. There was a linear correlation between Raman intensity and antigen concentration with minimal batch to batch variability. In conclusion, graphene-based plasmonic composite nanostructures opens a new avenue as a new class of SERS nanoprobes for advanced biosensing and bioimaging applications.

References

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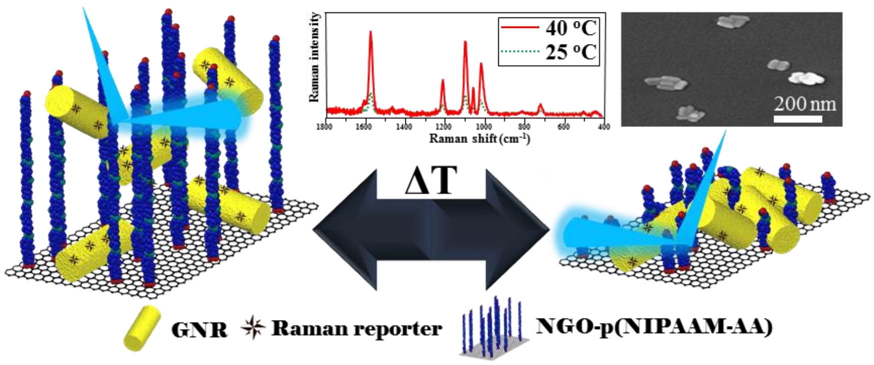
Figure



Cartoon for the preparation of stimuli-responsive graphene-based plasmonic composite nanostructures composed of gold nanorods (GNRs) and thermoresponsive poly(N-isopropylacrylamide-co-acrylic acid), poly(NIPAAM-co-AAc) brushes grown on nanoscale graphene (NG) via surface initiated atom-transfer radical polymerization. When Raman reporters were introduced to the GNRs, temperature-triggered collapse of p(NIPAAM-co-AAc) chains above the lower critical solution temperature (LCST) generated SERS signal higher than that observed below LCST, potentially because of decrease in distance between GNRs located on p(NIPAAM-co-AAc) brushes of the graphene.