Electronic Supplementary Information

Shape-diversified silver nanostructures uniformly covered on aluminium micro-powders as effective SERS substrates

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Formation mechanism of Ag nanostructures on Al powders

Following the discussion of sample preparation in the manuscript, the involving electrochemical reactions can be represented as below,[S1]

Cathodic reaction:
$Ag^+ + e^- \rightarrow Ag$ $E^0 = 0.79$ V (SHE)
Anodic reaction:
$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$ $E^0 = -1.67$ V (SHE)
$Al_2O_3 + 6H^+ + 12F^- \rightarrow 2AlF_6^{3-} + 3H_2O$

As indicated in Fig. S1a, the oxidation reaction of metallic Al surfaces is initiated by hole injection of Ag^+ ions in electrolyte solutions, leading to the redox process of Ag^+ ions and followed by nucleation of Ag seeds on Al powders. Meanwhile, the oxidized Al is removed by HF etchants and thus leaves the etching pits with oxide-removed Al surfaces exposed on powders for the succeeding galvanic reaction further, as evidenced in Fig. S1b. The continued growth of Ag is then sustained by the electric currents between Al surfaces and Ag^+ ions that further support the self-organization of 3D Ag nanostructures. Fig. 1c shows the TEM investigation of a representative Ag-coated Al powder, which was formed after 5-min galvanic displacement with the presence of $AgNO_3$ and HF reactants in EG medium.

In addition, the explicit dependence of solvents on affecting the reaction kinetics via galvanic displacement can be found. Representative comparisons of products fabricated through EG- and water-based process are sown in Fig. S2, where the faster growth of Ag structures but with less uniformity on Al powders are clearly demonstrated in water-based galvanic reaction. Fig. S3 further presents the measured contact angle in both a DI water drop [Fig. S3a] and an EG drop [Fig. S3b] on Al powders, respectively. Finally, the diffusivity of Ag^+ in aqueous solution is estimated by the following equation,[S2]
$D = AT/\eta P$
where D corresponds to the diffusion coefficient (cm^2S^{-1}); A is an empirical constant; η and P represent the solvent viscosity (Pa・s) and the viscosity exponent, respectively.

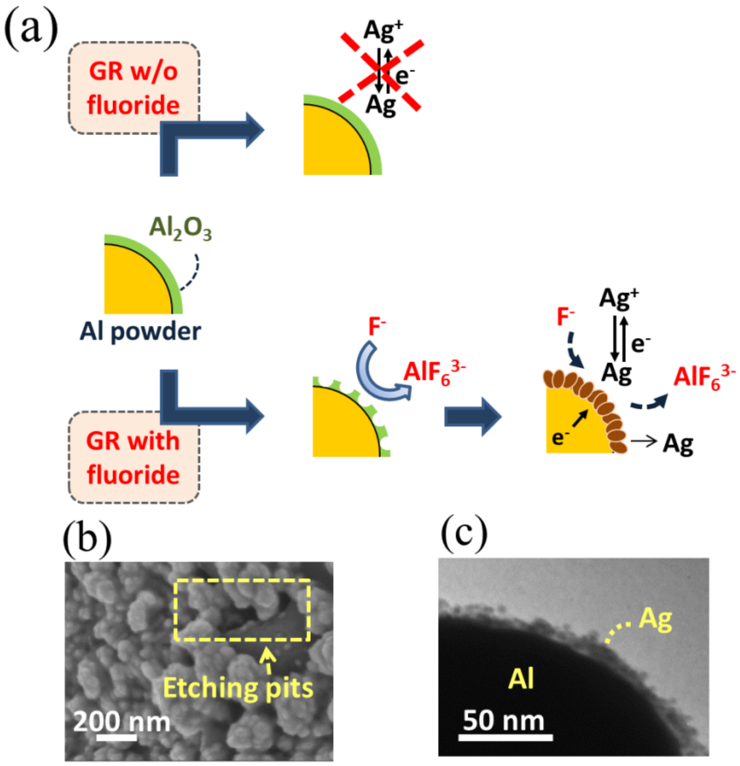

Fig. S1 (a) Schematic illustration of formation mechanism for Ag nucleation on Al powders. (b) SEM image of occurrence of etching pits on Al surfaces. (c) TEM image of an Al@Ag hierarchical powder. Notice that "GR" in Fig. S1a is referred as galvanic replacement

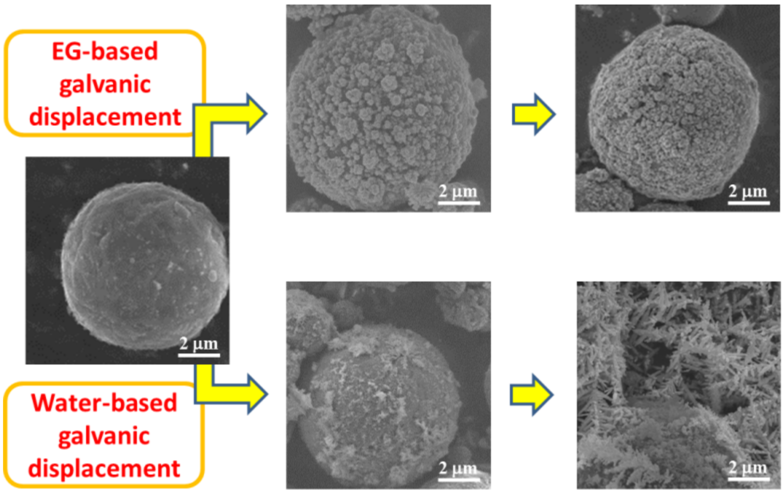

Fig. S2 SEM investigations of formed Ag nanostructures at different time intervals via galvanic displacement with EG as solvents (10 min and 15 min, figures above) and water as solvents (1 min and 5 min, figures below), respectively.

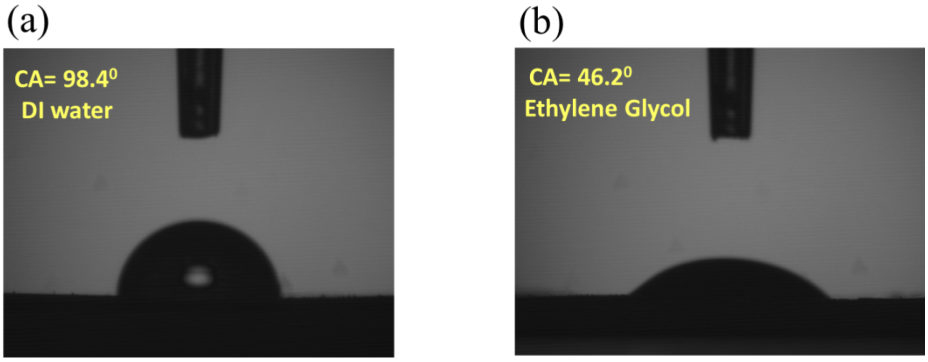

Fig. S3 Contact angle measurements of (a) a water drop and (b) an EG drop on the mono-layer Al powders attached on a tape.

References

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2 B. B. Hasinoff and S. B. Chishti, *Biochemistry*, 1983, **22**, 58.