Electronic Supplementary Information (ESI)

Digestive Ripening in the Formation of Monodisperse Silver Nanospheres

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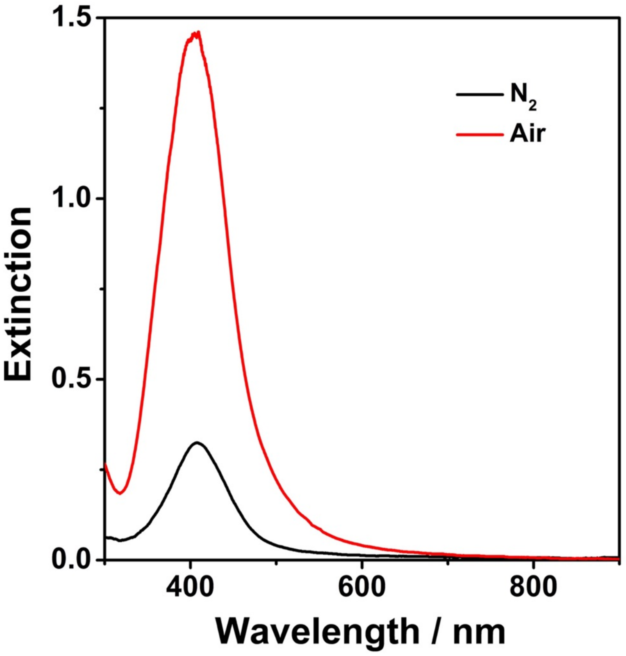

Figure S1. The oxidation of DEA into DEHA as a reducing agent. In this control experiment, the digestive ripening synthesis was conducted N_2 rather than the ambient air. The UV-vis spectrum suggests that the reduction of the Ag salt was significantly sluggish, due to the suppressed oxidation of DEA into DEHA. It confirms that DEHA formed by aerobic oxidation of DEA is the reducing agent for the synthesis of the polydisperse Ag nanoparticles. The Ag nanoparticles obtained from the experiment without air can be attributed to the reduction of $AgNO_3$ by DMF, which is a weak reducing agent.

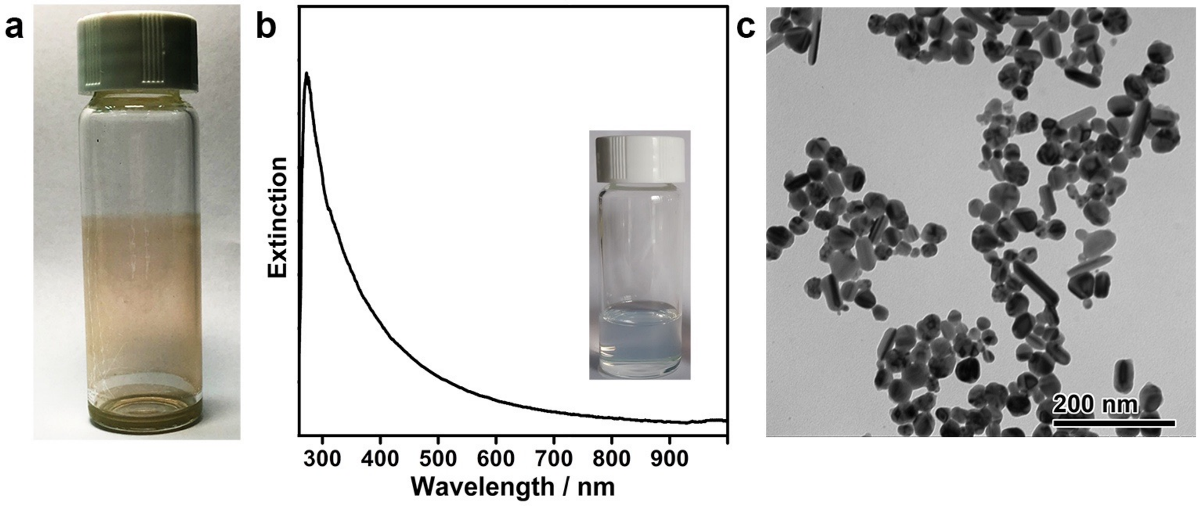

Figure S2. Role of PVP in the synthesis of the Ag nanospheres. (a) A photograph showing severe aggregation of the Ag colloid in the absence of PVP or any other surfactant. (b) UV-vis spectrum of the product obtained by using poly(acrylic acid) (PAA) in place of PVP in a typical digestive-ripening synthesis of the Ag nanospheres. No Ag nanospheres were obtained because PAA neutralized the DEA and hindered the formation of DEHA as a reducing agent. (c) TEM images of the product obtained by using cetyltrimethylammonium chloride (CTAC) in place of PVP in a typical synthesis. CTAC showed selectivity in the surface adsorption, which gave rise to non-spherical Ag nanocrystals (such as nanorods). It can be therefore concluded that PVP is an appropriate choice of surfactant, which ensures the colloidal property and the spherical shape of the Ag nanocrystals due to the homogeneous surface capping of PVP on the Ag surface.

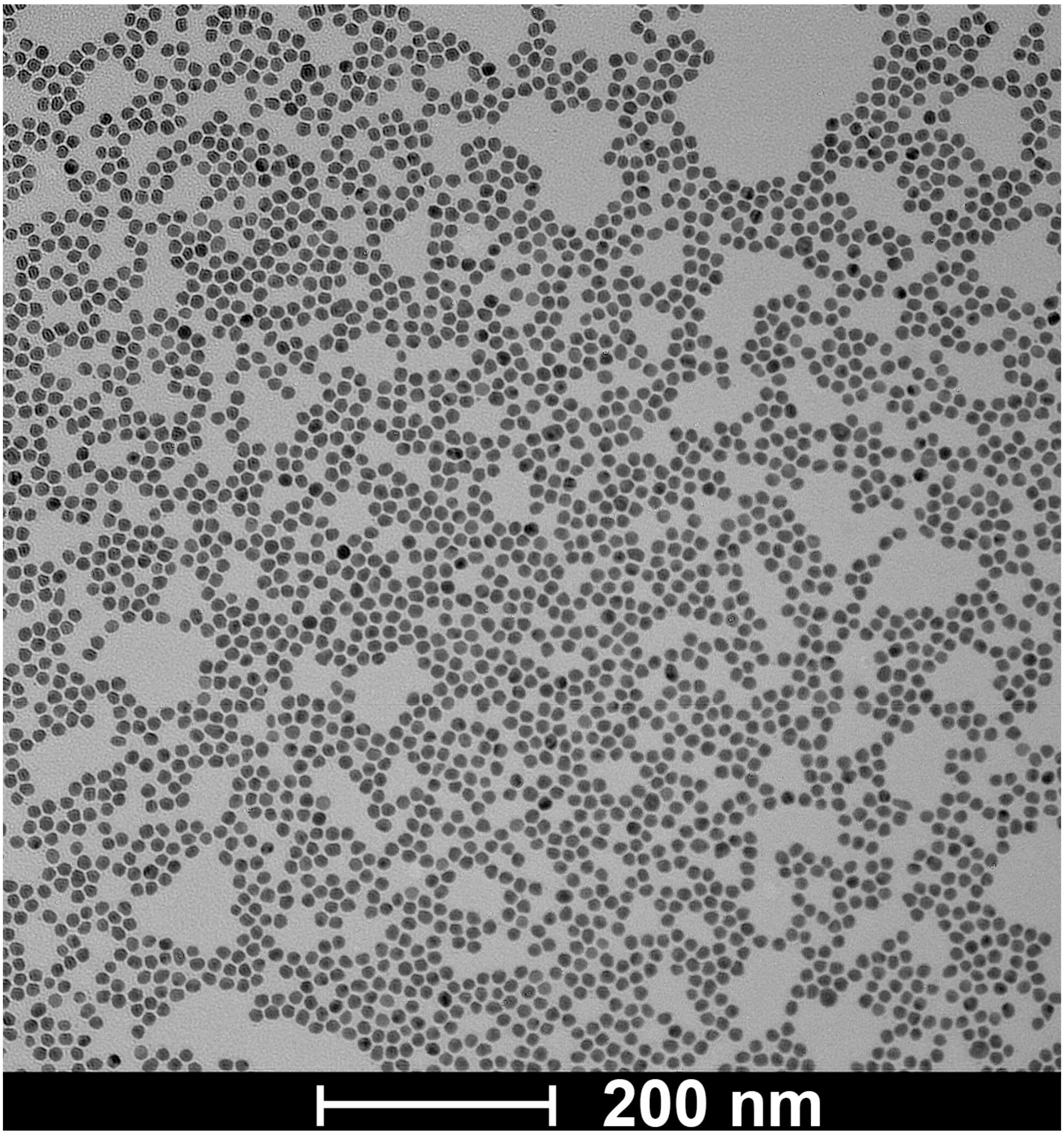

Figure S3. A low-magnification TEM image of the monodisperse colloidal Ag nanospheres obtained by the digestive ripening synthesis.

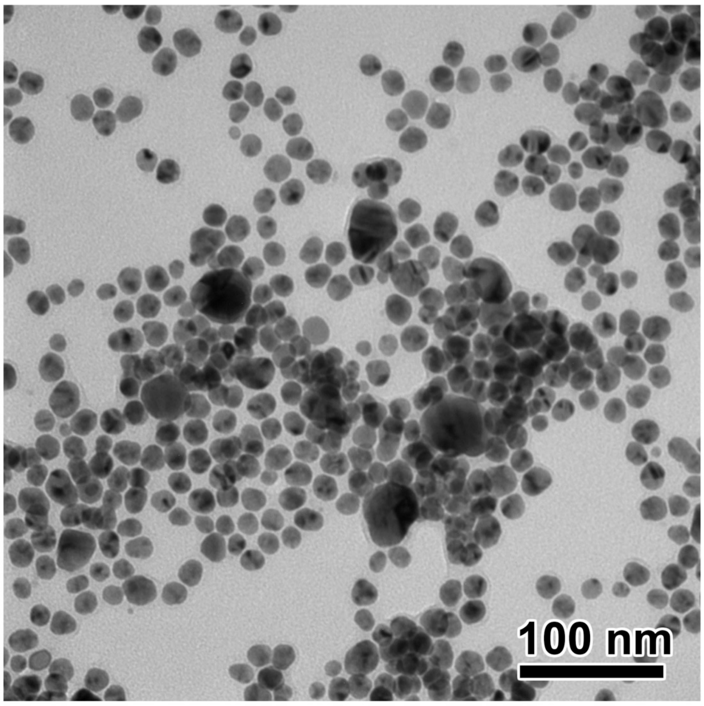

Figure S4. TEM image of the Ag nanoparticles obtained by the typical digestive ripening synthesis conducted in N_2. It is inferred that due to a lack of effective etching by Cl^-/O_2, only polydisperse Ag nanospheres can be obtained.

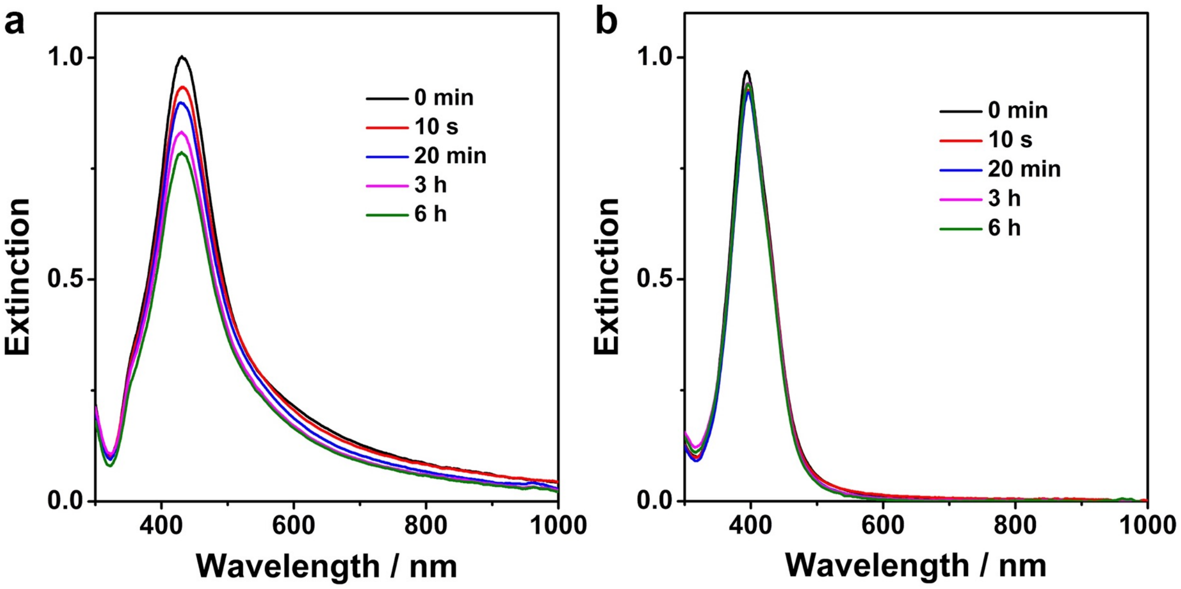

Figure S5. The strong adsorption of DEA on the Ag nanospheres. (a) PVP-capped Ag nanospheres without DEA. (b) PVP-capped Ag nanospheres with DEA. NaCl (0.1 M) was added into the two Ag sols. The UV-vis spectra of the two Ag sols were then recorded with time. The PVP-capped Ag nanospheres without DEA modification underwent a rapid decrease in the LSPR intensity in a period of a few minutes to hours, suggesting a rapid oxidative etching (a). In clear contrast, no spectral changes were observed in the DEA-stabilized Ag nanospheres (b). The enhanced stability of the Ag nanospheres confirms the strong adsorption of DEA on the Ag surface, which passivates the Ag surface and leads to enhanced resistance to the etching.

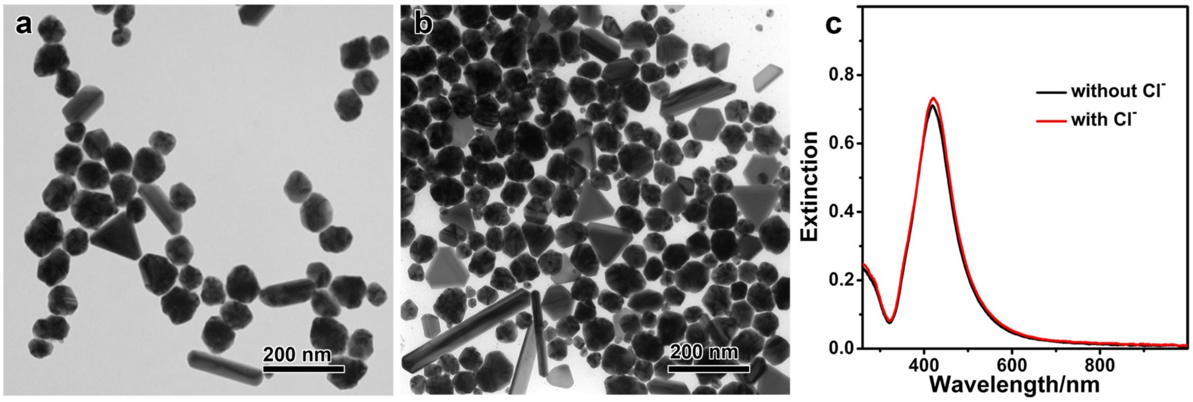

Figure S6. TEM images of the Ag nanoparticles obtained by replacing DMF with H_2O in a typical digestive ripening synthesis. (a) Before addition of Cl^-. (b) Obtained by sampling at 30 min after the addition of Cl^-). (c) The corresponding UV-vis spectra. The results confirm that H_2O is not an ideal solvent for the digestive ripening.

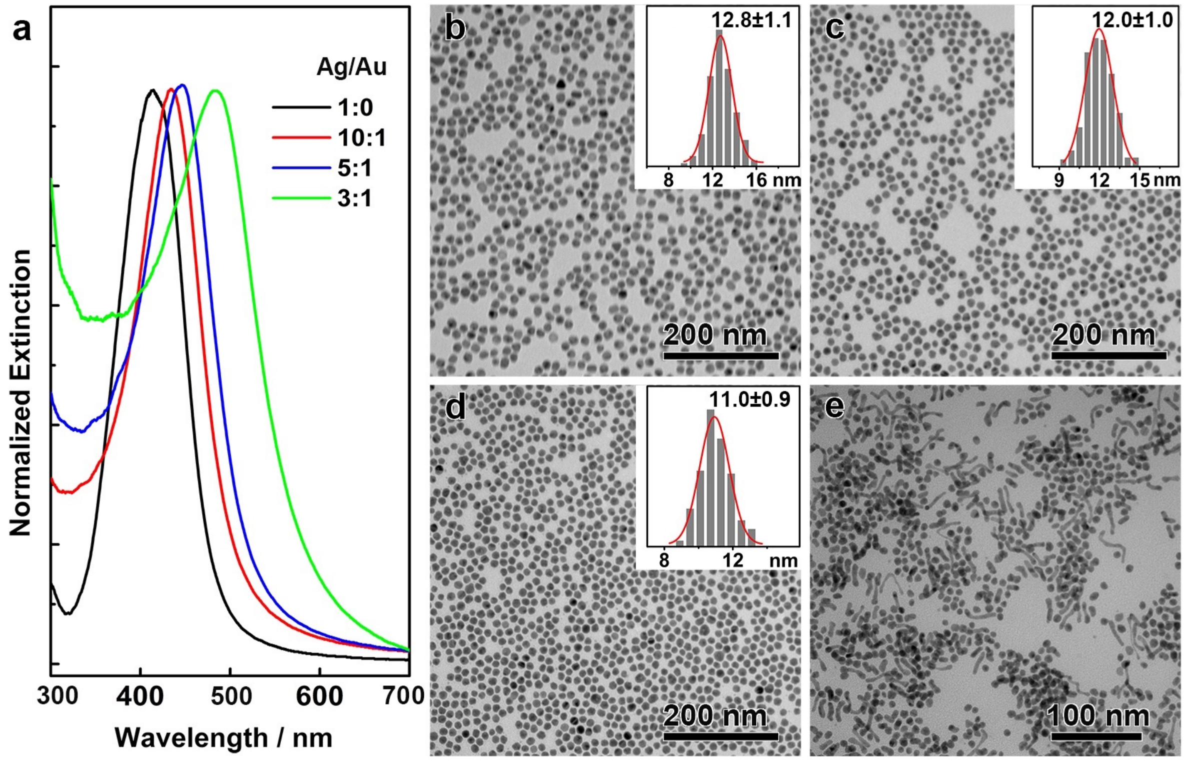

Figure S7. Synthesis of monodisperse Ag-Au alloy nanospheres by the digestive ripening mechanism. (a) Normalized UV-vis extinction spectra of the alloy nanospheres as a function of the Ag/Au ratio in the feeding precursor. (b–e) Corresponding TEM images of the Ag-Au alloy nanospheres. The Ag/Au ratios in the feeding precursors were 1:0, 10:1, 5:1, and 3:1, respectively. Inset: Size distributions of the Ag-Au alloy nanospheres. The mean sizes are expressed in terms of "mean ± standard deviation". Monodisperse Ag-Au alloy nanospheres were obtained at a high Ag/Au ratio (> 5:1). At a low Ag/Au ratio (3:1), short nanowires emerged, which is possibly due to the modification in the interaction between the metallic surface of the nanoparticles and the capping ligands.

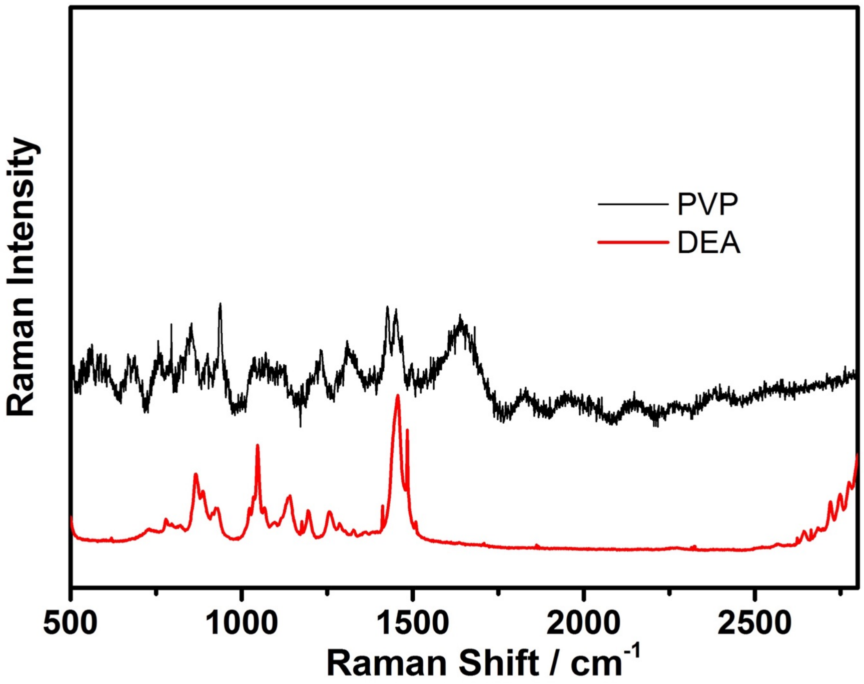

Figure S8. Raman spectra of PVP and DEA recorded from the substrate of Ag nanospheres. These peaks cannot be observed from the blue line of Figure 5c. It confirms that neither PVP nor DEA is present on the surface of the Ag nanospheres after drying on the silicon substrate.

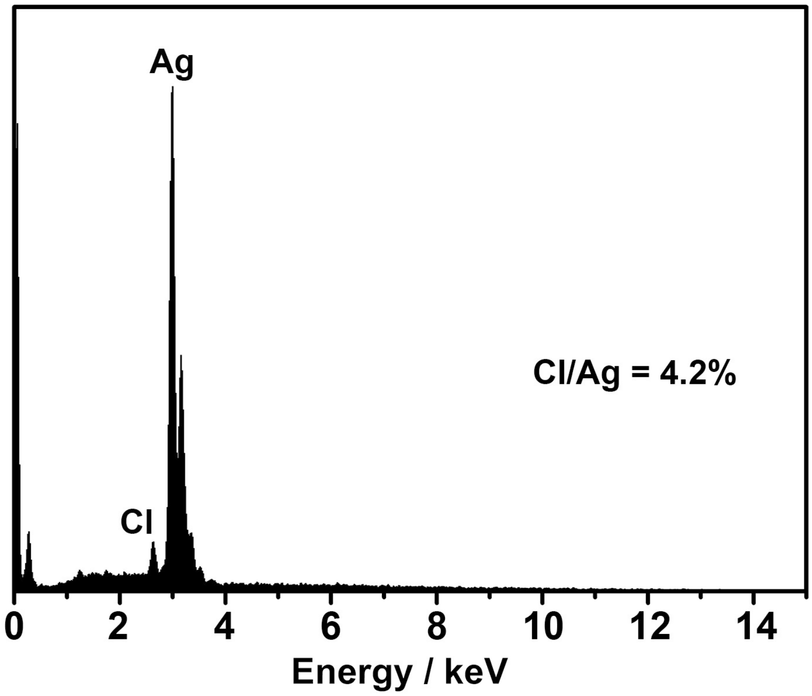

Figure S9. EDS spectrum of the monodisperse Ag nanospheres obtained by the digestive ripening, which suggests the presence of Cl^- on the Ag surface.