Supporting Information

"Ultrasmall Silver Nanopores Fabricated by Femtosecond Laser Pulses"
by F. Bian *et al.*

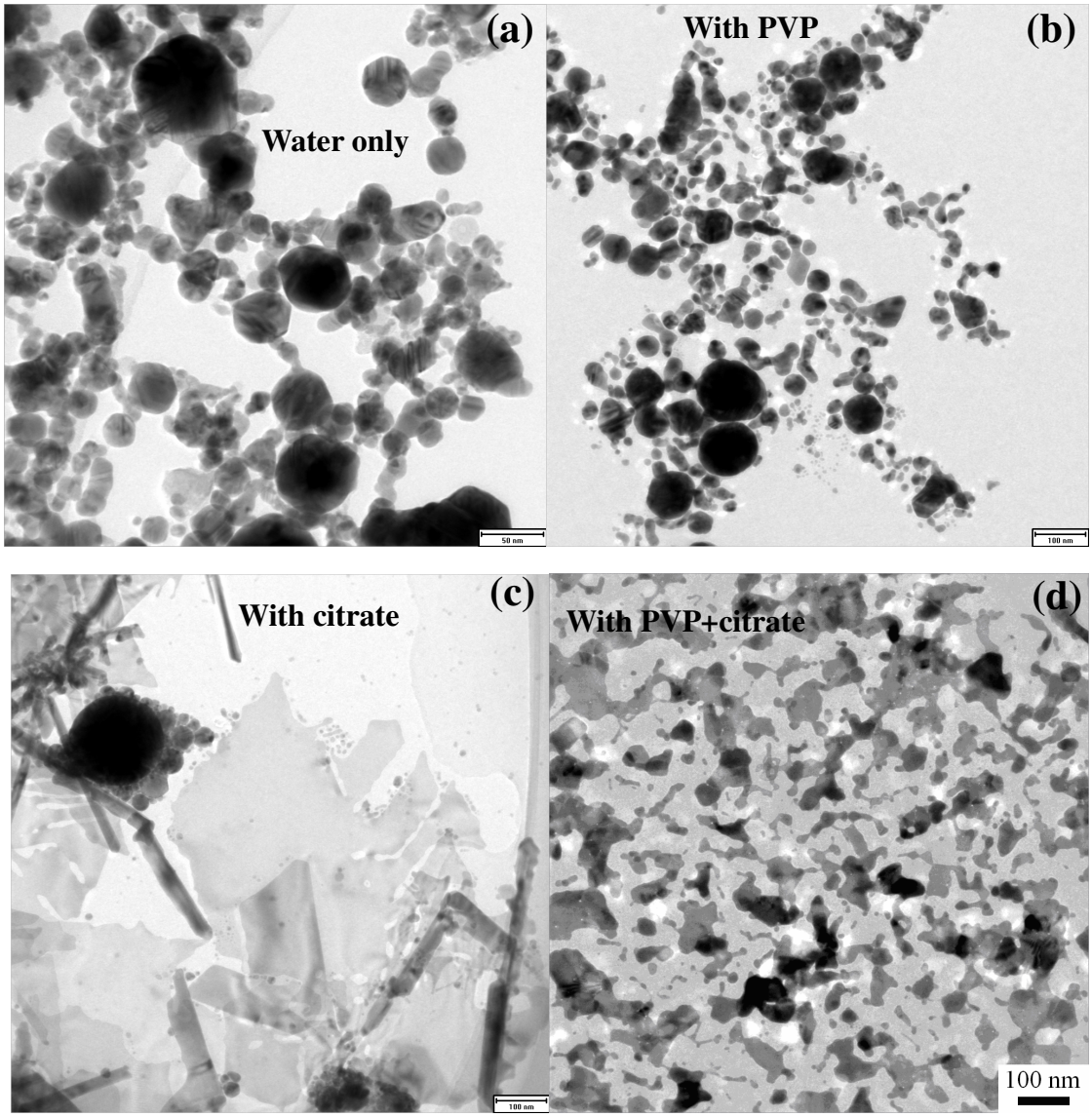

Figure S1. The effects of capping agent molecules in LAL. Here we show TEM images of Ag nanostructures fabricated in different aqueous solutions: (a) deionized water (Milli-Q, Millipore Co.) only; (b) solution with 0.1 mM polyvinylpyrrolidone (PVP, Aldrich); (c) solution with 0.3 mM sodium citrate ($Na_3C_6H_5O_7$, Alfa Aesar); (d) solution with both 0.1 mM PVP and 0.3 mM sodium citrate. Panel (d) is the same as that in Fig. 1, where small-area silver flakes (grey area) with dense 2-nm nanopores are observed. In panel (a) with pure water, nearly spherical nanoparticles are formed without the presence of any nanopores. From panel (a) to panel (b), where nanoparticles are more scattered, we find that the effect of PVP molecules is to prevent aggregation of metal particles. On the other hand, from panel (a) to (c), we identify that the effect of sodium citrate molecules alone is to allow the particles to grow into large areas of continuous thin film (again without nanopores).

Angles of 60° and 120° in the thin film are frequently observed, manifesting a re-crystallization process with the restriction that the growth direction is along Ag [111], under the influence of citrate molecules attached to Ag (111) surfaces. From above discussion, we conclude that *small-area* (created by PVP) *thin* films (assisted by citrates) are the requisites for the nanopore formation, confirming the nanopores are fabricated from abundant film enclaves, as shown in panel (d). Different ratios of PVP:citrate have been tested, and the highest yield of nanopores is observed with PVP:citrate = 1:3 as that in panel (d).

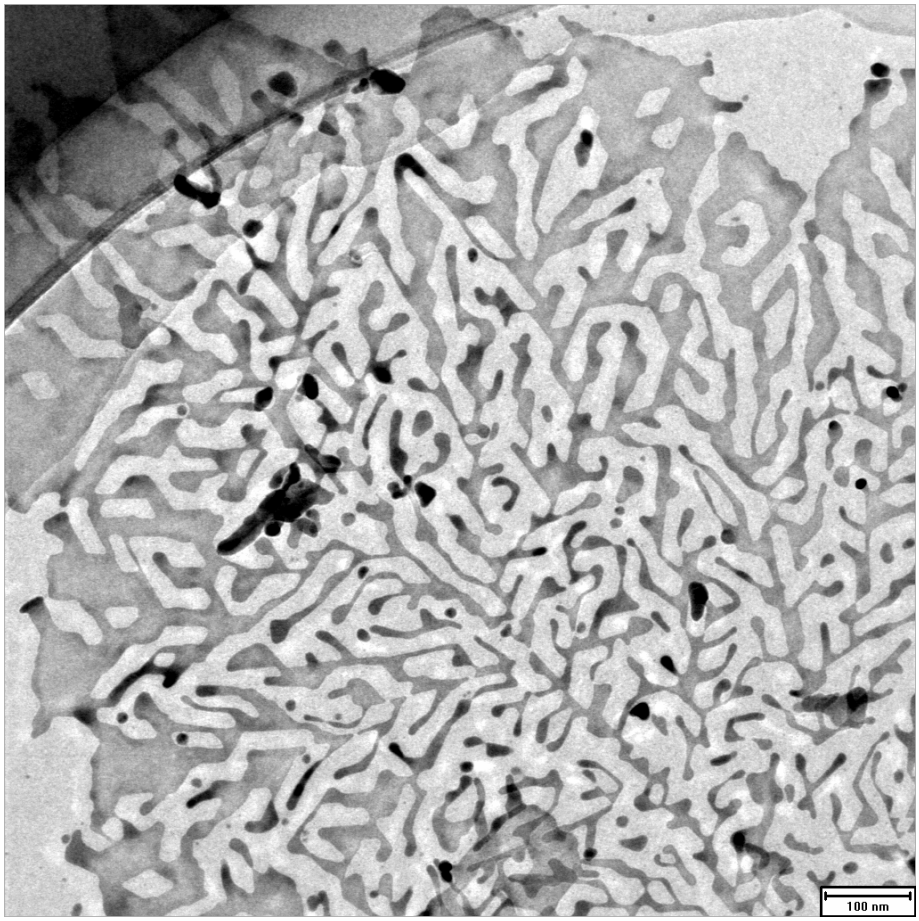

Figure S2. Nano-sized leaf as an example to show the diverse morphology that can be accessed by our modified LAL method. The nanostructure was obtained with nearly identical method described in the text except that the solution concentration is different.