Supplementary Information for:

Plasmonic Paper: A Porous and Flexible Substrate Enabling Nanoparticle-Based Combinatorial Chemistry

Abrin L. Schmucker¹, Sirimuvva Tadepalli², Keng-Ku Liu², Claretta J. Sullivan¹, Srikanth Singamaneni², and Rajesh R. Naik*¹

¹Materials & Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH 45433 and ²Institute of Materials Science and Engineering, Washington University in St. Louis, St. Louis, MO 63130.

Correspondence and requests for materials should be addressed to S.S. or R.R.N. (email: singamaneni@seas.wustl.edu or rajesh.naik@us.af.mil).

Additional Materials and Methods

Interrogating uptake on other papers.

A single 1.58 OD solution having λ_{max} at 642 nm was divided into aliquots for measuring the uptake efficiency for WhatmanTM (#1, 2, 3,54,5, 42, 50, 52, 54, 541, 3mm CHR), GETM(DE81, and 17CHR), and MilliporeTM (Amicon® 10kDa cutoff regenerated cellulose) papers. Disks generated using a simple office hole punch were incubated with 2mL of gold concave nanocubes. The extinction of the solution was measured before and after a 24 hour incubation period to determine particle uptake.

Paper blocking.

Paper substrates of Whatman[™] #1 and #4 were used to examine if blocking the paper substrates with well-known blocking agents like Poly-L-Lysine or bovine serum albumin resulted in lower uptake. Specifically, solutions of a 1%BSA, and .05% Tween® 20 (w/v) in PBS, and .002% (w/v) of poly-L-lysine (Aldrich #P4707) were prepared. Disks were incubated in blocking solution for 90 minutes, washed with water and dried before adding to solutions of gold concave nanocubes. The concentration was 1.68OD with λ_{max} at 611 nm. The extinction of the solutions was measured before and after a 24 hour incubation period with the blocked substrates.

Polystyrene functionalization.

Thiol terminated polystyrene (M.W. 56K, 30K) was added to 2 mL of THF to make a 5x10⁻⁴ M solution and stirred until the polymer dissolved. 1 mL of the polymer-THF mixture was quickly added to 1 mL of a 20 nM AuNR solution. The mixture was vortexed for 1 minute, and the remaining polystyrene was added, followed by another 2 minutes of vortexing. The solution turns from optically clear to a turbid mixture, and finally the polystyrene functionalized nanorods

(PS-AuNR) adhere to the sides of the vial. After the supernatant turns clear, it is decanted and the PS-AuNR are washed twice with ethanol, and once with hexane. Finally, the PS-AuNR are dried under vacuum at 200 mTorr to remove excess solvent. The PS-AuNR are then resuspended in toluene.

Supplementary Figures:

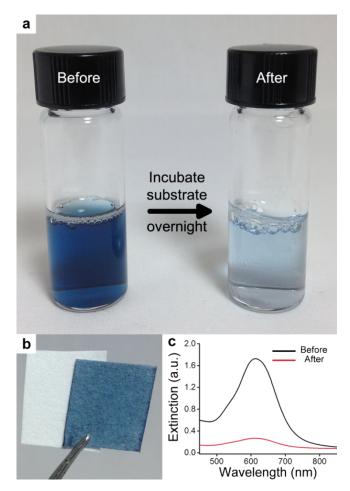


Figure S1. Creation of plasmonic paper. (**a**) Photographic image showing the efficiency of nanoparticle uptake by a ~1cm² swatch of WhatmanTM #1 filter paper following a 12h incubation period with gold concave nanocubes. (**b**) photographic image of ~1cm² swatches of #1 filter paper before and after exposure to the nanocube solution in (**a**). (**c**) UV-Vis extinction measurement of the nanoparticle solution before and after the incubation period, showing the substantial decrease in signal intensity.

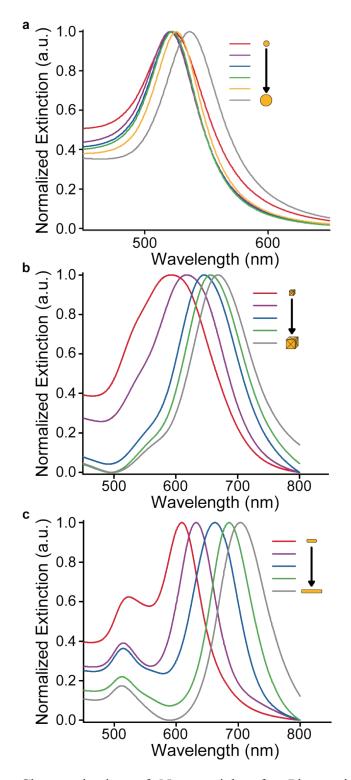


Figure S2. Solution Characterization of Nanoparticles for Plasmonic Paper. Normalized extinction spectrum of gold (a) spherical nanoparticles, (b) concave nanocubes, and (c) nanorods of increasing aspect ratio.

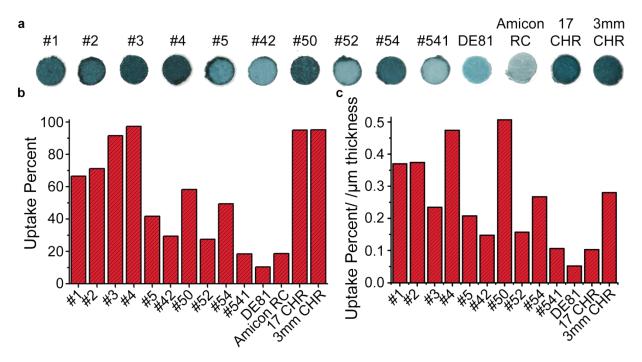


Figure S3. Nanoparticle Uptake on Different Papers. (a) Photographic image of a variety of uniform paper disks (~6mm) were produced by a standard office hole punch, illustrating that the adsorption effect is not confined to any particular brand of paper. (b) Ratio of extinction intensity before and after exposure to the various filter papers. (c) Percentage of nanoparticle uptake, normalized to paper thickness (where available) to interrogate relative adsorption efficiency.

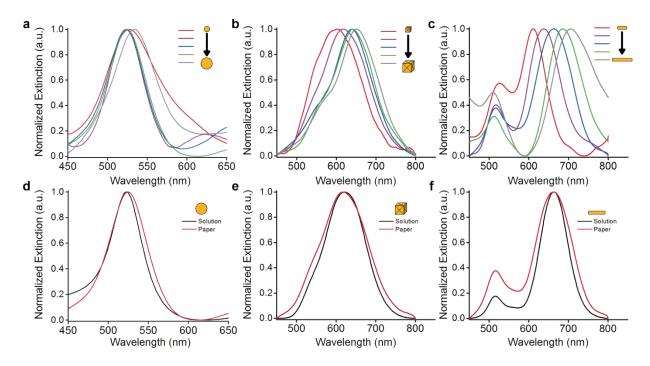


Figure S4 Characterization of plasmonic paper for other particles. Normalized extinction spectra of plasmonic paper incorporating spherical gold (**a**) spherical nanoparticles, (**b**) concave nanocubes and (**c**) nanorods. Normalized extinction spectra comparing the SPR peak position of gold (**d**) spherical nanoparticles, (**e**) concave nanocubes and (**f**) nanorods in solution to that when on hydrated paper.

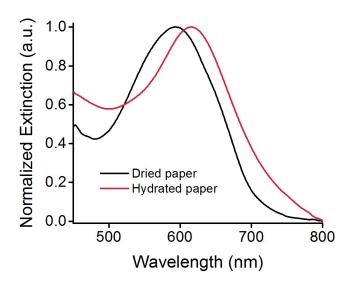


Figure S5. SPR Depends on Local Environment. Normalized extinction spectra of the SPR peak position of gold concave nanocubes as measured on dry paper and hydrated paper.

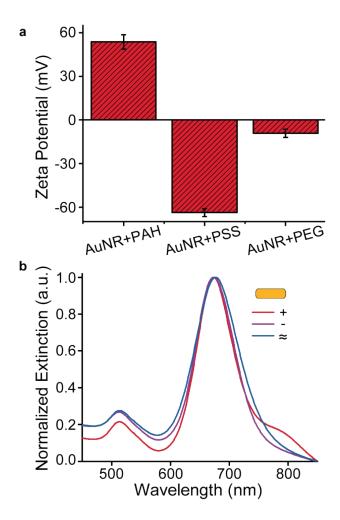


Figure S6. Nanorod Functionalization with different surface charges. (a) Zeta-potential measurement of three different samples of gold nanorods modified with ligands that are positively charged, negatively charged, and neutral. (b) Normalized extinction spectra of the different nanorod samples as measured in solution.

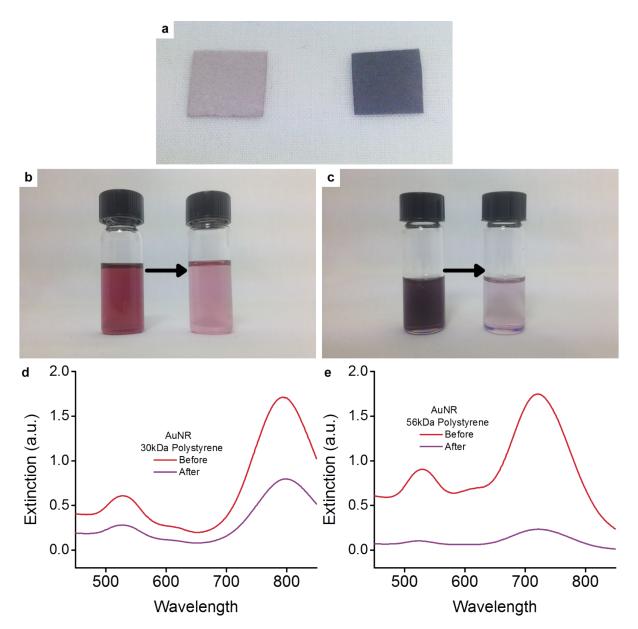


Figure S7. Uptake with Hydrophobic particles. (a) Photographic image illustrating nanorod uptake from hydrophobic toluene solutions using polystyrene-capped gold nanorods. Photographic images showing a visible reduction in the solution of (b) 30kDa polystyrene-capped and (c) 56kDa polystyrene-capped nanorods following overnight incubation with the paper substrate. Extinction spectra of nanorod solution containing (d) 30kDa polystyrene-capped and (e) 56kDa polystyrene-capped nanorods before and after incubation.

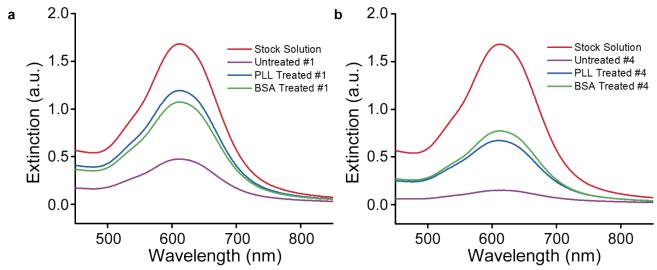


Figure S8. Reduction of uptake by surface blocking. Extinction spectra of gold concave nanocube solutions before and after incubation with WhatmanTM papers (**a**) # 1 and (**b**) # 4 that had been exposed to BSA or poly-L-lysine solutions.

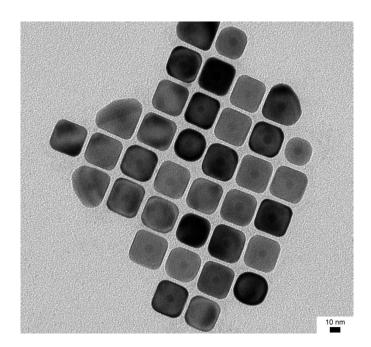


Figure S9. TEM of Au@Ag precursor nanoparticles. Transmission electron microscopy image of the Au@Ag nanocubes used for the etching and galvanic replacement reactions.