Electronic Supplementary Material (ESI) for Analyst.


# Supporting information for:

# Quantitative surface-enhanced Raman spectroscopy for kinetic analysis of aldol condensation using Ag-Au core-shell nanocube

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## Nanocube Characterization

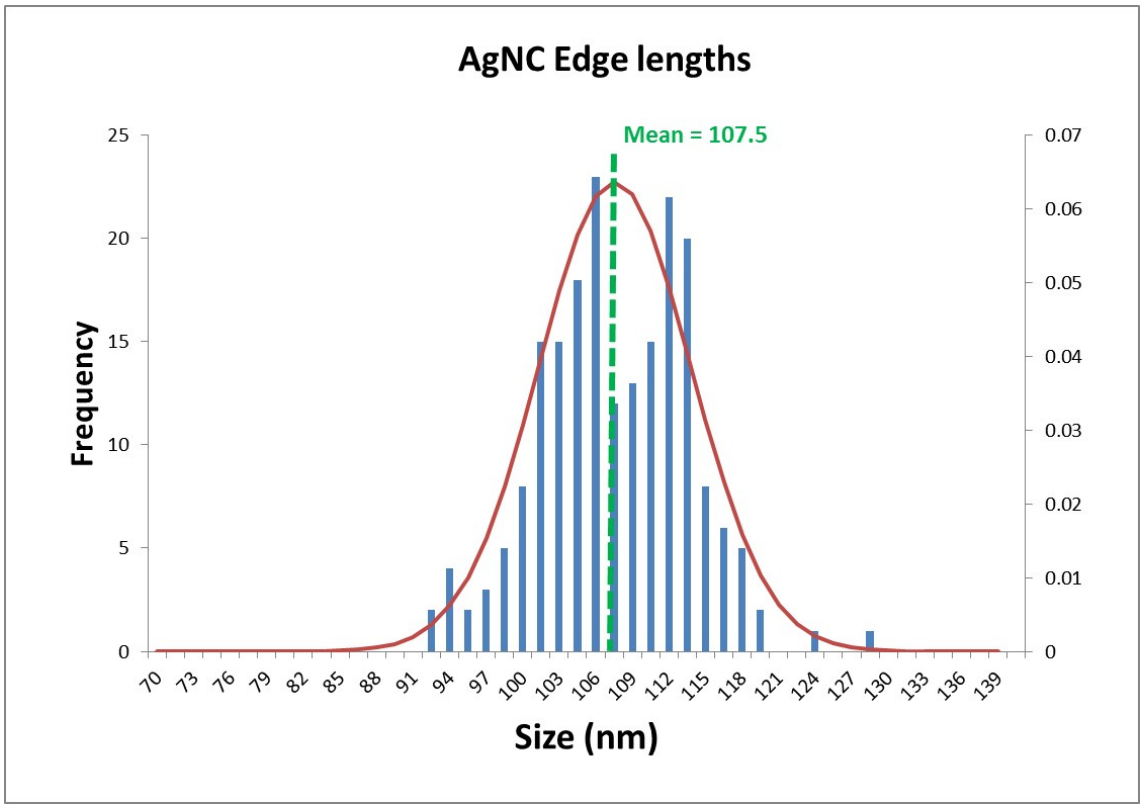


Figure S1. Size histogram of AgNCs used to make Ag@AuNC SERS substrate, overlaid with a fitted normal distribution.

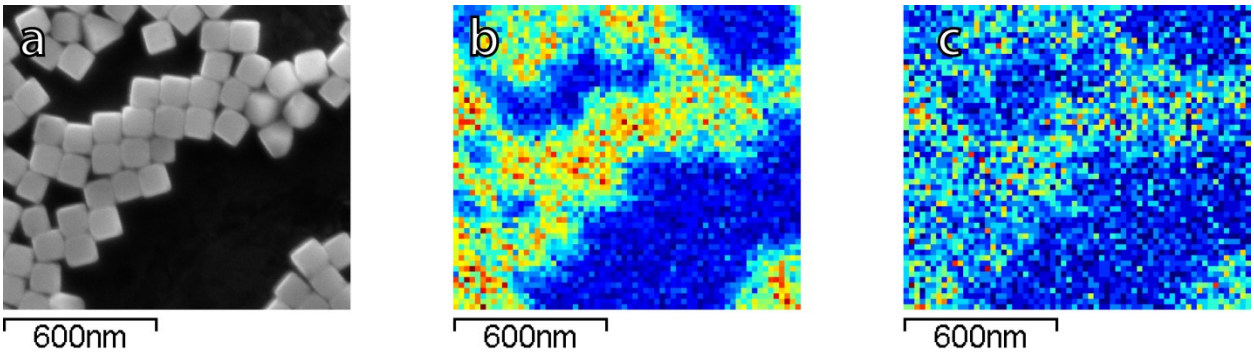


Figure S2. SEM image and EDX element maps for Ag@AuNCs. (b) and (c) are the element maps for Ag and Au, respectively, and correspond to the image in (a). (e) and (f) are the Ag and Au maps corresponding to the image in (d).

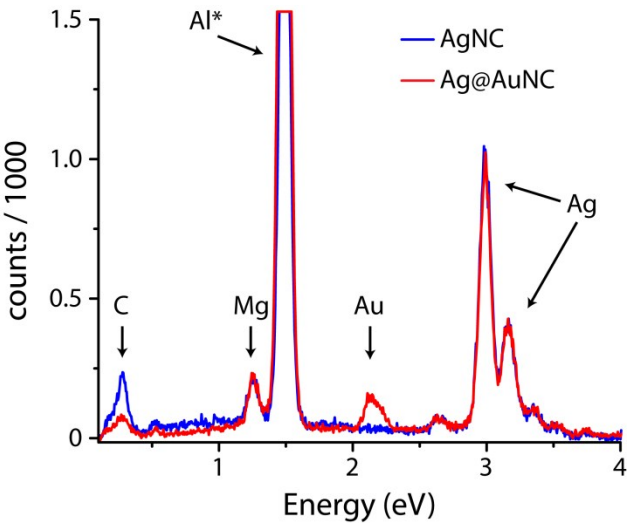


Figure S3. EDX spectra of AgNCs and Ag@AuNCs, with corresponding peak assignments. *The aluminum peak (from the SEM sample mount) is truncated.

## DFT Calculations

Density functional theory (DFT) calculations were carried out on NTP, MTBH, and 4-(4-methylthiophenyl)-3-buten-2-one adsorbed on Au surfaces, using the hybrid exchange-correlation functional B3LYP. Gold surfaces were represented by a cluster of 5 Au atoms in the case of NTP and 6 Au atoms in the case of MTBH and 4-(4-methylthiophenyl)-3-buten-2-one. The 6-311+G** basis set was used for C, H, O, N, S atoms. The modified LANL2DZ basis set was used for Au valence electrons and the corresponding relativistic core potentials were used for Au inner shell electrons. The solvent effects of ethanol were included by using the integral equation formalism polarization continuum model (IEFPCM). The molecule geometries were optimized (see Figure S4), after which the Raman scattering frequencies and activities were calculated. The Raman spectra were expanded by a Lorenzian expansion with a FWHM of 10 $cm^{-1}$ (see Figure S5).

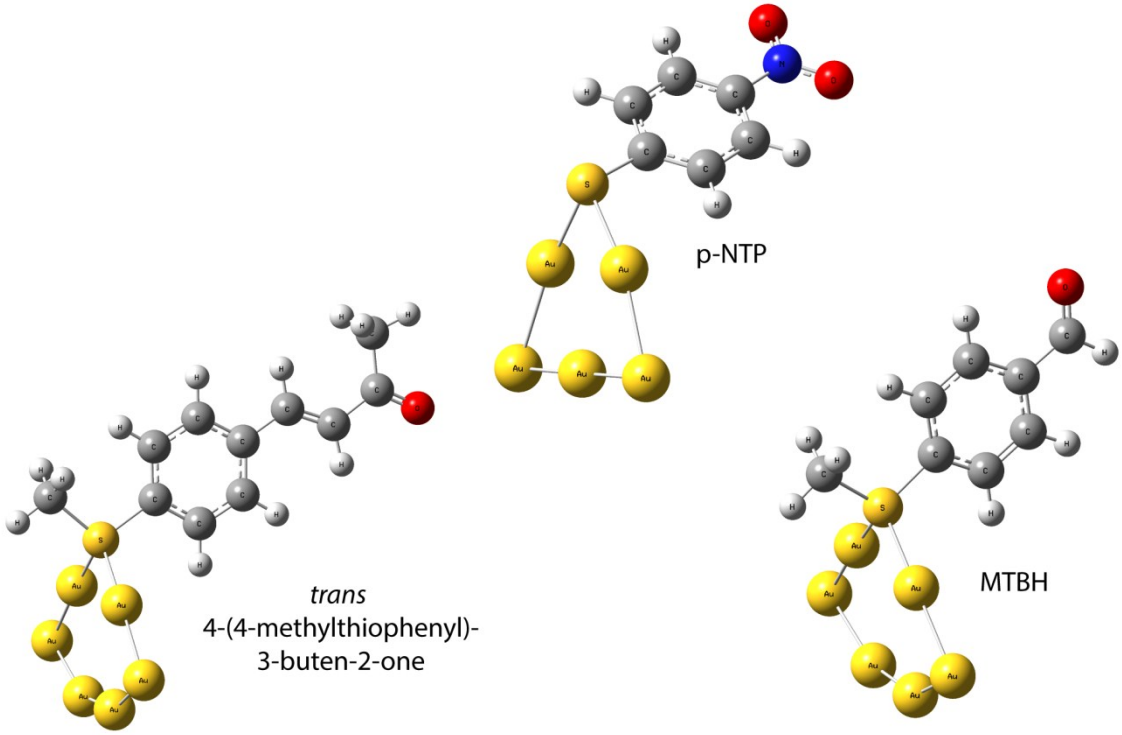


Figure S4. Optimized geometries from DFT calculations.

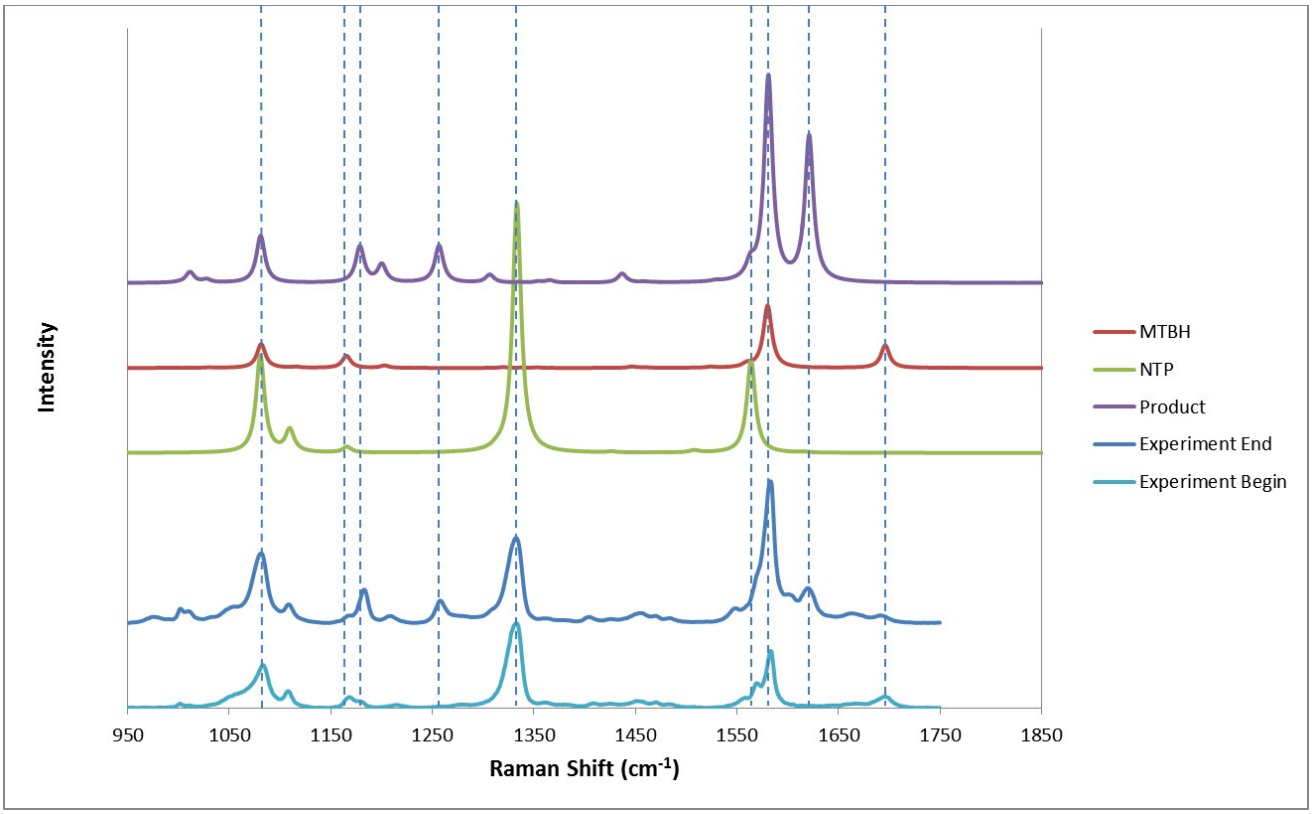


Figure S5. Simulated spectra for the three surface-adsorbed species present in the aldol condensation reaction (MTBH, NTP, Product). Calculated frequencies were scaled by a factor of 0.981 and offset for visual clarity. The IS-normalized experimental spectra of the first and last timepoints of an aldol condensation reaction are shown for comparison, again offset for clarity. Dashed lines are vertical guides to the eye.

## Aldol Condensation Reaction

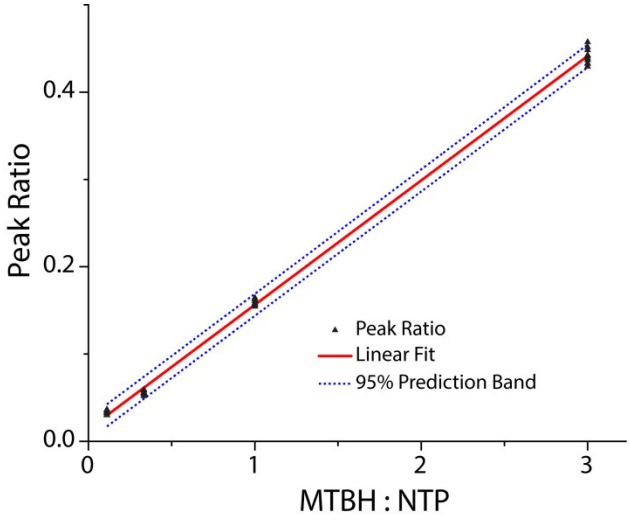


Figure S6. Linear regression of MTBH/NTP coadsorption. Ag@AuNCs were functionalized with MTBH and NTP. The adsorbing solutions were mixtures of pure MTBH and ethanolic NTP (a saturated NTP solution diluted 1:1000 with ethanol). The plot shows the intensity ratio of the peaks at 1700 $cm^{-1}$ (aldehyde C=O stretch, MTBH) and 1340 $cm^{-1}$ ($NO_2$ symmetric stretch, NTP) as a function of the volume ratio of MTBH and NTP solutions used in the adsorbing solution.

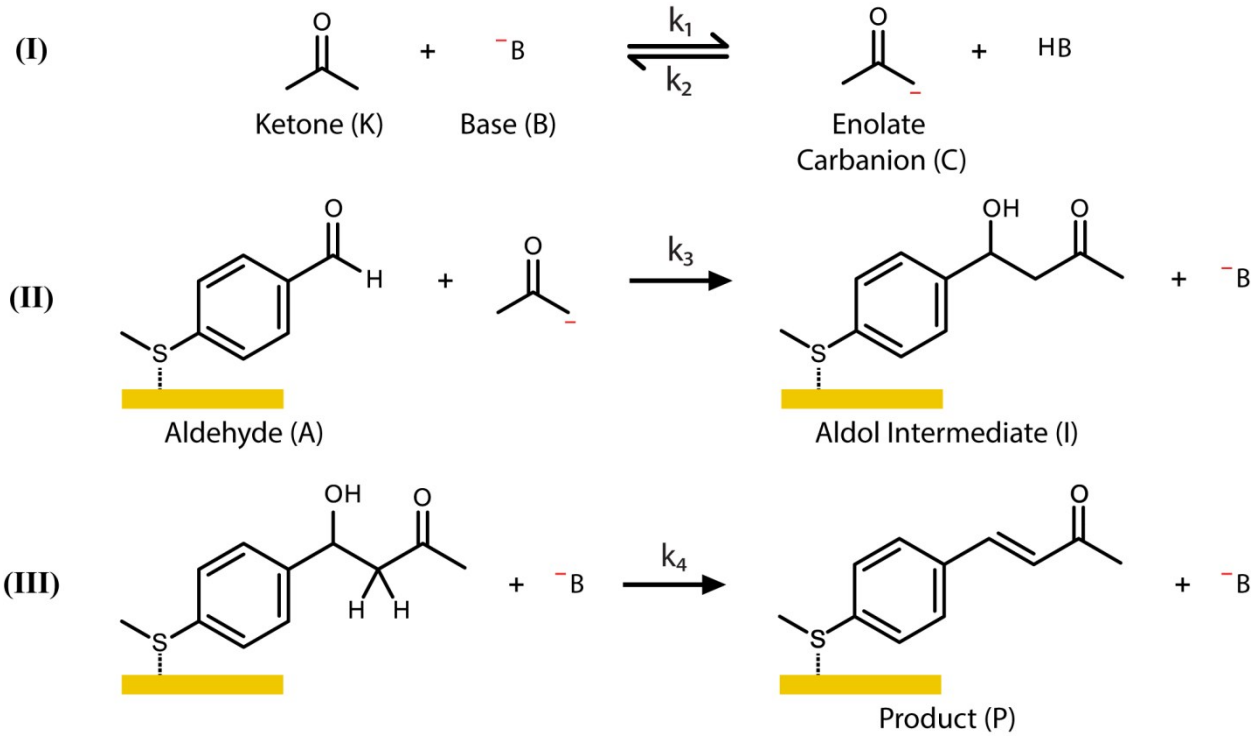


Figure S7. Reaction mechanism diagram for the aldol condensation of surface-adsorbed 4-(methylthio)benzaldehyde with free acetone.

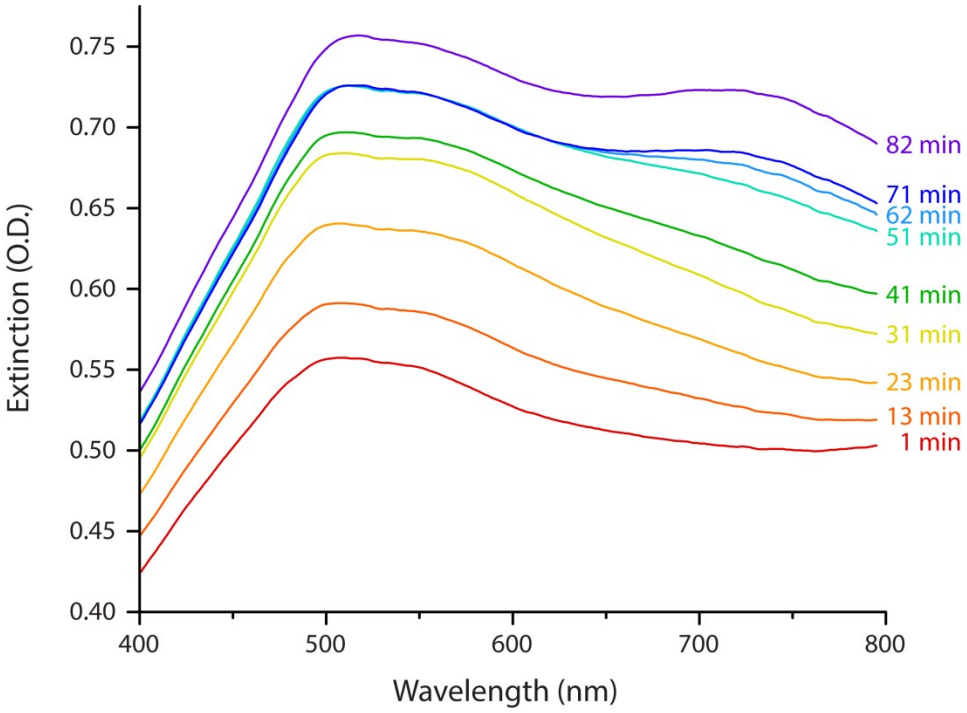


Figure S8. UV-Vis spectrum during reaction. Initial acetone concentration was 1.95 M. The initial NaOH concentration was set at 286 mM, and the reaction proceeded at room temperature.

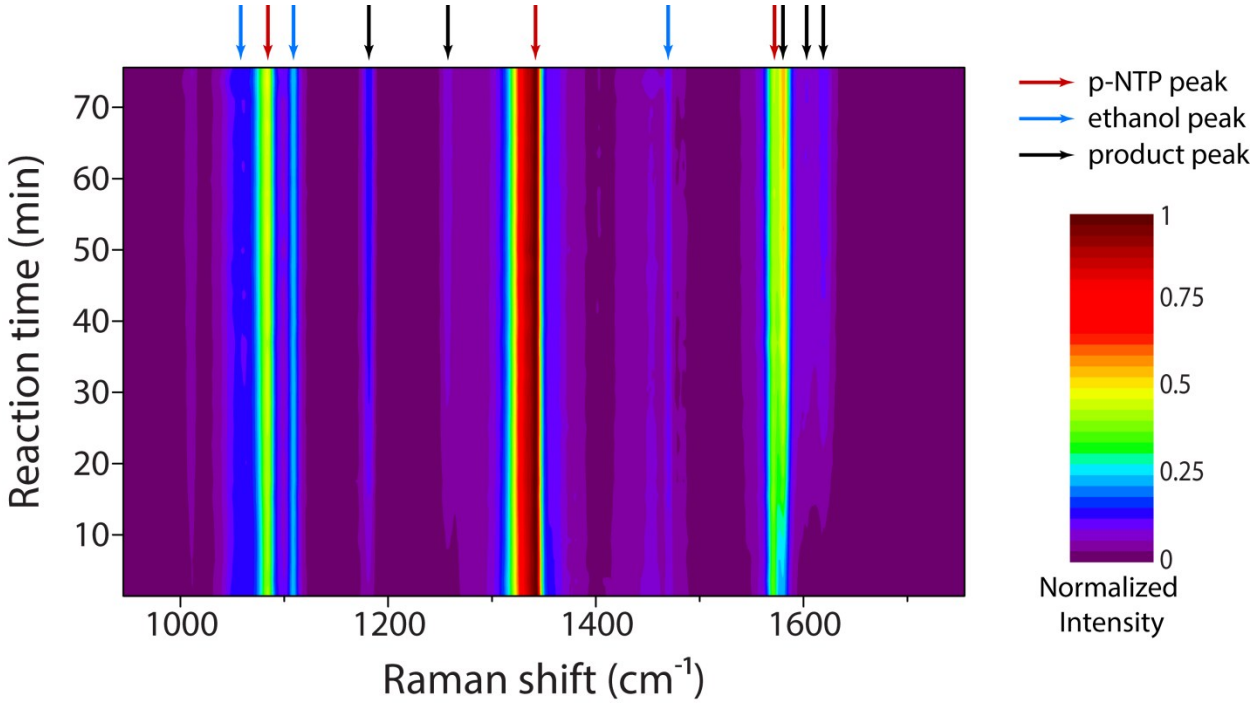


Figure S9. SERS results of aldol reaction (see Figure 6, main text) presented in a 2D Color map plot of the time-dependent SERS spectra. Note the constant peaks for ethanol and p-NTP, while the product peaks are increasing in intensity over time.