

**Supporting Information for**  
**Green synthesis of metal nanoparticles via natural extracts: the biogenic**  
**nanoparticle corona and its effects on reactivity**

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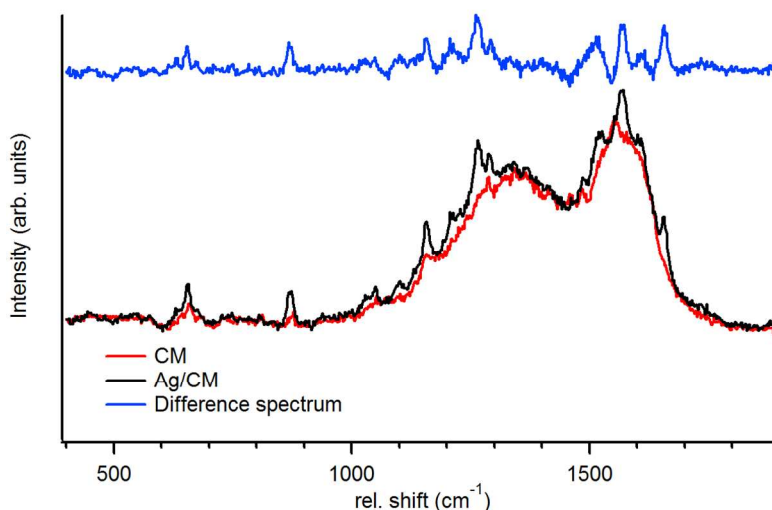
Figure S1: Example of spectral subtraction procedure used for calculating SERS spectra

Text S2: Adsorbate exchange experiments via Surface Enhanced Raman Spectroscopy

Figure S2: Example of SERS of the nitrile stretching modes

### Text S1. Background subtraction for Surface Enhanced Raman Spectroscopy of Ag/CM

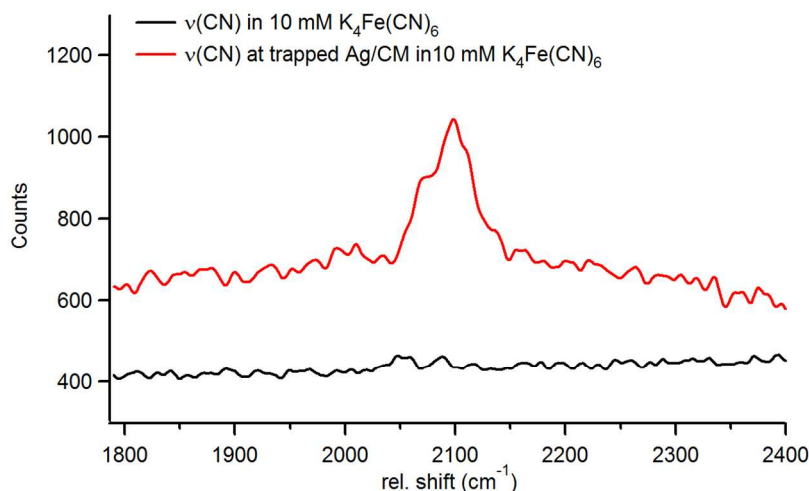
An example of the procedure used for obtaining Surface Enhanced Raman Spectroscopy (SERS) of organic adsorbates at Ag/CM is illustrated in Figure S1. Upon trapping of Ag/CM particles, Raman spectra were collected in sequence with a total of 1 s exposure. The spectra of trapped particles consists of an overlap of the broad D and G peaks of amorphous carbon and of sharp peaks due to molecular vibrations of the adsorbates (see Fig. S1, black trace). As the particle entered the optical trap, the signature of the carbon scaffold was typically seen first (see Fig. S1, red trace), followed by the spectral signature of carbon and adsorbates. A carbon spectrum collected during the same trapping event was used for background subtraction in order to obtain a difference spectrum with Raman contributions from the adsorbates (see Fig. S1, blue trace). This procedure ensured excellent background subtraction by using spectra collected under identical conditions and close in time.



**Figure S1.** Example of spectral subtraction procedure used for calculating SERS spectra of organic adsorbates on Ag/CM particles; excitation 532 nm, exposure time = 1 s.

## Text S2. Adsorbate exchange experiments via Surface Enhanced Raman Spectroscopy

$\text{Fe}(\text{CN})_6^{4-}$  ions display high affinity and chemisorb from solution onto Ag surfaces, furthermore, they possess Raman scattering peaks associated to nitrile stretching modes ( $\nu(\text{CN})$ ) at  $2000\text{--}2100\text{ cm}^{-1}$ ,<sup>1</sup> an area of little spectral overlap with organic compounds.  $\text{K}_4\text{Fe}(\text{CN})_6$  was added to Ag/CM suspensions in order to bring the  $\text{Fe}(\text{CN})_6^{4-}$  concentration to 10 mM; this solution yielded two weak  $\nu(\text{CN})$  Raman peaks at 2048 and 2089  $\text{cm}^{-1}$ . Immediately after  $\text{Fe}(\text{CN})_6^{4-}$  addition, the Raman of trapped Ag/CM particles yielded spectra as those shown in Figure 5 in the main text; however, after 20 min incubation it was possible to observe, upon particle trapping, the appearance of  $\nu(\text{CN})$  peaks of enhanced intensity with respect to those in solution. Figure SI2 shows a comparison the  $\nu(\text{CN})$  peak measured in 10 mM solution and that obtained from a trapped Ag/CM particle under identical conditions.  $\nu(\text{CN})$  peaks from Ag/CM particles were found to grow in intensity over approximately 1 h of immersion, however, after overnight incubation both the  $\nu(\text{CN})$  and peaks attributed to organic compounds disappeared entirely; we attribute this behavior to the etching of Ag nanoparticles by nitrile ligands.



**Figure S2.** Example of SERS of the nitrile stretching modes ( $\nu(\text{CN})$ ) of adsorbed  $\text{Fe}(\text{CN})_6^{4-}$  at Ag/CM particles (red trace), compared to the Raman spectrum of  $\text{Fe}(\text{CN})_6^{4-}$  in the same 10 mM solution of  $\text{K}_4\text{Fe}(\text{CN})_6$ .

## References

- (1) Loo, B. H.; Lee, Y. G.; Liang, E. J.; Kiefer, W., Surface-enhanced Raman scattering from ferrocyanide and ferricyanide ions adsorbed on silver and copper colloids. *Chemical Physics Letters* **1998**, 297, 83-89.