

# **Impacts of Select Organic Ligands on the Colloidal Stability, Dissolution Dynamics and Toxicity of Silver Nanoparticles**

## **Supporting Information**

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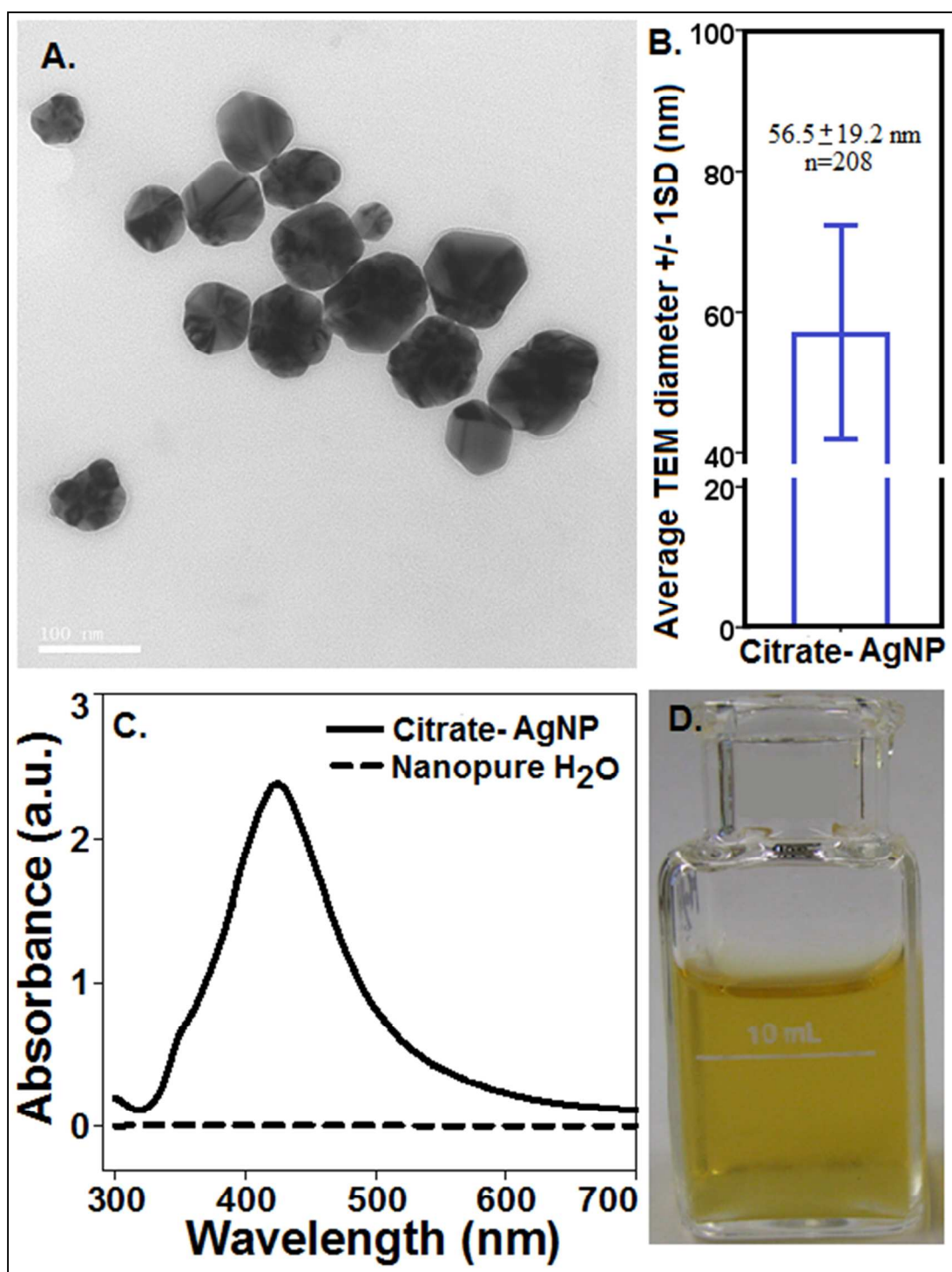
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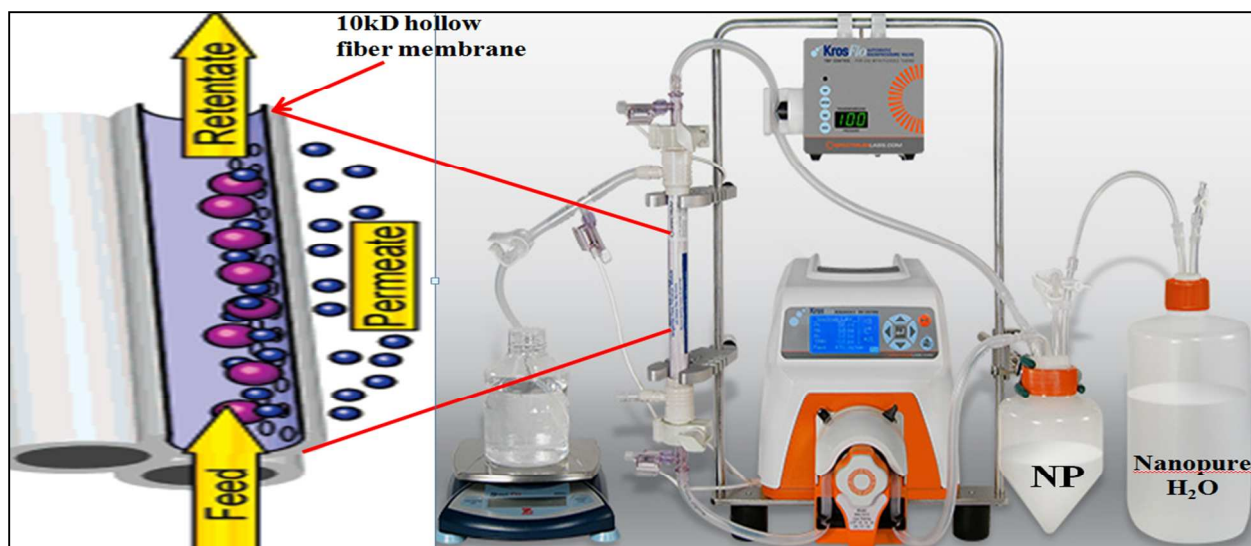
**Total Pages: 8 (including cover page)**

**Total Figures: 4**

**Total Tables: 3**



**Figure S1.** Representative TEM imagery (A), TEM particle size distribution (B), surface Plasmon resonance spectrum (C), and the stable colloidal suspension (D) of stock Citrate-AgNPs. Scale bar = 100 nm (taken from our previous publication<sup>1</sup>).



**Figure S2.** Photograph showing Kros *Flo* Research Ili Tangential Flow Filtration (TFF) System (right panel) equipped with 10 kD polysulfone hollow fiber diafiltration membranes (left panel) used for the purification of Citrate-AgNPs; adapted from <http://www.spectrumlabs.com/>; NP, nanoparticle suspension. Applying suitable shear pressure (15 - 20 psi) via a peristaltic head that pumps the suspension through pharmapure#16 tubings, highly pure nanoparticles are obtained as retentate as nanosuspension is pass through the hollow fiber membranes (size = 10 kD, surface area=145 sq. cm) under tangential flow maintained by multiple pressure transducers and soluble impurities and ions are buffer exchanged with nanopure water.

**Table S1.** Purification protocol applied for cleaning as-synthesized Citrate-AgNPs using Tangential Flow Filtration (TFF) system.<sup>2</sup>

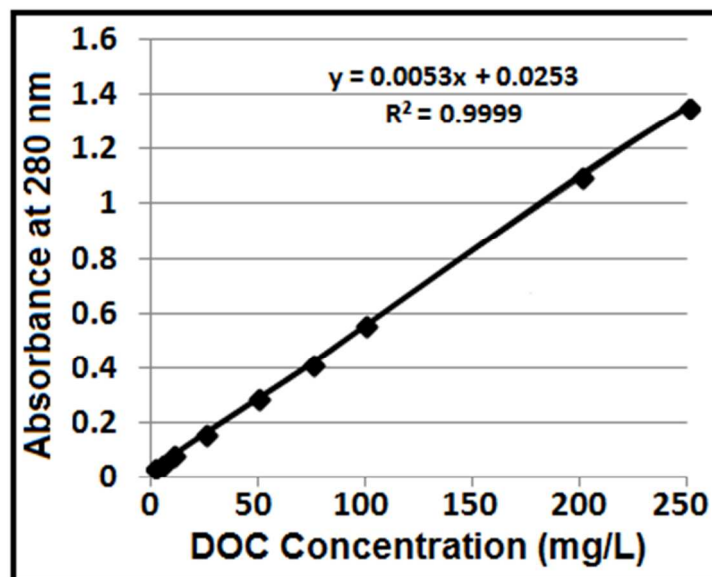
PURIFICATION OF UNCLEAN CITRATE- NAG	ELECTRICAL CONDUCTIVITY ( $\mu\text{S}/\text{CM}$ )
STARTED VOLUME = 500 ML	1095
ENDED VOLUME = 70 ML	1162
VOLUME INCREASED TO 500 ML BY ADDING NANOPURE WATER	185
ENDED VOLUME = 100 ML	283
VOLUME INCREASED TO 500 ML BY ADDING NANOPURE WATER	36
ENDED VOLUME = 75 ML	68
VOLUME INCREASED TO 500 ML BY ADDING NANOPURE WATER	11
ENDED VOLUME = 150 ML	20
VOLUME INCREASED TO 500 ML	5*

\* obtained as clean Citrate-AgNP suspension with electrical conductivity 5  $\mu\text{S}/\text{cm}$ .

**Table S2. Characteristics of Citrate-AgNPs.**

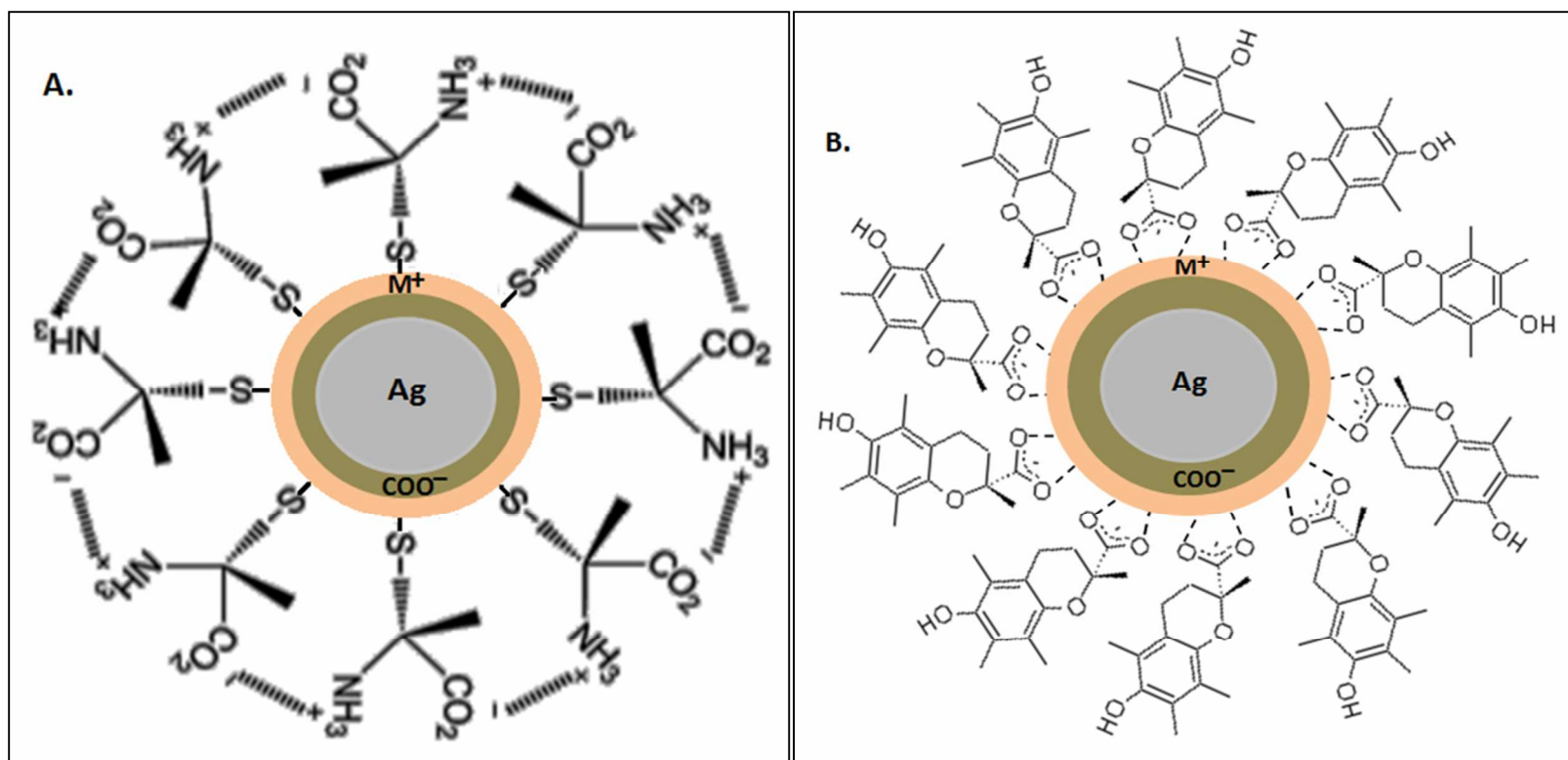
MATERIAL <sup>A</sup>	PH	PARTICLE SIZE DISTRIBUTION		ZETA POTENTIAL (MEAN $\pm$ S.D.) (mV)	PLASMON RESONANCE		AVERAGE CIRCULARITY
		HYDRODYNAMIC DIAMETER (MEAN $\pm$ S.D.) NM	TEM DIAMETER (MEAN $\pm$ S.D.) NM		$\lambda_{\text{MAX}}$ (NM)	ABSORBANCE (AU)	
CITRATE- AGNP	7.2	14.8 $\pm$ 0.9	56.5 $\pm$ 19.2 (N = 208)	-22.5 $\pm$ 1.8	445	2.38	0.88

<sup>a</sup> all measurements were taken at 2 mg/L Citrate-AgNPs; SD, Standard deviation of the sample; Smoluchowski equation estimated mean  $\zeta$  potential from the electrophoretic mobility of the particles; mV, millivolt.  $\lambda_{\text{max}}$  represents maximum wavelength at which the peak was observed; n = number of particles analyzed for estimating particle diameter from Transmission Electron Microscopy (TEM) images using ImageJ 1.44. For stock nanosuspension,  $\zeta$  potentials remained fairly similar before (-21.43 mV) and after (-25.13 mV) purification.



**Figure S3.** DOC calibration curve produced by UV-vis absorbance measurement at 280 nm and the concentrations were verified by persulfate-UV oxidation procedure.

**Quality Control (QC).** All containers used for this study were soaked in 5% HNO<sub>3</sub> overnight, cleaned several times using nanopure water (resistance = 18.3 MΩ-cm), and air dried before use. Typical metal analysis, using an Atomic absorption spectroscopy (AAS)-Flame/Furnace, comprised of the method blank, digested samples, sample duplicate, spiked sample, and appropriate internal standards. The rinse blank consisting of 2% HNO<sub>3</sub> made in nanopure water was used to clean the system following analysis of every ten samples. Maintenance of AAS is routinely performed through permanent maintenance contract with the manufacturer. Total Ag recovery was in the range 104.8 – 112.4 %, and five-point calibration curves were typically developed for Ag analysis using AAS.



**Figure S4.** Schematics showing: (A) thiolate bonding of CYS with metallic ions  $M^{+}$  interacting with carboxylate coating of AgNPs<sup>3</sup> which may explain our observation of the slight blue-shift (shifted to the left) of the localized SPR peaks (Figure 2C), and suggests potential surface modification of Citrate–AgNPs with increasing CYS concentrations; (B) potential coordination at an oxygen site with the cations  $M^{+}$  interacting with the available  $COO^{-}$  on AgNP surface; the interaction is likely influenced by the planar benzene

ring and the carboxylate substituent of the 6-membered, non-aromatic ring of the trolox molecule. The sketches are only meant for visualizing potential interactions, and are not to scale.  $\text{COO}^-$  denotes carboxyl ion coating on AgNP surface acquired during synthesis of Citrate-AgNPs;  $\text{M}^+$  represents cations such as  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^+$  or  $\text{K}^+$  readily available in moderately hard water used as the test medium. Ag denotes AgNP's core.

**Analysis of Water Quality Parameters.** Water quality parameters such as pH, temperature, dissolved oxygen (DO), conductivity, hardness, alkalinity, and ammonia-nitrogen were assessed in the test media after every three days until the completion of the experiments, and were found to have acceptable quality as per the USEPA guidelines for *D. magna* culture (Supporting Information Table S3).<sup>4</sup> Total hardness, total alkalinity, and ammonia-nitrogen were measured using standard colorimetric HACH methods as described by the manufacturer (HACH Company, Loveland, CO). Water conductivity, pH, dissolved oxygen, and temperature were determined using Hanna Instrument HI9828 multiparameter meter (Transcat Inc., Rochester, NY).

**Table S3. Water quality parameters of moderately hard reconstituted water used as the *Daphnia magna* bioassay test medium.**

PH	TEMP (°C)	CONDUCTIVI TY (μS/CM)	DO (MG/L)	ALKALINI TY (MG/L AS $\text{CaCO}_3$ )	HARDNES S (MG/L AS $\text{CaCO}_3$ )	$\text{NH}_3\text{-N}$ (MG/L)	NOMINAL CONCENTRATIONS (MG/L)			
							$\text{NaHCO}_3$	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{MgSO}_4$	$\text{KCl}$
7.0	20.5	379	8.42	45	85	0.14	96	60	60	4

## References Cited in Supporting Information

1. Pokhrel, L. R.; Dubey, B.; Scheuerman, P. R.; Maier, K. J.; Tolaymat, T. M. Natural water chemistry (dissolved organic carbon, pH, and hardness) modulates citrate-coated silver nanoparticle stability, dissolution rate, and antibacterial activity. (in revision).
2. Pokhrel, L. R.; Dubey, B.; Silva, T.; El Badawy, A. M.; Tolaymat, T. M.; Scheuerman, P. R. Rapid screening of aquatic toxicity of several metal-based nanoparticles using the MetPLATE™ bioassay. *Sci. Tot. Environ.* **2012**, *426*, 414-422.
3. Liu, h.; Ye, Y.; Chen, J.; Lin, D.; Jiang, Z.; Liu, Z.; Sun, B.; Yang, L.; Liu, J. In situ photoreduced silver nanoparticles on cysteine: An insight into the origin of chirality. *Chem. Eur. J.* **2012**, *18*, 8037–8041.
4. *Procedures for conducting Daphnia magna toxicity bioassay*; United States Environmental Protection Agency; EPA/600/8-87/011; 1987.