Supporting Information

Size and Surface Effects on Chemically-induced Joining of Ag Conductive Inks

Yingsi Wu, Zhaomin Wang, Xinyu Zhao and Mei Chee Tan*

Engineering Product Development, Singapore University of Technology and Design,
8 Somapah Rd, Singapore 487372.
*To whom correspondence should be addressed. Email: meichee.tan@sutd.edu.sg

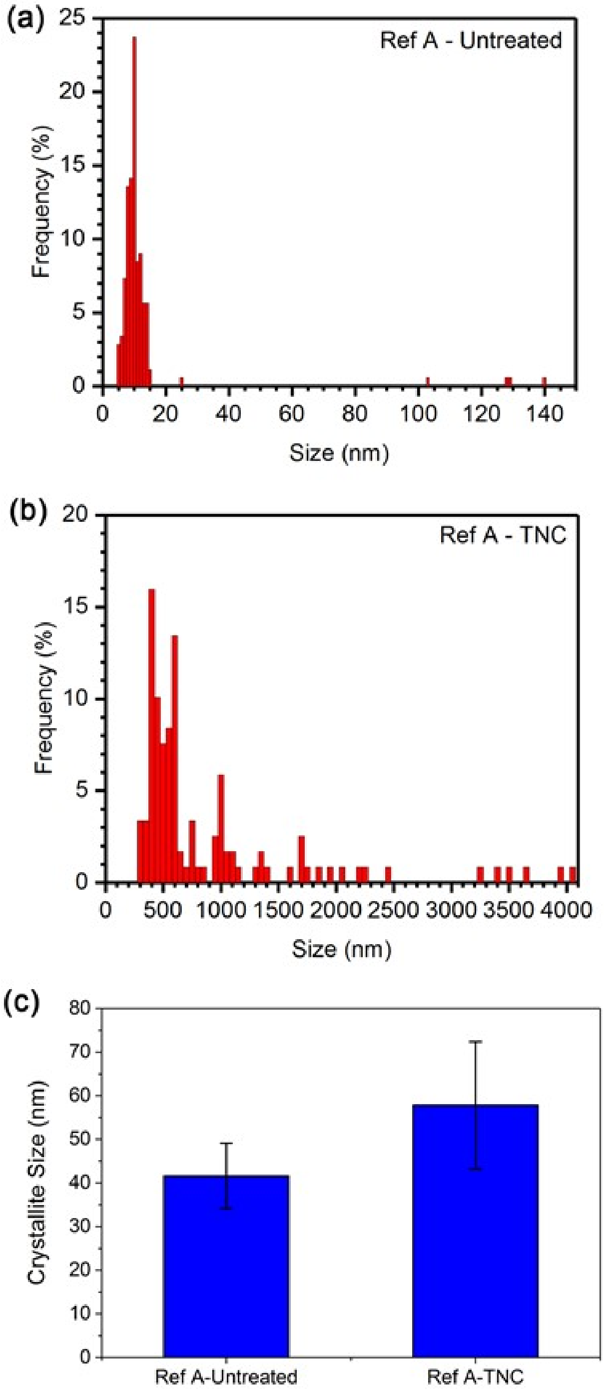

Figure S1. SEM particle size distribution of Ref A samples, (a) untreated and (b) treated with NaCl (TNC). (c) Estimated crystallite sizes of untreated and TNC Ref A samples calculated from the full width half maximum of their respective XRD profiles.

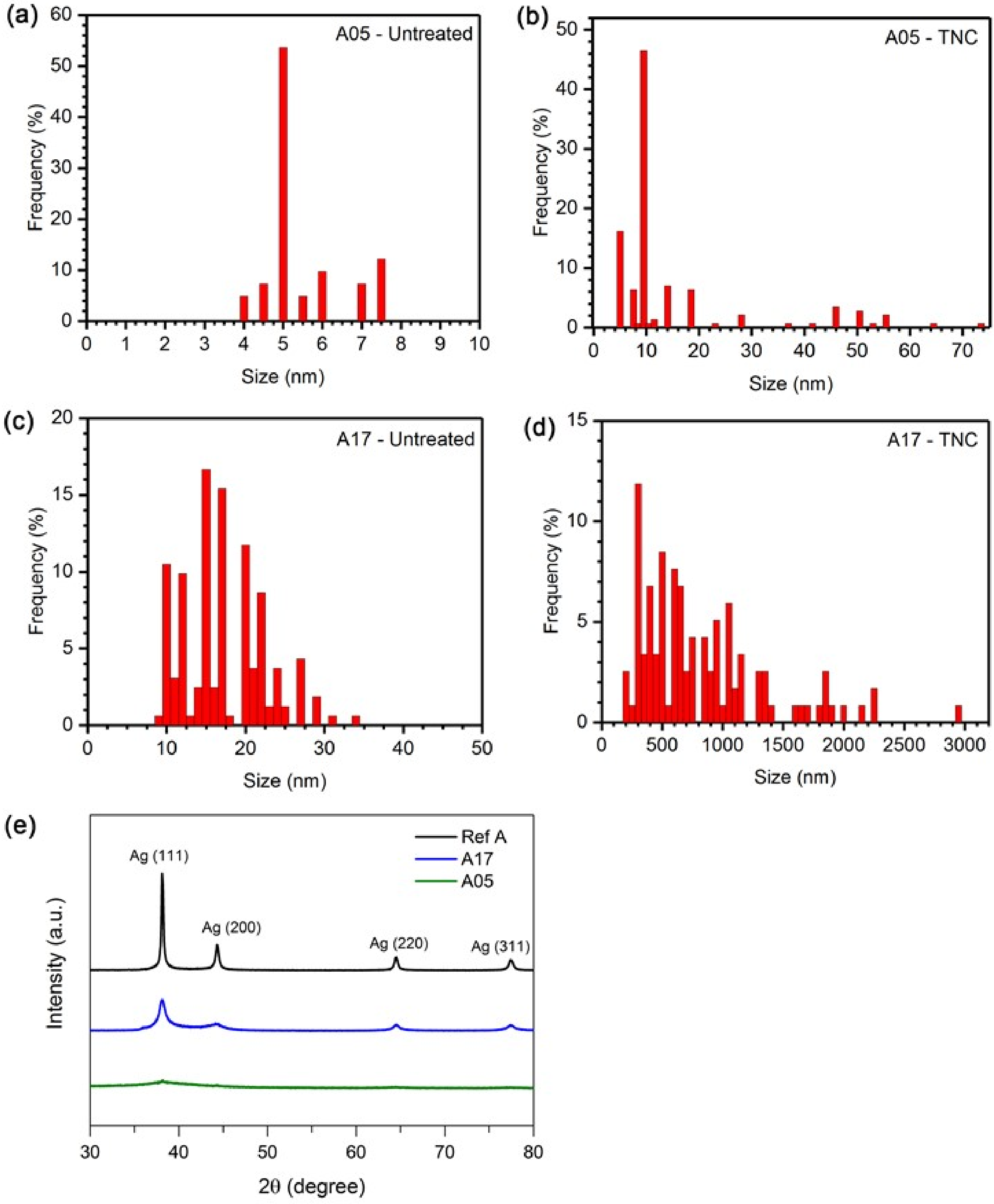

Figure S2. SEM particle size distribution of Ag nanoparticles with average sizes of (a, b) 5 and (c, d) 17 nm that were untreated and treated with NaCl (TNC). (e) XRD profiles of untreated Ag nanoparticles with average sizes of 5 and 17 nm compared to Ref A samples.

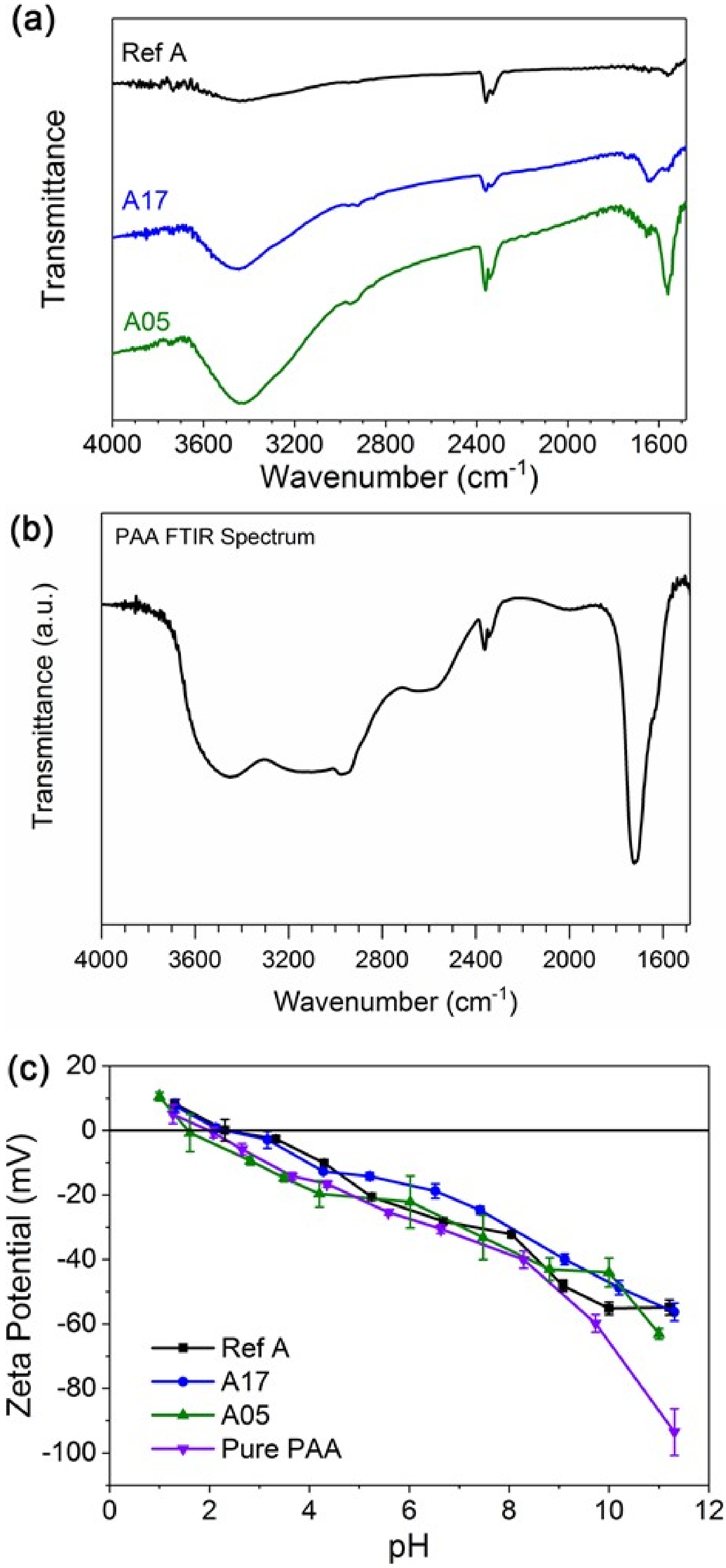

Figure S3 Surface characteristics of (a) PAA-modified Ag nanoparticles with different sizes and distribution compared to (b) pure PAA based on FTIR measurements. (c) Surface charges and isoelectric point of PAA-modified Ag nanoparticles with different sizes and distribution.

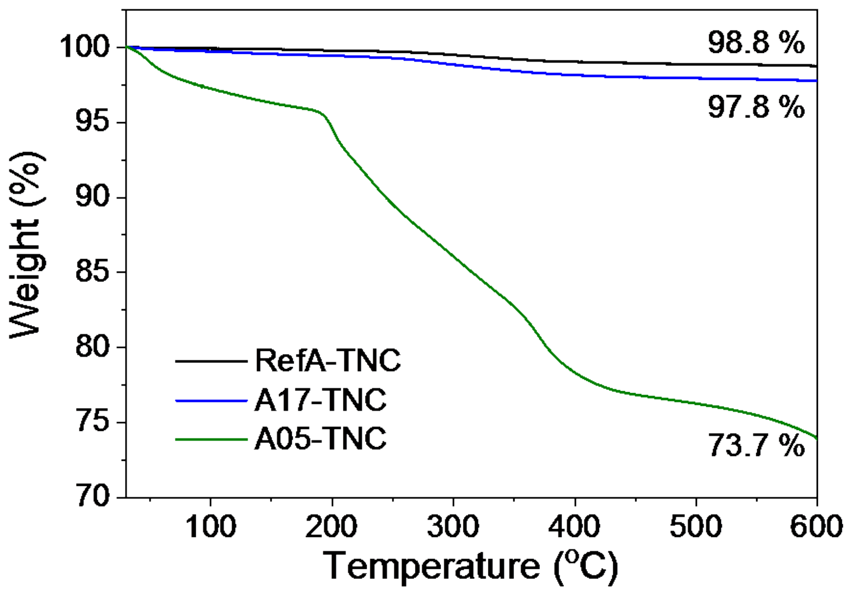

Figure S4 Measured weight loss using the TGA under an inert N_2 atmosphere for Ag nanoparticles after treatment with NaCl.

Table S1. Two-point probe measurements of resistance of printed conductive lines comprising of Ag particles of different sizes and treatments. Length is measured as the distance between the 2-point probes, as estimated from the optical micrographs. Diameter of the printed line was estimated from SEM micrographs of their cross sections. Linear resistivities and conductivities were calculated from the measured resistance, where the average and standard deviation were next computed.

Samples		Length (μm)	Diameter (μm)	Cross Sectional Area (μm^2)	Resistance (Ω)	Resistivity (Ω.cm)	Conductivity (S/cm)	Average Conductivity(S/cm)
Ref A	Untreated	281	10.0	78.54	3.05×10^5	8.52×10^0	1.17×10^{-1}	
					3.52×10^5	9.84×10^0	1.02×10^{-1}	$(1.37 \pm 0.48) \times 10^{-1}$
					1.87×10^5	5.23×10^0	1.91×10^{-1}	
Ref A	TNC	308	12.3	118.82	1.76×10^0	6.79×10^{-5}	1.47×10^4	
					1.91×10^0	7.37×10^{-5}	1.36×10^4	$(1.44 \pm 0.07) \times 10^4$
					1.74×10^0	6.71×10^{-5}	1.49×10^4	
A17	Untreated	182	0.62	0.32	5.60×10^5	9.90×10^{-2}	1.01×10^1	
					4.92×10^5	8.70×10^{-2}	1.15×10^1	$(1.08 \pm 0.07) \times 10^1$
					5.27×10^5	9.32×10^{-2}	1.07×10^1	
A17	TNC	327	1.20	1.13	8.90×10^0	3.08×10^{-6}	3.25×10^5	
					12.0×10^0	$4.15 \times 10\text{-}^{6}$	2.41×10^5	$(2.96 \pm 0.47) \times 10^5$
					9.00×10^0	3.11×10^{-6}	3.21×10^5	
A05	Untreated	318	16.1	203.58	2.39×10^8	1.53×10^4	6.54×10^{-5}	
					3.29×10^8	2.11×10^4	4.75×10^{-5}	$(5.72 \pm 0.90) \times 10^{-5}$
					2.66×10^8	1.70×10^4	5.87×10^{-5}	
A05	TNC	274	13	132.73	0.67×10^8	3.25×10^3	3.08×10^{-4}	
					1.91×10^8	9.25×10^3	1.08×10^{-4}	$(1.65 \pm 1.25) \times 10^{-4}$
					2.60×10^8	12.6×10^3	0.79×10^{-4}	

1. Thermochemistry of AgCl(s) Formation Reaction at Room Temperature, 298K

Values were taken from Zumdahl, Steven S. (2009). Chemical Principles 6th Ed. Houghton Mifflin Company. p. A23. ISBN 0-618-94690-X.

$Ag^{+}(aq) \quad + \quad Cl^{-}(aq) \quad \rightarrow \quad AgCl(s)$

$\Delta H_f^0(Ag^+(aq)) = 105.6$ kJ/mol; $\quad S^0(Ag^+(aq)) = 72.7$ J/(mol.K);

$\Delta H_f^0(Cl^-(aq)) = -167.2$ kJ/mol; $\quad S^0(Cl^-(aq)) = 56.5$ J/(mol.K);

$\Delta H_f^0(AgCl(s)) = -127.1$ kJ/mol; $\quad S^0(AgCl(s)) = 96.2$ J/(mol.K).

$$\Delta H_{rxn} = \sum \Delta H_f^0(products) - \sum \Delta H_f^0(reactants) = -127.1 - 105.6 - (-167.2) = -65.5 \text{ kJ/mol} \quad (6)$$

$$\Delta S_{rxn} = \sum S^0(products) - \sum S^0(reactants) = 96.2 - 72.7 - 56.5 = -33 \text{ J/(mol.K)} \quad (7)$$

$$\Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} = -65.5 - 298\times(-33\times10^{-3}) = -55.7 \text{ kJ/mol} \quad (8)$$

The AgCl formation reaction is spontaneous and exothermic at 298 K.

2. Estimated Upper Temperature Limits of Surrounding Water around Each Particle

By assuming that all heat release during AgCl formation is absorbed by surrounding water (i.e., no further heat loss), we could estimate the upper temperature limits of the surrounding.

$-\Delta H_{rxn} = m \times C_p \times \Delta T$

where ΔH_{rxn} = heat released due to AgCl formation for each particle

m = mass of water surrounding each particle for an assume solvation shell thickness

C_p = heat capacity of water = 4184 J/kg.K; note that most polymers will have a lower heat capacity, which means the increase in temperature could be much higher if one considers that most of the heat is absorbed by PAA

Table S2. Estimated Upper Temperature Limits for Different Initial Ag Sizes.

	Initial	**After Treatment with NaCl**			**1 nm H_2O shell**	**5 nm H_2O shell**
Ave Untreated Particle Size (nm)	**Ag Mass (g)**	**AgCl (wt%)**	**Ag (wt%)**	**Heat Released (J)**	**ΔT (K)**	**ΔT (K)**
5	6.87×10^{-19}	68.97	31.03	4.74×10^{-19}	454	30
17	2.70×10^{-17}	10.27	89.73	2.77×10^{-18}	51	7

The estimated ΔT for 1 and 5 nm shell of water around the particle for each particle size was used as a guideline to estimate the temperature gradient of the surrounding (i.e., how rapidly the temperature decreases away from the particle). This will give us a ballpark estimate of the sphere of thermal influence of the heat released due to AgCl formation.

3. Melting Temperature of Ag Nanoparticles

For spherical nanoparticles,

$$\frac{T_m\ (D)}{T_{m0}} = \left(1 - \frac{1}{\frac{12D}{D_0} - 1}\right) \exp\left(-\frac{2S_{b0}}{3R}\frac{1}{\frac{12D}{D_0} - 1}\right)$$

D is particle diameter

Bulk melting temperature, T_{m0} = 1235 K

Bulk solid-vapor transition entropy, S_{b0} = 104.7 J/mol.K

Atomic diameter, h = 0.289 nm and D_0 = 6h for spherical nanoparticles

Table S3. Estimated Melting Temperatures for Different Initial Ag Sizes.

Ave Untreated Particle Size (nm)	T_m (K)	T_m (°C)
5	933	660
17	1139	866

From Lu, H. M.; Li, P. Y.; Cao, Z. H.; Meng, X. K., Size-, Shape-, and Dimensionality-Dependent Melting Temperatures of Nanocrystals. The Journal of Physical Chemistry C 2009, 113 (18), 7598-7602.