SUPPLEMENTARY INFORMATION: Rheological characterization of yield stress gels formed via electrostatic heteroaggregation of metal oxide nanoparticles

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SHEAR MODULI

Below are frequency sweep plots for all tested silica-titania and titania-alumina gels

at various particle concentrations and ratios. Data was collected using methods described



Figure S1: Shear modulus vs frequency plots for silica-titania (a-b) and titania-alumina (c-d) gels at various particle concentrations and ratios.

in the main text. An additional plot (Fig. S2) illustrates the differences in the critical strain and linear viscoelastic region between gels made with different particle species pairings, as discussed in the body of the main text.



Figure S2: Amplitude sweeps of gels made with different particle species pairings at a total particle volume fraction of 2.5% and at the 'optimum' particle ratio as described in the main text of the article.

APPARENT VISCOSITY

Apparent viscosities were measured at shear rates ranging from 10^{-6} s⁻¹ to 2500 s⁻¹, and Figure S2 contains flow curves that show how gel viscosity profiles change with



Figure S3: Apparent viscosity vs shear rate plots for silica-titania (a-c) and titania-alumina (d-f) dispersions at various particle concentrations, particle ratios, and solution pHs.

particle concentration, particle ratio, and solution pH. Gaps or abbreviations in the flow curves are related to one of two experimental limitations; 1) shear rates that require stresses near the yield stress of the gel are very difficult to produce using a stress-controlled rheometer and result in noisy, irreproducible viscosity values, and 2) low viscosity fluids cannot be measured at low shear rates because the torgue exerted by the fluid is below the minimum measureable torque of the rheometer. All of the gels and particle display dispersions power-law shearthinning behavior at shear rates below some critical value and therefore lend

Table S1: Ostwald-de Waele and Herschel-Bulkley power law fitting parameters for particle dispersions and colloidal gels, including pre-exponential consistencies, power-law indices, and shear rates where shear-thinning behavior transitions to Newtonian shear-rate independence.

Sample	Consistency (cP)	Power Law Index	Power-Law to Newtonian Transition (s ⁻¹)
Nanoparticle Dispersions			
2.0vol% Aerosil 200	254	0.242	255
2.0vol% TiP90	105	0.356	160
2.0vol% Aeroxide AluC	398	0.202	255
Silica-Alumina Gels			
1.0vol% 75-25 pH=7	199	0.2	150
1.5vol% 75-25 pH=7	13660	0.065	>2200
2.0vol% 25-75 pH=7	6164	0.133	1300
2.0vol% 50-50 pH=7	16001	0.154	1300
2.0vol% 75-25 pH=7	49084	0.015	>2000
2.5vol% 75-25 pH=7	125060	0.014	>2000
2.0vol% 75-25 pH=2	613	0.287	460
2.0vol% 75-25 pH=10	248	0.302	275
Silica-Titania Gels			
1.0vol% 75-25 pH=5	293	0.154	160
1.5vol% 75-25 pH=5	4455	0.096	1050
2.0vol% 25-75 pH=5	4376	-0.019	460
2.0vol% 50-50 pH=5	5160	0.117	1200
2.0vol% 75-25 pH=5	13730	0.033	>2000
2.5vol% 75-25 pH=5	25213	-0.021	>2000
2.0vol% 75-25 pH=2	269	0.27	255
2.0vol% 75-25 pH=8	279	0.338	450
Titania-Alumina Gels			
1.0vol% 50-50 pH=7	550	0.264	415
1.5vol% 50-50 pH=7	5161	0.051	>2000
2.0vol% 25-75 pH=7	12291	0.057	>2000
2.0vol% 50-50 pH=7	10652	0.049	>2000
2.0vol% 75-25 pH=7	7764	-0.017	>2000
2.5vol% 50-50 pH=7	18851	0.053	>2000
2.0vol% 50-50 pH=4	164	0.316	255
2.0vol% 50-50 pH=10	798	-0.014	255

Power Law Fitting Parameters

thmselves to analysis using the Ostwald-de Waeleⁱ (OdW) or Herschel-Bulkleyⁱⁱ (HB) model for relating viscosity and shear rate. The OdW and HB models both model viscosity and shear rate using a power-law relationship, but the HB model adds an additional term to account for a yield stress, if present. The basic relationship used by both models is:

$$\mu_{app} = K * \left(\frac{d\gamma}{dt}\right)^{n-1}$$
 Eqn. S1

Where μ_{app} is the apparent viscosity, K is a pre-exponential factor commonly referred to as the consistency, dy/dt is the shear rate, and n is exponential term commonly referred to as the power law index. This equation was used to fit the viscosity vs shear rate curves in Figure S2 and the best-fit values for the consistency and power law index parameters for each sample are shown in Table 2 along with the shear rate where the sample transitions from power-law to Newtonian behavior. The data in Table 2 lends itself to a few generalizations about the gel behavior. First, the 'strength' of the gel can be approximated by the consistency value, which agrees with previous results in that the silica-alumina gels have a much higher viscosity than the corresponding silica-titania and titania-alumina gels. Consistency values also reinforce the previous trends noticed regarding particle ratio, with consistency being a strong function of particle ratio for silicacontaining gels, but less of a factor for the titania-alumina gels. A similar trend is observed with power-law index values, where stronger gels and increased network strength results in indices close to zero, while samples at low concentrations and pHs outside of the gelation window display power-law indices in the range of 0.2-0.3, which is similar to the indices observed for dispersions of only a single species of fumed nanoparticle. Four of the tested gels have power-law indices that are <0, a property that is not theoretically possible, but has been observed in a variety of biomass dispersions.^{iii,iv} Padmanabhan theorized that the negative indices were a result of some combination of molecular degradation of the sample, viscous dissipation, and fluid slip. Since molecular degradation of the fumed metal oxide nanoparticles is relatively unlikely at these shear rates and stresses, the negative indices observed here are therefore likely due to viscous dissipation

and wall slip, however, non-linear degradation of particle agglomerates could also be a contributing factor.

The particle mixtures demonstrate a very strong and reversible, relationship between viscosity and solution pH, as shown in Figure S2c, f, and i. The apparent viscosity drops by two orders of magnitude or more when the solution pH is pushed below or above the IEPs of both of the metal oxides. Similar behavior has been observed in clay dispersions where the various facets of the clay particle have different IEPs^v and in alumina dispersions near the IEP, where positively charged and negatively charged surface groups coexist and maximize interparticle electrostatic interactions.^{vi} In addition to the large drop in viscosity, the low- and high-pH dispersions do not exhibit a yield stress, implying that there is no long range structure present.

Since all of the tested dispersions at pHs within the gelation window display powerlaw behavior and a similar power law index, it was hoped that there would be a single descriptive factor that could relate how the viscosity profile changes for different particle mixtures, concentrations, and ratios. Figure S3a. shows a combined viscosity profile for



Figure S4: Normalized viscosity vs shear rate plot (a) and consistency vs max. +/- pairings plot (b) for all gels that exhibit yield stress behavior. Viscosities were normalized using the fitted consistency value found in Table 2.

all of the samples that exhibited gel-like behavior after being normalized using the consistency values reported in Table 2. The normalized viscosity data for all of the samples collapses onto a single power-law profile, so if a single variable or set of variables could be found that relate each gel sample to its measured consistency would allow us to predict viscosity profiles for other particle mixtures. One possible parameter would be the maximum number of +/- pairings in a given gel mixture, since the number of interparticle bonds should, in theory, be strongly correlated to the overall strength of the particle network and its viscoelastic behavior. A value for the maximum number of +/pairings can also be easily calculated using the specific surface charges reported in the literature. However, a plot of consistency vs max. number of +/- pairings, shown in Figure S3b, shows that there is no overall correlation between the two across different nanoparticle pairings, though within each pairing there is a weak correlation between the two variables. All of this implies that there are additional factors that important to understanding the gel structure and behavior for the different nanoparticle pairings beyond a simple charge balance between negatively charged surface sites and positively charged surface sites. Other potential factors may be sintered aggregate size, aggregate fractal dimension, relative polydispersity of the aggregates, etc. All of these factors will require additional study using dynamic light scattering, small-angle scattering, and other techniques in order to determine how they affect the bulk rheology of the gel.

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FLOW HYSTERESIS/WALL SLIP

As mentioned in the paper, all of the shown rotational rheology data were



Figure S5: Viscosity vs shear rate plot for a 1.5 vol% $SiO_2 - 0.5$ vol% Al_2O_3 gel. Closed symbols were measured using a low-to-high shear rate ramp, open symbols were measured using a high-to-low shear rate ramp.



Figure S6: Stress vs shear rate plot for a 1.5 vol% $SiO_2 - 0.5$ vol% Al_2O_3 gel, measured using a plate-plate geometry while ramping the shear rate from low-to-high (a.) and from high-to-low (b.). More repeatability, especially at low shear rates, is observed only when measuring from high-to-low.

measured in descending order of shear rates because this method proved to be more reproducible from sample to sample than the reverse. As shown in Figure S4, large deviations in the flow curve are often observed at very low shear rates, possibly due to wall slip, non-uniform yielding as the shear rate increases, and differences in the shear history of samples. Overall, the flow curves are very similar (though deviations are made less apparent due to the axes being on a logarithmic scale spanning several orders of magnitude). Figure S5 contains further evidence that the sample provides more reproducible rheological measurements when measured in a descending shear rate ramp. When the shear rate ramp is run from high-to-low, the low shear rate plateau is much more reproducible when measured in this manner, likely because it ensures that the shear history of the samples are very similar, which results in a more reproducible gelation mechanism.

Figure S6 addresses concerns about wall slip, showing stress curves for the same 1.5 vol% silica/0.5 vol% alumina gel measured using a 50 mm plate-plate geometry at

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Figure S7. Stress flow curves for a representative sample (1.5 vol% $SiO_2 + 0.5$ vol% Al_2O_3 gel at pH 6.5) measured at four different gap heights using a plate-plate geometry; showing no obvious evidence of wall slip.



Figure S8. Stress evolution at low shear rates showing that the rheometer control loop is capable of maintaining a constant shear rate during low shear rate experiments using same sample used in Fig. S7.

four different operating gaps. The data demonstrate no obvious evidence of wall slip, though there is some scatter in the data near the yield point.

The Anton-Paar MCR 301 rheometer used in this study is a stress-controlled instrument that uses a control loop to maintain a constant shear rate during shear rate controlled tests. Anomalous and inaccurate data would be measured if this control loop cannot sufficiently control the shear rate during an experiment. For these samples, this problem is most likely to occur at low shear rates where the required stress to maintain a given shear rate is very close to the yield stress and where the measured shear rate is very sensitive to small changes in shear stress. Fig. S7 shows how the stress and shear rate evolve in a shear rate controlled experiment for a 1.5 vol% SiO₂ + 0.5 vol% Al₂O₃ gel at pH 6.5. During the test, the shear rate is initially held at 10^{-2} s⁻¹ for 15 minutes, then changed to 10^{-3} s⁻¹ for 5 minutes, and finally held at 10^{-4} s⁻¹ for 10 minutes. The

rheometer does an excellent job of maintaining a constant shear rate even at shear stresses very near the yield stress of the gel.

Along a similar vein of inquiry, it is important to ensure that when the rheometer is operated in stress-control mode it provides a constant stress and to understand how the shear rate evolves at a given applied stress, as seen in Fig. S8 for the same sample.



Figure S9. Shear rate evolution at constant applied stress demonstrating the yield stress and flow behavior of the gels.

For stresses less than the yield stress (~30 Pa, for this sample) the measured shear rate oscillates above and below zero, between -0.00011 s⁻¹ and +0.00009 s⁻¹, after the initial 5-10 s (as seen in Fig. S8, inset), reinforcing that these gels exhibit a yield stress. For an applied stress just slightly above the yield stress (35 Pa), the shear rate gradually reaches a steady state without any slip. At a slightly higher stress (40 Pa) the fluid takes a very different route to equilibrium which is consistent with wall slip. The measured shear rate quickly increases, reaches a maximum and then slowly settles into an equilibrium shear rate after a few minutes.

SMALL ANGLE NEUTRON SCATTERING OF SINGLE PARTICLES



SANS was used to characterize the gels and nanoparticle mixtures to determine

Figure S10. 1-D plots of SANS data obtained for particle dispersions and gels with each of the different particles used: silica (a.), alumina (b.), and titania (c.)..

the fractal dimension of the gel network (shown in Figure 2 of main text). Additional SANS experiments were carried out on dispersions of the individual nanoparticle species in order to get accurate form factor scattering patterns for each nanoparticle species. This data was used to determine structural information for the different nanoparticles and to deconvolute the structure factor arising from the gel network. Figure S9 contains 1-D scattering curves obtained from quiescent samples of silica, alumina, and titania in aqueous solutions with D₂O/H₂O ratios where the neutron scattering length density of the liquid phase is contrast matched to that of one of the other nanoparticle species (a contrast variation series was run for each nanoparticle species and the contrast match points for silica, titania, and alumina were

determined to be 62%, 43%, and 88% D₂O, respectively). In all of these cases, the high g scattering is essentially identical for the single particle dispersions and the gel mixtures, indicating that all scattering at $q < 0.07 \text{ }^{-1}$ is coming from the sintered fractal aggregates. Deviations of the scattering curves at low g are due to the long range structural differences between the gels and dispersions. The continued power law slope in the gel samples is indicative of the long-range fractal network present in the gelled nanoparticle mixtures, while the low-g elbow/plateau in the dispersion scattering curves provides information regarding the average size of the sintered aggregates. Unified power law fits of the single species dispersions were used, along with electron microscopy, to determine the primary particle sizes, fractal dimensions, and aggregate diameters listed for the different nanoparticle species in the 'Materials' section of the primary text. In addition to the low-g elbow/plateau, Fig. S9 a. and c. also show evidence of an interaction peak at approx. q = 0.03 nm⁻¹. in the single species dispersions. This peak/bump is due to electrostatic repulsion of the like-charged particles and is not present in the alumina-only scattering curve because of the much lower concentration present in that sample, limiting the amount of particle-particle interaction.

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