Structure and Rheology of Self-Assembled Micelle-Nanoparticle Plasmonic Nanogels: Experiments and Molecular Dynamics Simulations

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Summary Self-assembly in wormlike micelle solutions is used to distribute various metallic nanoparticles to produce stable plasmonic nanogels with exceptional color uniformity and robustly tunable optical properties. Such gels exhibit rich rheological behavior including shear thickening, rheopexy and shear thinning as the nanoparticle concentration is progressively increased. The mechanisms contributing to the rheological and structural properties of the plasmonic nanogels are studied by using Molecular Dynamics simulations.

PLSMONIC NANOGELS SYNTHESIS

Typically, metal nanoparticles (NPs) in a solution tend to agglomerate. This often leads to phase separation. We use self-assembly of the NPs with cetyltrimethylammonium bromide (CTAB) wormlike micelles (WLMs), which are elongated and semiflexible cylindrical aggregates of amphiphilic CTAB molecules in aqueous solutions, to create well-separated stable suspensions. At sufficiently large concentrations, the micellar chains entangle to form a viscoelastic network with a linear dimension (ξ_M) on the order of $(k_bT/G_0)^{1/3}$ where G_0 is the plateau storage modulus and k_b and T represent the Boltzmann constant and absolute temperature respectively. SAXS and rheological experiments suggest a mechanism of self-assembly in which the nanoparticles bridge the micelle fragments to form a stable double network. In this way, different types of nanoparticles can be uniformly incorporated in the WLMs network.[1, 2] As shown in figure 1(a), plasmonic nanogels (PNGs) consisting of different types of NPs provided a fascinating range of colors. Light trapping can be achieved in a wide range of wavelength by changing NP type and shape. As shown in figure 1(b), a plasmonic nanogel sample exhibited four peaks at ≈ 420 nm, ≈ 520 nm, ≈ 640 nm and ≈ 750 nm. Such PNGs have potential application as a simple and direct method of optimizing light trapping layers over the whole visible spectrum in photovoltaic devices.

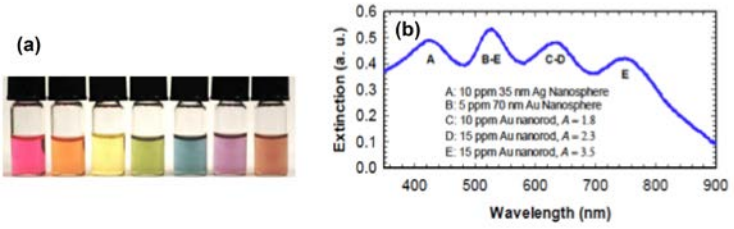

Figure 1: (a) Multicomponent plasmonic nanogels with tunable optical properties.[1] (b) A multicomponent PNG with a relatively uniform extinction spectrum over the visible range.

RHEOLOGICAL STUDY OF PLASMONIC NANOGELS

Figure 2 shows the steady shear viscosity vs. shear rate of the CTAB/NaSal samples with different amount of Ag NP loading. Pure micellar solution with CTAB concentration, C_D = 0.05 M and the molar ratio of sodium salicylate salt to the surfactant, R = 0.30 is shear thickening at a critical shear rate of ~180 s^{-1}. Addition of Ag NPs causes shear-induced-structure (SIS) formation and shear thickening, followed by a shear thinning regime. A three-fold viscosity increase is observed by comparing the maximum in the viscosity and the zero shear viscosity in the Newtonian regime. The viscosity maximum in the shear thickening region, η_{max} of different samples increases as nanoparticle concentration, C_N, is increased. However, a Newtonian regime is absent for the samples with intermediate C_N. This is the signature of rheopectic phenomenon, i.e., the slow increase in viscosity with time when a fluid is subjected to shear at a constant shear rate. Rheopexy in the pure micellar solution is the result of a continuous kinetic coagulation process during which long micelles or large micellar structures are formed. To examine the effect of NP addition on rheopectic behavior, we performed Peak Hold experiments on samples with 0.1 *wt*.% Ag in which the shear rate was held at a constant value over a certain time period and the viscosity was measured as a function of time. As the shear rate was increased from 0.01 to 0.1 s^{-1} the plateau viscosity increased indicating NP-micelle complex formation. As the shear rate was increased from 0.1 to 100 s^{-1}, the plateau viscosity decreased implying that NP-micelle bonds are prone to breakage at high shear rates. The time required to achieve the plateau decreased with increasing shear rate suggesting that the kinetics of SIS formation (due to NP-micelle self-assembly) is faster at higher shear rates. This may be due to the enhanced flow alignment-tumbling events of micelle fragments as well as increased rates of collision between NPs and micelles.

Micellar solutions with relatively large R, e.g., R = 0.4, are shear thinning viscoelastic fluids. Figure 3 shows the viscosity η as a function of the shear rate $\dot{\gamma}$ under steady shear flow. Under large deformations or at higher shear rates,

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η decreases as a function of $\dot{\gamma}$ due to flow alignment and breakage of the network structure. The zero shear viscosity η_0 of all the samples are also calculated by fitting the viscosity data obtained in the flow experiments to the Carreau model. We plot the calculated η_0 as a function of the nanoparticle concentration in weight percentage C_N in figure 3. It is apparent that there is a large difference between the experimental data and the predictions of the Stokes-Einstein theory for the effective viscosity of dilute hard sphere suspensions. This is an indication of the formation of micelle-NPs junctions. Under strong shear flow or at Weissenberg number, $We \equiv \lambda_r \dot{\gamma} > 1$ where λ_r denotes the fluid relaxation time, the network is strongly deformed and ruptured, causing shear thinning. The zero shear viscosity first increases as C_N is increased. After reaching a maximum value corresponding to a saturation of the NP-micelle network, the viscosity decreases with the addition of more NPs.

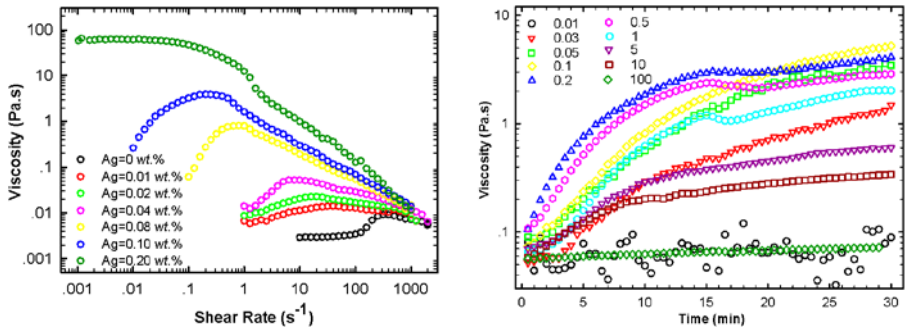

Figure 2: (Left) Log-log plot of viscosity vs. shear rate for C_D = 0.05 M and R = 0.30 with different concentrations of Ag NP addition. (Right) Plot of viscosity vs. time for R = 0.30 and C_N = 0.1 *wt.*% at different shear rates in Peak Hold experiments.

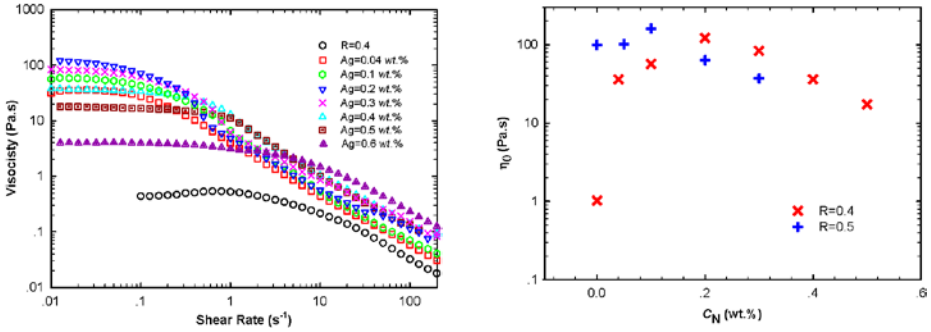

Figure 3: (Left) Log-log plot of viscosity vs. shear rate for C_D = 0.05 M and R = 0.40 with different concentrations of Ag nanoparticle addition. (Right) Plot of zero shear viscosity vs. shear rate for C_D = 0.05 M and R = 0.40 & R = 0.50 with different concentrations of Ag nanoparticle addition.

MOLECULAR DYNAMICS SIMULATIONS

We applied Molecular Dynamics (MD) simulations to study the mechanisms contributing to the rheological and structural properties of the plasmonic nanogels. The relevant time and length scales are on the order of μs to ms and several 10 nm respectively. Hence, atomistic MD simulations of such systems which consists of $O(10^5)$ atoms are computationally infeasible. Hence, we have developed coarse grained (CG) MD simulations, capable of representing the chemical details of surfactant, salt, NPs and also explicit solvent interactions based on the MARTINI force field framework.[3, 4] The results suggest that vesicular NP-surfactant structure can form stable bridges with cylindrical micelles through two mechanisms: end-cap opening and lateral attachment. Figure 4 below illustrates NP-micelle junction formation via the end-cap opening mechanism.

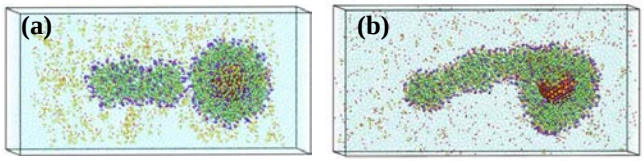

Figure 4: (a) Schematic of initial condition of simulation system. CTA^+ surfactant (green tails & purple heads) in the presence of sodium salicylate salt (salt to surfactant molar ratio of unity) adsorbs as a double layer on the negatively charged NP (orange) making a vesicular structure. (b) The vesicular structure forms an electrostatically stabilized junction with a CTAC micelle by an end-cap opening mechanism.

References

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