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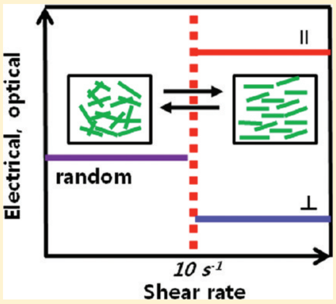
# Reversible Macroscopic Alignment of Ag Nanowires

Hu Zhou,[†] Patrick Heyer,[§] Ho-Jong Kim,[‡] Jung-Hoon Song,[‡] Longhai Piao,[*,†] and Sang-Ho Kim[*,†]

[†]Department of Chemistry, Kongju National University, Chungnam, 314-701, Korea
[§]Anton Paar Germany GmbH, Helmuth-Hirth-Str. 6, D-73760 Ostfildern, Germany
[‡]Department of Physics, Kongju National University, Chungnam, 314-701, Korea

S *Supporting Information*

**ABSTRACT:** The macroscopic arrangement of one-dimensional nanowires (NWs)/nanorods is crucial for many technological applications, because of their structure-dependent physical properties. Using a simple flow-induced alignment method, reversible structural changes between aligned and random states were demonstrated in Ag NW suspensions. The alignment of the NWs was induced under high shear rates and was stable for at least 6000 s, because of depressed Brownian motion. An aligned Ag NW suspension could return to its original random state under low shear, because of the rotation of the Ag NWs. The practical implications of flow-induced alignment are shown through the dielectric, electric, and optical properties of the dispersions. Although the alignments were not perfect, these properties still exhibited marked direction dependence. It is remarkable that the macroscopic, reversible structural change between aligned and random states and the related changes of physical properties can be easily scalable to large areas for many potential applications.



**KEYWORDS:** Ag nanowire, alignment, rheology, printing, electrical and optical properties

## INTRODUCTION

Rheology examines bulk phenomena, but it reflects microscopic variables.[1−4] For example, the rheological behavior of polymers, such as the frequency dependence of shear moduli, is strongly influenced by the polymer chains' interactions with each other and with the solvent.[1,2,4] Therefore, modification of the molecular interactions of colloidal suspensions can be reflected as a change of frequency dependence. Such control over bulk rheological properties has been studied with the aim of aligning custom fillers, such as glass fibers[5] and magnetic particles.[6] Work with custom fillers has demonstrated great potential for generating structures of nanomaterials with alignments reaching macroscopic levels. Another method of creating aligned structures is self-assembly,[7,8] where spontaneous organization of molecules occurs either directly, through specific interactions between molecules, or indirectly, through interaction with their environment. However, self-assembly is often limited by thermodynamics and dynamics, with macroscopic structures taking impractical amounts of time to form and such arrangements often only form at microscopic, rather than macroscopic, levels.[9] Therefore, rheological control through flow phenomena is favorable for creating macroscopic arrangements of nanomaterials.

Unlike isometric fillers, one-dimensional (1D) particles can strongly affect the rheological behavior of suspensions, even at the very low loading, because of their large aspect ratios.[10] Suspensions of custom 1D fillers, such as glass or carbon fibers, have been widely studied, and their main rheological behaviors are physically well understood.[11] However, rheological study of NW/nanorod suspensions is less common. These nanomaterials are hybrids of filler and nanoscale additives. Their lengths are macroscopic, while their cross-sectional dimensions remain close to molecular scales, and therefore they have potentially variable rheological behaviors.

Carbon nanotube (CNT) suspensions have gathered recent research interest for their unique rheo-optical behavior based on their alignment under simple shear flow.[12−14] However, their flexibility (afforded by extremely large aspect ratios) makes aligning CNTs under shear flow difficult as they easily overlap and aggregate.[13,14] Ag NWs, unlike CNTs, are rigid and do not tangle easily, making them a good model system for macroscopic assembly studies. They also have potential uses in many electronic devices, because of their high electrical conductivity.[15,16]

This paper reports the bulk rheological properties of Ag NW suspensions, with respect to their molecular interactions. These rheological properties were used to control macroscopic arrangements of NWs and their resulting physical properties. Specifically, aligned structures form under intense shear, which can be reversibly controlled by different shear rates. The practical implications of flow-induced alignment are shown through the dispersions' dielectric, electric, and optical properties having significant structural dependency. Since Ag NWs have high aspect ratios (>50) and mechanical rigidity, they can be aligned in structures with length scales reaching macroscopic (greater than millimeter size) through rheological control. Therefore, the potential applications of alignments of Ag NWs controllable at macroscopic levels are

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likely to increase as the understanding of macroscopic arrangements of nanomaterials improves.

## EXPERIMENTAL SECTION

**Material Preparation.** All the reagents were purchased from Sigma−Aldrich and used as received. Ag NWs were synthesized by polyol reduction of silver nitrate in the presence of PVP-55K (55 000 g/mol).[17] Ag NW suspensions were prepared by adding PVP-360K (360 000 g/mol) in batches to ethylene glycol (EG) suspensions of Ag NWs. A more detailed description of the experimental procedure can be found in the Supporting Information.

**Measurement.** Rheological tests were performed on a Physica MCR 301 rheometer (Anton Paar Germany GmbH) equipped with 25-mm-diameter parallel plates set 1 mm apart. A separation of 0.3 mm was used in all the thixotropic experiments. Simultaneous rheo-dielectric tests were carried out on a Physica MCR 501 rheometer equipped with a P-PTD 200/56/DI (lower plate with Peltier temperature control and dielectric option) with an H-PTD 200. Parallel plates 25 mm in diameter and with a separation of 1 mm were used in all the simultaneous rheo-dielectric tests. Absorbance spectra were measured under ambient conditions, using a multichannel detector (Hamamatsu C10027-02), combined with an optical microscope (Olympus Model BX51WI). Optical microscopy images of the Ag NW dispersions were obtained using a microscope (Olympus Model JP/IX-71−22FL/PH, Japan) equipped with a camera. Screen printing was carried out by a commercially available screen printing machine (type GP-600FV, Dae Young Tech, Korea). The morphologies and sizes of the NWs were investigated by a Hitachi Model S-4800 field-emission scanning electron microscopy (FESEM) system at an acceleration voltage of 10 kV. Electrical conductivities were measured using a Keithley Series 2400 SourceMeter instrument equipped with a Probershop PE-4X mini probe station.

## RESULTS AND DISCUSSION

For suspensions of 1D particles, the effect of fillers often depends on their aspect ratio ($R$) and volume fraction ($\phi$). Hence, it is often useful to distinguish three concentration regimes: dilute ($\phi R < R^{-1}$), semidilute ($R^{-1} < \phi R < 1$), and concentrated ($\phi R > 1$), according to the Doi−Edwards model of monodisperse fiber suspensions, derived from the effect of steric repulsion on free rotation.[10] At sufficiently high concentrations, highly anisotropic rodlike particles have a strong tendency to form ordered nematic phases. Onsager[18] first explained that isotropic hard-rod suspensions will become unstable at $\phi R > 3.29$, forming an ordered nematic state due to steric effects. Study of the rheological properties of Ag NW suspensions and their structural changes under flow was undertaken on three thermodynamically stable dispersions of Ag NWs in EG: semidilute (**A**) and concentrated (**B** and **C**) (see Table 1; their stabilities are discussed in the Supporting Information).

The dispersions' rheological properties are shown in Figure 1. Amplitude sweeps were carried out to determine the dispersions' linear viscoelastic regions and deformation behavior. This involved the suspensions being subjected to an increasing deformation or strain at a fixed frequency, establishing their shear moduli ($G'$ and $G''$; see Figure 1a). $G'$ represents the "stiffness" or elasticity of the material and $G''$ is a measure of viscous resistance to deformation. The moduli of the concentrated Ag NW suspensions (**B**, **C**) decreased markedly under large strains. The decrease of anisotropic particles' shear moduli under large strains usually suggests alignment of the material in the direction of flow.[11] The semidiluted dispersion (**A**) had these moduli decrease only slightly under large strains. At the higher concentrations, Ag NWs overlapped greatly and could not move individually, because of their restricted free rotation space; whereas the semidilute Ag NWs were sufficiently far apart for relatively weak confinement of the particles' motion.[10,19] As a result, shear thinning was observed only in the concentrated region.

**Table 1. Ag Nanowire (NW) Dispersions**

| sample | weight fraction (wt %) | volume fraction, $\phi$ (vol %) | aspect ratio, $R$[a] | $\phi R$ | regime |
|---|---|---|---|---|---|
| **A** | 9.0 | 0.89 | 60 | 0.54 | semidilute |
| **B** | 45.0 | 4.30 | 60 | 2.58 | concentrated |
| **C** | 27.0 | 2.69 | 100 | 2.69 | concentrated |

[a] The average diameter of the Ag NWs was ca. 100 nm, and the average length of the Ag NWs was ca. 6 $\mu$m (ca. 10 $\mu$m in **C**).

Frequency sweeps were then undertaken (Figure 1b), in which dynamic frequency was used at a fixed strain amplitude. This determined whether the samples were more liquidlike or solidlike through the frequency dependence of the shear moduli in the linear viscoelastic regime.[20] Similar to the unfilled PVP solution, **A** showed terminal relaxation characteristics of $G' \approx \omega^{1.74}$ and $G'' \approx \omega^{0.94}$, while **B** and **C** had different dynamic responses of $G' \approx \omega^{1.36}$ and $G'' \approx \omega^{0.94}$. This implies that the Ag NW dispersions did not form a physical gel, because both shear moduli varied with frequency, even in the concentrated region.[3] The frequency dependency of the shear moduli of Ag NW dispersions is much different from those of CNT dispersions at high concentrations. In CNT dispersions, the flexible nanotubes can entangle with each other at high concentrations, forming gel-like structures.[3,14,21] Unlike CNTs, Ag NWs lack such flexibility and, therefore, do not mesh with each other. This difference suggests that the rheological behaviors and structure of Ag NWs should be quite different from those of CNTs.

The stabilities of these shear-driven structures were investigated through thixotropic experiments, which involved measuring time-dependent changes of moduli (Figure 1c) and viscosity (Figure 1d) in oscillatory and rotational modes, respectively. Small oscillations were applied to obtain $G'$ and $G''$ of the initial state (step I, Figure 1c). In step II, sudden high shear was applied to break the initial state. The progression of $G'$ and $G''$ with small oscillations then was monitored in step III, where the applied perturbation was in the linear response range and, hence, the microstructure's recovery to its original form was not influenced by the perturbations (it is thought that the recovery process is spontaneous and driven by thermodynamics). In this way, the development of $G'$ and $G''$ after the cessation of intensive shear could be observed, thus characterizing the temporal evolution of the microstructure. It was found that Ag NW dispersions barely recovered their moduli under oscillatory conditions, even after 6000 s. This suggests that the new structures were stable and were unlikely ever to return spontaneously to their initial state. This contrasts with the relaxation time of PVP chains of ca. 0.3 s, which shows that PVP solutions quickly recover under similar conditions. (See Supporting Information for the PVP experiment.)

The development of viscosity $\eta$ was measured in rotational mode (see Figure 1d). In step I, low shear rate was applied to obtain the initial viscosity. In step II, high shear was applied, followed by an interval where again a low shear rate is applied in step III. Note that, in step III, the perturbation was beyond the

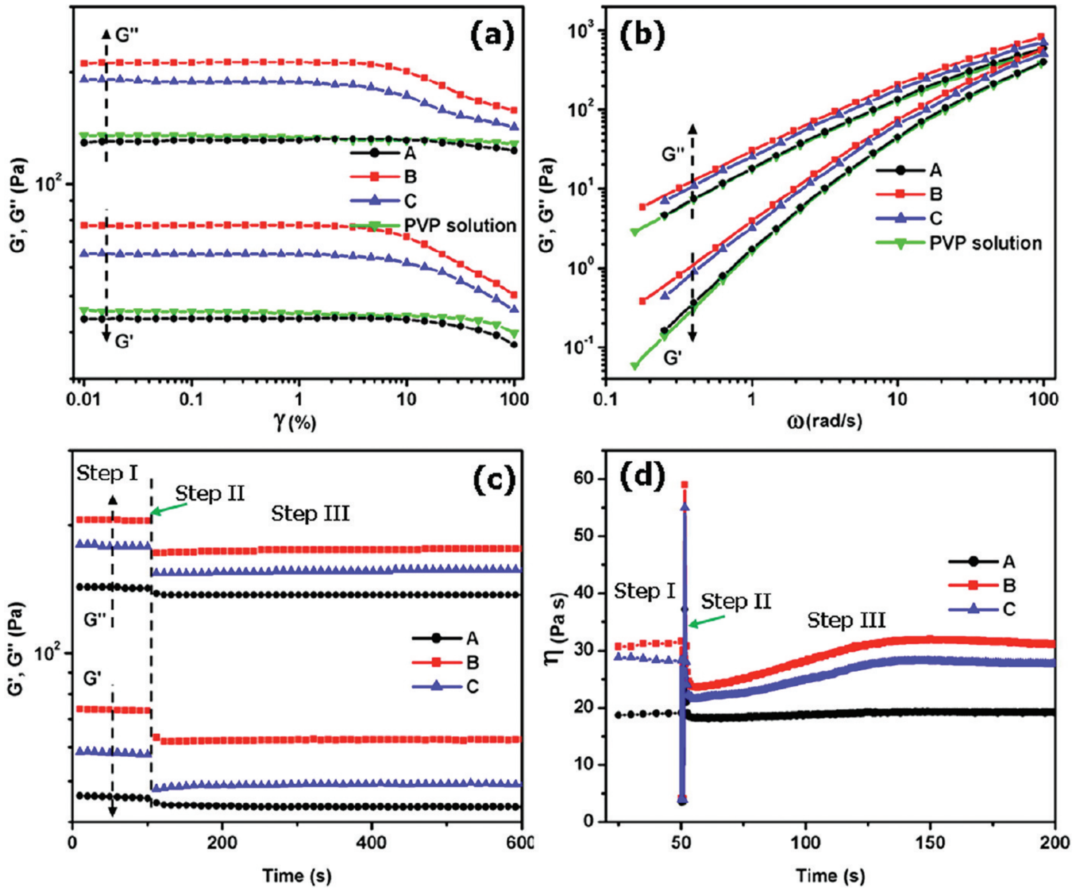

**Figure 1.** Rheological behavior of the Ag NW suspensions. The storage modulus ($G'$) and loss modulus ($G''$) of PVP solution and the Ag NW dispersions were measured as functions of (a) strain and (b) frequency. The recovery of (c) $G'$ and $G''$ and (d) viscosity ($\eta$), measured after the cessation of intense rotational shear, also are shown. In panel (d), the sudden increase of viscosity after the cessation of shear is thought to be the result of inertial effects.

linear range. Interestingly, the three dispersions showed slow recovery at low shear rates, whereas under simple oscillation (Figure 1c), no recovery at all was observed. The viscosities returned to the initial values after 90 s, suggesting the recovery of the original structure. Figure 1c shows that the orientated state formed after high shear did not spontaneously return. However, when the deformation was beyond the linear range (i.e., continuous low-rate rotational shear), the Ag NW suspensions could return to the original random state (Figure 1d). Therefore, two stable states, aligned and randomly distributed NWs, can be constructed and reversibly controlled by shear.

Then, the deformation−recovery of the concentrated dispersions (**B**) was examined by monitoring the shear moduli under an oscillation−rotation cycle. This experiment allowed re-examination of the reversible transition between the random and aligned states. More importantly, the corresponding physical structures of the Ag NWs were observed using an optical microscope. The rheological measurements in Figure 2a were performed as follows: in steps I, III, and V, small oscillations were applied to obtain the shear moduli of **B** after the cessation of the rotational shear (applied in steps II and IV). This measures the initial state in step I and the microstructure's evolution in steps III and V. In steps II and IV, continuous rotational shear was applied to break the prior state: high-rate shear was used in step II to obtain the aligned state and low-rate shear was applied in step IV to break it. The shear moduli decreased markedly from the initial state after the application of the high shear interval, they returned almost to their original values after the low shear interval, in agreement with the results in Figures 1c and 1d. After the high and low shear interval (points A and B in Figure 2a), samples of the dispersions were carefully transferred to glass slides for structural characterization. Since the recovery time for the Ag NW dispersions was found to be more than 6000 s, the structures were assumed to be unchanged during observation. Although it was not perfect, the optical microscope images (Figure 2a) show alignment of the NWs along the shear direction when intensively sheared and also the random structure after the low shear interval. These observations suggest that the decrease and recovery of the moduli and viscosities of the dispersions was ascribable to the alignment and disordering of the Ag NWs in flow fields. The critical shear rate of such a transition is found to be ca. 10 $s^{-1}$ (see section 9 in the Supporting Information). Interestingly, in sticky CNT suspensions, Hobbie et al.[14] also observed that the flow-induced aligned state becomes stable above the critical shear rate of ca. 10 $s^{-1}$. Although they intuitively believed that above the critical shear stress, there is sufficient force to break bonds between CNTs contacted through the overlap of neighboring Jeffery orbits. This similarity between these two markedly different systems suggests some universal role behind this transition, which warrants future investigation.

The rheological behavior is explicable through the structures of the dispersions. In the concentrated dispersions, randomly

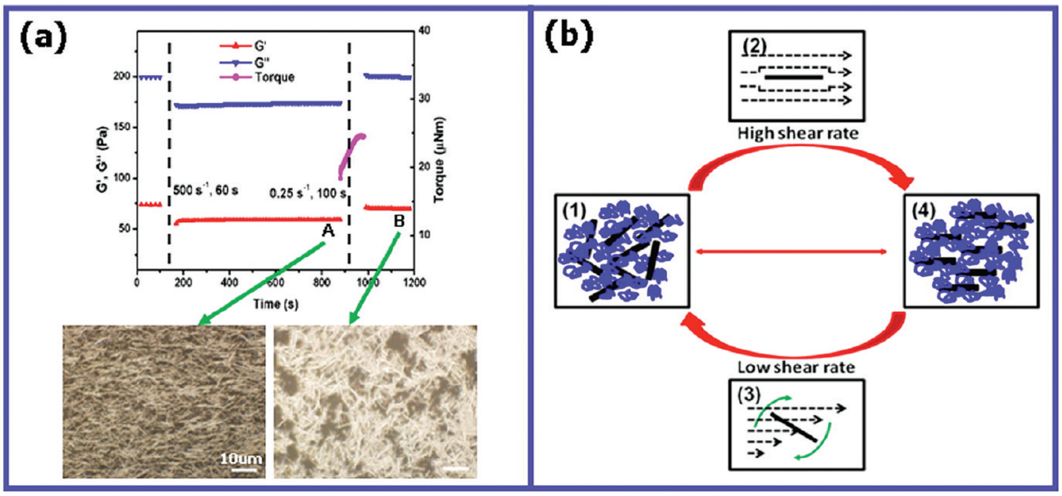

**Figure 2.** Shear-driven alignment of Ag NWs. (a) Storage moduli ($G'$) and loss moduli ($G''$) of **B**, as functions of time in the oscillation−rotation cycles, and optical microscope images from points A and B, respectively. (b) Reversible orientation and disordering of NWs or rods in a shear field. In panel (a), the duration of low-rate shear (100 s) was longer than the time (ca. 90 s) required for the full recovery of viscosity under rotational shear. In panel (b), insets (1) and (2) show the oriented and random states and insets (3) and (4) show the rotation and orientation of NWs and rods in a flow field.

oriented NWs strongly interacted because of their confinement[10,19] so that resistance to deformation under shear was great, resulting in high moduli and viscosity in the random state. In order to decrease such resistance, alignment of the NWs occurred under the intense shear, since the probability of two-body collisions decreased due to the extra translational free space.[18] Perturbations in the linear viscoelastic regime did not affect the structure of the Ag NWs, so their mechanical and rheological properties did not change. However, under sufficiently large strains and stresses, the structure was disrupted. As a result, reversible alignment and disordering of the Ag NWs was successfully undertaken by the introduction of shears (see Figure 2b).

Theoretical explanation of these observations can be found by characterizing the fluid flow. Generally, 1D fillers such as these Ag NWs, tend to align to minimize the resistance against a shear flow. However, the alignment can be strongly affected by the polymer matrix. Therefore, the dimensionless Weissenberg number ($Wi$, which is the ratio of the relaxation time of the fluid to a specific process time, $Wi = \dot{\gamma}\lambda$) was estimated for the polymer solution. PVP solutions were found to have $Wi$ values of 0.3−3 in the transition region of $\dot{\gamma} = 1{-}10\ \mathrm{s}^{-1}$. Generally, $Wi = 1$ is the threshold of anisotropy and orientation, with higher values indicating a predominance of orientation over isotropy.[22] The resulting $Wi$ value at high shear rates (e.g., $\dot{\gamma} = 10\ \mathrm{s}^{-1}$) therefore explain the alignment of Ag NWs as an extension of the PVP chains in a flow field would aid the alignment of the Ag NWs. The elastic effect caused by extension of the polymer chains could drive the alignment of the Ag NWs in the direction of flow, to decrease this effect.[23,24]

However, alignment always competes with thermal relaxation, with some aligned states not being maintained in some 1D suspensions. Relaxation can be characterized by the Peclet number, $Pe$ (defined as the ratio of the shear rate to the rate of particle reorientation by Brownian motion), and the Reynolds number, $Re$ (the ratio of inertial to viscous dissipation energies). The Peclet number can be estimated from the rotary diffusion coefficient of the Ag NWs:

$$Pe = \frac{\dot{\gamma}}{D_r}$$

where $D_r = k_B T \ln(R)/3\eta_s L^3$, $k_B$ is the Boltzmann constant, and $\eta_s$ is the shear viscosity of the matrix.[25] The large matrix viscosity and the highly extended nature of the Ag NWs make the Peclet number very large ($Pe = 10^5{-}10^7$), and the Reynolds number very small ($Re = 10^{-6}{-}10^{-3}$). As a result, Brownian motion of the Ag NWs is depressed so that the strong interactions between the Ag NWs can maintain the aligned state for a long time (remaining unchanged for more than 6000 s in this work). Therefore, Ag NW dispersions are not able to recover their previous structure spontaneously at an experimental time scale after intense shear.

Low shear rates, however, led to the disordering of the Ag NWs through their rotation. When the aligned Ag NWs were under a simple shear flow, asymmetric torque caused the 1D particle to rotate. Similar behavior is known from macrofibers in Newtonian and/or weakly elastic fluids, which always rotate along various Jeffery orbits under a low Reynolds number.[26] Therefore, the induced rotation of the NWs breaks the aligned structure and allows it to return to the initial random orientation.

Such stably aligned structures and reversible return to the random state are unique to Ag NWs. For molecular or polymer systems, aligned structures can be formed, but they relax quickly due to strong Brownian motion. However, for micro 1D particle arrangements, the aligned structures cannot be easily broken, because of weak Brownian motion. In Ag NW suspensions, Brownian motion is between the molecular and microparticle systems, so that the stable aligned states and the random states can be reversibly switched many times. Over 100 reversibility operations were tested in this work.

The collective electrical and optical properties of 1D nanomaterials, such as nanorods and NWs, can be greatly influenced by their orientation.[27] Therefore, structure-induced physical properties of the aligned and disordered Ag NWs were measured. The application of shear is simple and relatively easy, up-scalable, and therefore can potentially be used to induce tailored physical properties. Simultaneous rheo-dielectric measurements were performed on Ag NW suspensions to monitor the change of dielectric constant under shear. Simultaneous shear moduli and dielectric response measurements were taken (Figure 3) when

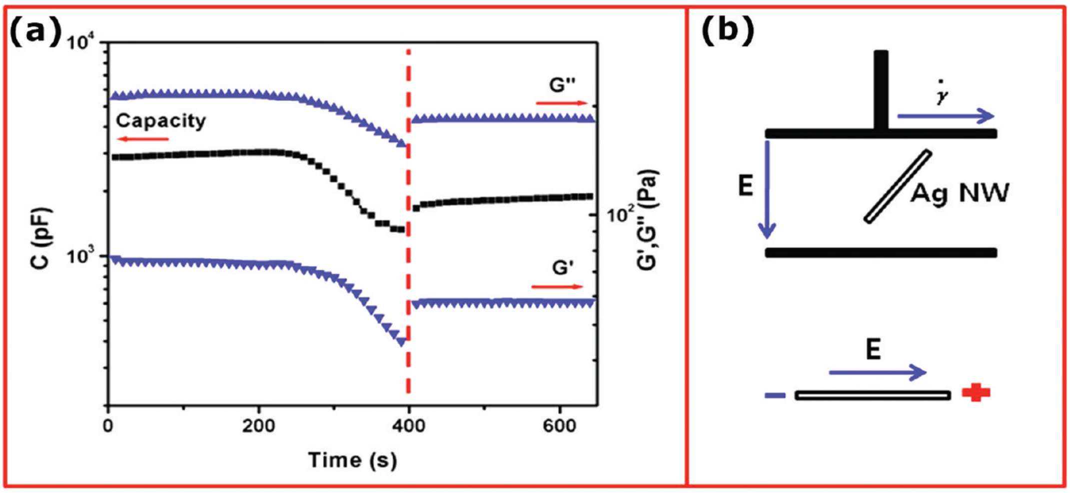

**Figure 3.** Simultaneous rheo-dielectric measurement of Ag NW suspensions: (a) *G*′ and *G*″ vs time measured from suspension **B** and (b) schematic diagram, where *E* is the electric field intensity.

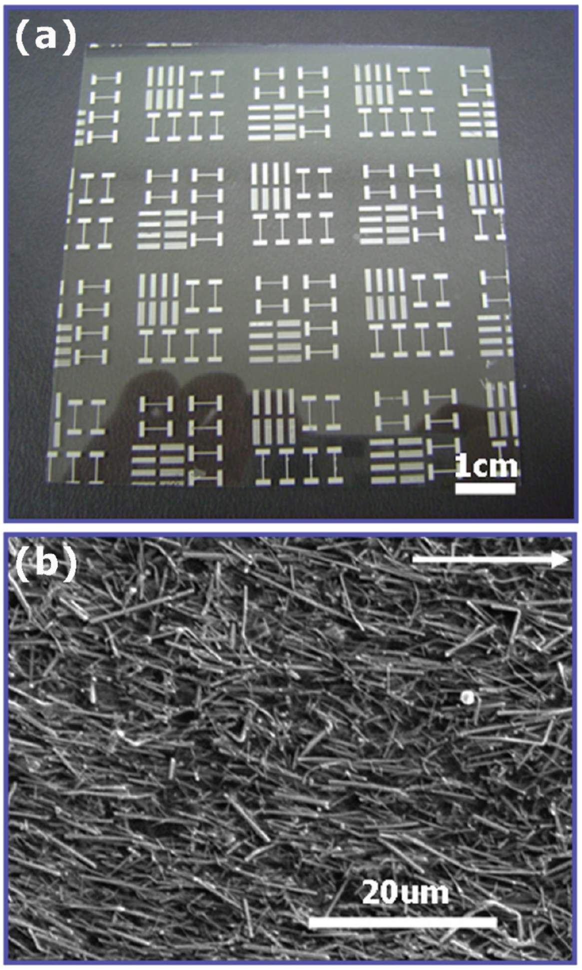

**Figure 4.** Screen-printed Ag NW electrodes: (a) photograph of silver electrode formed by screen printing Ag NW suspension **B** on a glass substrate and (b) SEM image of the printed electrode. The arrow denotes the printing direction.

sequential oscillatory shears were applied as shown in Figure 1c. As expected, the capacitance of the Ag NW suspension followed the changes of shear moduli; this strongly suggests that shear-induced structural changes of the Ag NWs were reflected in the suspension's dielectric response. In an electric field, Ag NWs covered with PVP and EG can act as highly effective dielectric materials.[28] Intuitively, the1D structure affords them the ability of changing the dielectric property with alignment. This is supported by later optical polarization experiments. Therefore, such similar changes happened in simultaneous rheo-dielectric measurements.

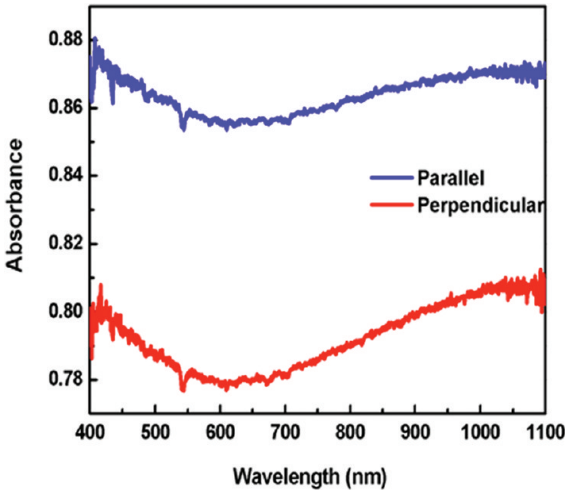

**Figure 5.** Typical optical absorption spectra with different polarizations from Ag NW dispersions after alignment. "Parallel" denotes along the alignment direction.

Shear-driven structural changes can also be reflected in the asymmetric conductivity of electrodes. Since screen printing involves high shear processes, Ag NW suspension could be effectively printed onto a substrate with their aligned state being formed in the printing direction. This was demonstrated by screen-printed Ag NWs forming electrodes with the Ag NWs aligned in the printing direction (Figure 4). Half of the electrode patterns were formed parallel to the printing direction and the other half, vertical. After the samples were dried at 150 °C for 30 min, the electrodes' series resistances were found to be ca. 100 Ω along the printing direction and ca. 10 kΩ perpendicular to it, i.e. a variation of 2 orders of magnitude as direction changed from parallel to perpendicular. Since Ag NWs are highly conductive along their length, this result supports the shear-driven alignment of Ag NWs. The resulting anisotropic electric properties are potentially useful in many electric devices, such as asymmetric conductive films (ACFs).

In addition to the dielectric and electrical properties of the shear-driven structural changes, optical properties were also investigated through the polarization of absorbance spectra (Figure 5). The shapes of the spectra did not show any specific difference with different polarizations. However, absolute absorbance was ca. 10% larger when the incident light was polarized parallel to the oriented direction. This was consistently observed in several samples, indicative of larger dipole−oscillator strength in the parallel direction[27] and consistent with the Ag NWs being oriented along the shear direction. This polarization dependency of the aligned Ag NWs is a good example of an NW polarizer.

## ■ CONCLUSIONS

Ag nanowire (NW) suspensions demonstrated reversible structural changes between aligned and random states. They exhibited strong shear thinning at high concentrations ($\phi R > 1$), because of the alignment of the Ag NWs. Their terminal relaxation behavior shows that the Ag NW suspensions did not form a physical gel (or disordered solid material) even at high concentrations; likely imputable to the stiffness of the Ag NWs, unlike flexible carbon nanotubes (CNTs). The alignment of the NWs was affected under high shear rates and was stable for at least 6000 s, because of depressed Brownian motion. Aligned Ag NW suspension could return to its original random state under low shear, because of the rotation of the Ag NWs. This interesting rheological behavior was explicable through the rheology of 1D particles. The stable alignment and reversible return to isotropy is unique to Ag NWs, which is attributable to the Brownian motion of nanometer-sized 1D particles. Collective physical properties of Ag NWs were also investigated. Although the alignments were not perfect, they displayed many interesting physical properties. Dielectric responses followed changes in the shear moduli, showing correlation with the structural transitions. Screen-printed electrodes consisting of Ag NWs also exhibited direction-dependent electric resistances. The absorption spectra of Ag NW films showed polarization dependency as predicted by NW polarizers. These macroscopic, reversible structural changes between aligned and random states and the related changes of physical properties are important, because this simple shear flow method can be used to form extended alignments of 1D nanomaterials, scalable to large areas, for many potential applications.

## ■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Formulation of Ag NW suspensions, SEM and TEM images of the Ag NWs, thermogravimetric analysis (TGA) of the Ag NWs and PVP, the dispersion stability of the Ag NW suspensions, the details about simultaneous rheo-dielectric tests, absorbance spectra measurement, rheological measurement, recovery of PVP solutions in the thixotropic experiments, recovery of Ag NW dispersions after application of various shear rates, and calculations about Reynolds, Peclet, and Weissenberg numbers. A description of the material is included. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*Tel.: +82418500455 (L.P.), +82418508492 (S.-H.K.). Fax: +82418568613 (L.P.), +82418568613 (S.-H.K.). E-mail: piaolh@kongju.ac.kr (L.P.), sangho1130@kongju.ac.kr (S.-H.K.).

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