Multi Responsive, Anisotropic Colloidal Mixture Using 2D α-ZrP Nanoparticles

P. A. N. S. Priyadharshana, Seung-Ho Hong, Jang-Kun Song*
Department of Electrical and Computer Engineering, Sungkyunkwan University, Suwon, Gyeonggi-do, Korea[1]
*jk.song@skku.edu

Abstract- The electric field-assisted orientation of colloidal nanoparticles has attracted significant attention in recent years, mostly due to its operational simplicity. However, this alignment is only temporary and gradually disappears after the removal of the electric field. Essentially, polymer-hybrid nano systems make it easier to achieve well-ordered permanent structures even under termination conditions. However, reversible stabilization of the structure is still a challenging goal for energy-saving stand-alone devices with structural switching capability. To begin with, we synthesized a dual responsive anisotropic hydrogel by dispersing an aqueous solution of exfoliated α-ZrP nanosheets with Pluronic F-127. The temperature-dependent sol–gel-sol phase transition behavior of Pluronic provided an excellent thermosensitive characteristic to the composite hydrogel mixture. Moreover, the embedded ZrP nanosheets endow the hydrogels with electrical responsiveness at their sol state, which could be aligned under high-frequency electric fields. Stabilization of nanoparticles with proper alignment was achieved at a non-flowable gel state, by increasing the temperature above the sol-gel transition temperature. Upon increasing and/or decreasing the temperature from the gel state, the electric alignment completely disappeared in a reversible manner due to the gel-sol transition

Keywords: liquid crystals, Polymer colloid, multi stimuli responsive

I. Introduction

Two-dimensional (2D) materials have been drawing immense attention for the fabrication of electronics and optoelectronics devices in the field of academic research due to their extraordinary and unique properties. [1,2] In nature they exist in bulk layered phase, where the monolayers are hold together by the van der Waals forces, and single layer flakes can be obtained by mechanical exfoliation. The exfoliated nanosheets are usually obtained as colloidally dispersed particles and due to this particular 2D shape specifically they can exhibit lyotropic liquid crystal (LC) phase behavior. Unlike the conventional LCs, colloidal LC can be selectively and easily mixed with polymer colloidal mixtures when they have a common solvent. The α- zirconium phosphate (α-ZrP) is an inorganic 2D material which can exhibit the lyotropic liquid crystalline properties in aqueous solution, owing to their anisotropic shape. Similar to the conventional LC, orientational direction of these nano particles can manipulate using AC electric fields. However, lack of multi responsive nature of colloidal mixtures have produce several restrictions on industrial applications of colloidal-based opto-electronic devices. In this study, we introduce a novel method to enhanced the intrinsic electro optical properties of α-ZrP nano colloidal mixture by simply mixing with PF-127; hereafter simply referred to as ZPF colloid. Aqueous Pluronic F-127 (PF-127) is a well-known triblock copolymer which can exhibit reversible sol-gel-sol phase transition characteristics in response to external temperature variations. Interestingly, we were able to graft the unique thermal properties of polymer colloids into nano colloidal LC in order to obtain multi responsive nature. Moreover, we supposed to control the nanosheets orientation of ZPF colloids (at their sol state) by electric fields over a tunable range of temperature as one of the most significant features of our technique.

II. Materials and Methods

Two dimensional, layered α-zirconium phosphate (α-ZrP, [Zr(HPO4)2·H2O)] nanoparticles were synthesized via a hydrothermal method. The nanoparticles were functionalized using tetrabutylammonium hydroxide (TBAOH), and a stable colloidal was obtained by mixing with deionized (DI) water. The top image (TEM) of fig. 1(a) revealed the stratified nature of the obtained α-ZrP nano particles with an irregular hexagonal shape. This particular shape induced the LC properties to the α-ZrP colloidal mixture (in DI water) which can easily observe through two cross polarizers as shown in the bottom image of fig.1(a). A set of thermo-sensible ZPF colloidal mixtures were prepared using different concentrations of PF-127 (10–25 wt %.) at a fixed total formulation concentration of α-ZrP (0.44 wt%.) by simply mixing the exfoliated α-ZrP and PF-127 powders in an aqueous medium at 0 °C. [3] The thermo-responsive behavior of pure PF-127 colloidal mixture and ZPF colloidal mixtures were studied by means of the tube inversion method. The temperature-dependent sol-gel-sol transition phase diagrams for both colloidal mixtures at various polymer concentrations are shown in Fig. 1(b).

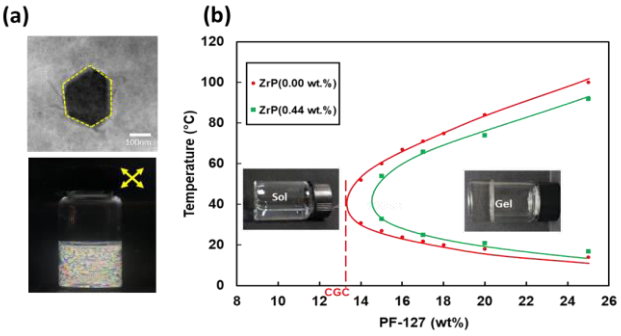

Fig. 1 Material characterization (a) TEM image of ZrP monolayer platelets after exfoliation (top) and LC phase behavior under cross polarizers (bottom) (b) Sol-gel-sol phase diagrams of prepared hydrogels at given α- ZrP concentrations

II. Results and Discusssion

In general, Pluronic in aqueous solution is undergoes a sol-gel-sol transition, that occurs via construction and destruction of small sets of micellar structure that correspond to the temperature increment. Essentially, for the composite ZPF hydrogel mixtures, while adding the α-ZrP nano particles, exhibited slightly different phase transition curves with a shift to the right along with a narrowing of the gelation temperature range, compared to the PF-127 only hydrogel. The critical gelation concentration (CGC) values of the ZPF colloidal mixtures with α-ZrP concentrations of 0.44 wt %. were ~15 wt %, which numbers are slightly higher than for the PF-127 hydrogel (~13 wt%%., labeled in red dash-dotted line.). The presence of α-ZrP nanoparticles in the medium possibly perturbs both the packing density and integrity of the well-ordered micellar networks of the ZPF hydrogel mixtures. The right shift of the phase transition curves indicates that the addition of α-ZrP nanoparticles effectively increases the CGC values as it requires a higher polymer concentration to complete the gelation process. Consequently, the CGC and the gelation temperature range were significantly altered depending upon the α- ZrP concentration.

The orientation of the nano sheets in both ZPF composite (at sol state) and pure α-ZrP samples can highly and facilely control by utilizing square wave AC electric fields. A cell with patterned electrodes was prepared by assembling two indium tin oxide (ITO) electrodes with a 5 mm inter-electrode gap and 1mm cell gap was utilized to control the nano particle orientation (fig. 2(a)). Under the application of 10 kHz; 100V square wave electric field, long axis of the α-ZrP nano particles tend to align parallel to the electric field and it can be easily observed by placing the cells between two crossed polarizers. However, as can be seen in the fig. 2(b), the electrically induced alignment of the nano sheets is gradually disappeared after removal of the electric filed within a few second in the cells filled with α-ZrP samples and the ZPF samples which have a low polymer concentration (below their CGC).

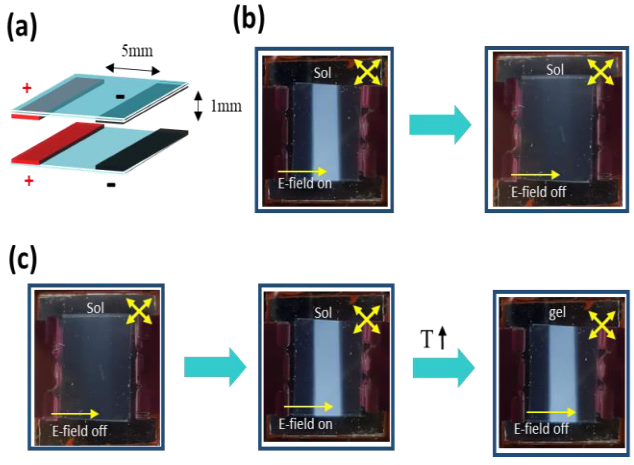

Fig. 2. Multi responsive nature (a) Electrode configuration of ITO cell (b). Electrically induced alignment of α-ZrP nano colloid (c) Electrically induced alignment of ZPF nano colloidal mixture at their sol and gel states.

In addition, the samples at a higher polymer concentration (above the CGC) still follow a relaxation of the induced alignment with the termination of electric field, especially at their sol state. Nevertheless, the ZPF hybrid mixtures at a higher polymer concentration (above their CGC) facilitate to maintain the obtained alignment in between the sol-gel phase transition temperature (T_{sg}) and ge-sol phase transition temperature (T_{gs}). Accordingly, we examined the stabilization of α-ZrP nano sheets by using a polymerizable mixture of ZPF hydrogel, prepared by mixing 0.44 wt%. of α-ZrP with 17wt%. of PF-127. As illustrated in the fig. 2 (c) alignment of the composite mixture was able to maintained under retention of the electric filed by using the self-assemble temperature-induced gelation mechanism in between 35°C and 80°C. Interestingly, this temperature region can easily control by altering the PF 127 concentration according to the phase diagram which illustrate in fig.1(b)

IV. Conclusion

In conclusion, we have introduced a new type of dual responsive anisotropic hydrogel from an aqueous solution mixture of exfoliated α-ZrP nanosheets and Pluronic F127. The vial inversion tests were carried out for PF-127 only and the ZPF hydrogel was examined for its thermo-reversible gelation behavior. High (10 kHz) frequency alternating electric fields were used to control the α-ZrP nanoparticles in the ZPF hydrogels. Stabilization of alignment was achieved through the sol-gel phase transition of PF-127 copolymer. The nanosheet alignment was retained for more than two weeks between the T_{sg} and T_{gs} even after the termination of the electric field. Our study further confirms that PF-127 concentrations is vital factors for controlling the T_{sg} and T_{gs} values.

Acknowledgements

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