Real-Space Visualization of Charged Polymer Network of Hydrogel by Double Network Strategy and Mineral Staining

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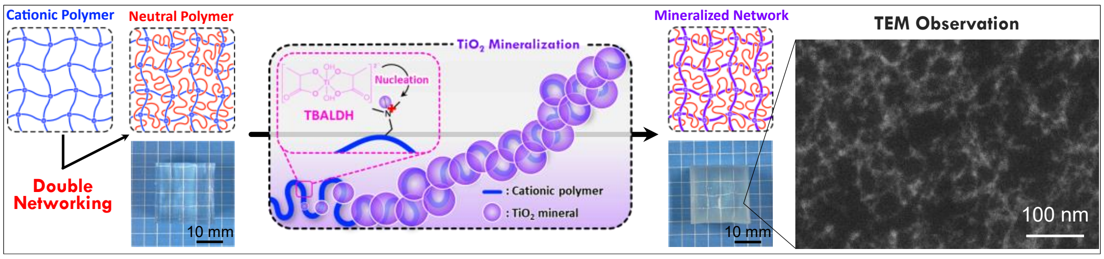
Keywords: Mineral staining; Transmission Electron Microscopy; Hydrogels; Nanostructure

Hydrogels consist of three-dimensional polymer networks and water, and the network structure affects their physical properties. Synthetic hydrogels inevitably possess a hierarchical inhomogeneous network structure, and specific properties, such as fracture and subsequent crack propagation, strongly depend on the "local" structure. Thus, the local structure is essential for predicting such a phenomenon, and ideal techniques for analysis are required. Among the methods for structural analyses of hydrogels, the real-space imaging of a polymer network of hydrogel on a nanometer scale is one of the optimal ones; however, it is highly challenging. A well-known technique to enhance the electron density is electron staining with heavy element compounds such as uranyl acetate[1)] and phosphotungstic acid.[2)] However, synthetic polymer strands are thin, flexible, and susceptible to aggregation during staining or resinification. Then, the structural information at the mesh size scale is lost during sample preparation.

In this study, we propose a direct observation technique for cationic polymer networks using transmission electron microscopy (TEM). By combining the double network strategy and a TiO_2 mineral staining technique, we overcame the polymer aggregation and the low electron density of the polymer. An objective cationic network was incorporated into a neutral skeleton network to suppress shrinkage during subsequent staining. Titania mineralization using titanium bis (ammonium lactate) dihydroxide along the cationic polymer strands provided sufficient electron density for the objective polymer network for TEM observation.[3)] This observation technique enables the visualization of local structures in real space and is complementary to scattering methods for soft matter structure analysis.



Scheme 1. Strategy of the present study.

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