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Exploring the toughening behavior of double network gels using TEM

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Double network hydrogels (DN gels) consist of a hard, brittle 1st network and a soft, stretchable 2nd network, resulting in exceptional strength. Their high toughness is attributed to the sacrificial bond theory: the first network fractures preferentially, while the second network suppresses crack propagation by stretching. However, nanoscale local deformation mechanisms of the networks remain unclear. Nanoscale characterization techniques such as transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) face challenges when applied to DN gels. In TEM, low electron density of polymer chains makes them indistinguishable from the background. SAXS enables direct analysis of bulk gels without complex preparation, providing average structural information, but dominance of the second network obscures first-network-specific information.

To address these limitations, we developed a targeted electron-staining method: iron oxide nanoparticles were selectively grown on the polyelectrolyte first network, enhancing its electron density for both TEM and SAXS (Fig.1). This approach enabled dual-space structural analysis—real-space imaging (TEM) and reciprocal-space quantification (SAXS).

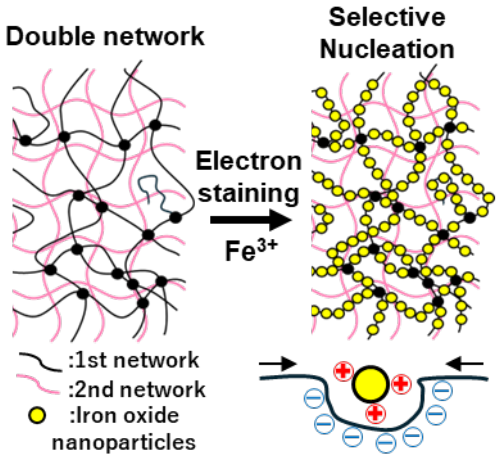

Figure 2. Selective staining method of DN gel for TEM/SAXS observation.

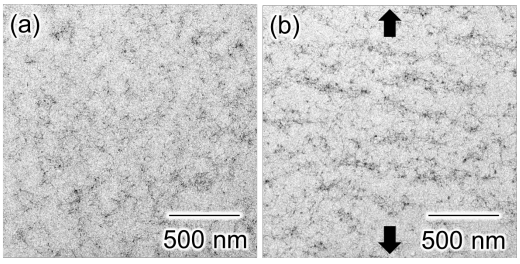

Figure 1. TEM images of DN gel (a) without stretching and (b) stretched to necking region. Tensile direction is shown as arrow.

In unstretched DN gels, no structural deformation was observed (Fig.2(a)). Upon yielding, however, aligned stripe-like domains with widths of 100–200 nm emerged perpendicular to the tensile direction (Fig.2(b)). SAXS analysis revealed anisotropic scattering profiles, with a pronounced intensity increase along the stretching axis, consistent with the TEM-observed fracture patterns. Strikingly, Fourier transforms of the TEM images exhibited anisotropy ratios matching the SAXS data, confirming that the nanoscale fracture architecture is representative at both real-space and reciprocal-space levels. Furthermore, the anisotropic swelling behavior of the yielded gel correlated with these nanoscale fracture patterns, linking macroscopic properties to nanoscale architecture.

References

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