

Study on Viologen-Incorporated Hydrogel and Its Redox-Driven Deformation

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Among many hydrogels that show reversible deformation in response to external stimuli, redox driven hydrogels are of particular interest, because quick and reversible redox reactions give fast and large-amplitude deformation of the gels and find applications for artificial muscles and actuators. When using polymer-based hydrogel actuators, their deformation is frequently limited by the inefficient transmission of the redox driving force throughout the gel. Reversibility and quickness of the deformation are the keys to realize a flexible and self-directive motility of a molecular robot that is composed of a gel actuator. In general, to accelerate electron transfer fast and wide in the gel electric conductive fillers are used. To attain such redox-driven deformable hydrogels as actuators, incorporation of electronic conductive polymers, conductive fillers, or high density reversible redox sites should be most effective. Extensively investigated deformable redox driven hydrogel contains ferrocene, hydroquinone, or viologens. Some of them are combined with photo-excitation induced redox reactions.

A deformable molecular robot may be directly placed on an electrode surface in water, on which direct electron transfer processes can readily drive the redox actuation of the gel. We imagine an ameba-like gel crawling on a solid electrode surface. The electrode

surface plays two roles: (i) energy supply to attain fast, reversible, and repeatable locomotion with a large amplitude and (ii) fine and precise regulation of the movement.

Using a viologen unit as the key redox site to give the targeted motion, we designed viologen pendant poly-*L*-Lysine based glutaraldehyde cross-linked hydrogel (PLLV-GA-gel, Fig.1). The core design is the mechanism of contraction upon reduction of viologens and re-expansion upon reoxidation. One-electron reduction of a viologen dication (V^{2+}) to viologen radical cation ($V^{\bullet+}$) induces the stacking of $V^{\bullet+}$ units and desolvation from the viologen sites. The stacking process to form $V^{\bullet+}$ dimers hauls the polymer chains to entangle them and accelerates inter-site electron transfer processes. Simultaneously, the desolvation process drains water from the gel. A decrease of positive charges on viologens upon reduction results in the reduction change of osmotic pressure and helps water egress from the gel. All these changes upon reduction contribute to the

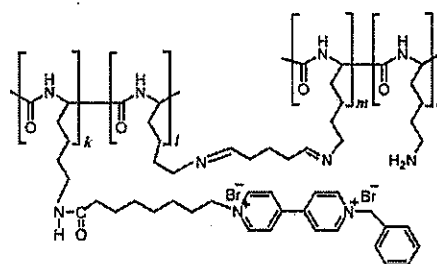


Figure 1. Structure of PLLV-GA-gel.

contraction of the hydrogel. On the other hand, oxidation of V^{+} to V^{2+} induces electrostatic repulsion of V^{2+} and contributes to re-expansion of the hydrogel.

This thesis consists of seven chapters. Introduction to this doctoral dissertation research is given in Chapter 1. Chapter 2 contains experimental methods including synthesis of PLLV-GA-gel, video recording of deformation by chemical redox as well as the measurements of cyclic voltammograms (CVs), electroreflectance (ER), and surface-enhanced Raman scattering (SERS) spectra.

In Chapter 3, I focus on the characterization of PLLV-GA-gel by CVs and ER measurements. The surface and the cross-sectional surface structures of the gel were observed by scanning electron microscopy. The UV-vis absorption spectra of precursor viologen-pendant PLL (PLLV) with an excess of sodium dithionite in phosphate buffer solution indicated dimer rich features, whereas the viologen solution as pendant site did monomer rich features. The deformation of the gel by redox chemicals and by redox-inactive salts was demonstrated.

Chapter 4 shows the further characterization of PLLV-GA-gel by Fourier-transform infrared spectroscopy, Raman scattering spectroscopy, elemental analysis, electron spin resonance. Estimation of viologen concentration in the gel from the pendant rate and the dimer content is also shown.

In Chapter 5, I describe the implication of SERS data in terms of heterogeneity and dimerization of V^{+} forms. In situ SERS measurements revealed the state of PLLV-GA-gel in the vicinity of the interfacial region at a Au electrode surface with a focus on the position-specific micro-environment under redox control. Because the actuation of the gel is driven by dimerization of V^{+} -forms, regulation of the V^{+} -dimer content in the gel is one of the keys for the gel actuator to be designed at will.

Chapter 6 shows the optimization of the viologen pendant rate and the effects of cross-linking structure and viologen unbound gel. The deformation was largely affected by the pendant rate, cross-linker, and the way of viologen attachment. The structures played an important role in deformation. In addition, the effects of incorporation of conductive fillers, gold nanoparticle, graphene nano-platelet, and single-walled carbon nanotube and as well as the impact of the incorporation of an anionic polymer, poly(styrene sulfonate) are also shown. The conductive fillers are expected to form electron transfer pathways especially when the shrinkage of the gel shortens the mutual distance between the fillers. The incorporated PSS may partly convert the anion egress/ingress to cation egress/ingress accompanied by water drain/uptake due to the osmotic pressure difference originated by the redox of viologens in the PLLV-GA-gel.

In Chapter 7, I conclude this thesis with a summary of PLLV-GA-gel and the achievement in the experimental works. Perspectives are also described.