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Simple and precision design of porous gel as a visible indicator for ionic species and concentration

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Here we report the design and synthesis of a novel porous gel for an ionic visible indicator. The rapid-responsive porous gel which reveals color changes depending on a potassium ion concentration was prepared using a templating technique.

Porous materials are of great interest because of their high specific surface area.[1] In particular, materials which possess an interconnecting porous structure have a potential for use as catalysts and molecularly recognizable materials. The omni-directional, interconnecting pores allow for the diffusion of solutes into the pores. If such a porous material having a well-ordered and periodic structure can be made on the submicron length scale, they will have a strong potential for controlling visible light.[2] We call such materials that possess a periodic index of refraction “photonic crystals”. Since the color tone is due primarily to three dimensional fine structures formed in the material, the color is often referred to as “structural color”. The periodically ordered porous gels created by a templating method using closest-packing colloidal crystals as templates also act as “photonic crystals” (Scheme 1).[3] These gels are rapidly tunable photonic crystals depending on changes in their environment: the structural color can be changed quickly with the swelling ratio of the gels because the interconnecting porous structure allows the solvent to diffuse more rapidly into/out of the gels. Many gels will undergo reversible volume changes in response to change in pH, anionic strength and organic compounds.[4] Thus, these structural colored porous gels have a potential use as rapid-responsive visible indicators of chemical species in solution. Here we report the design and synthesis of a novel porous gel as a visible indicator for a specific ion in aqueous solution.

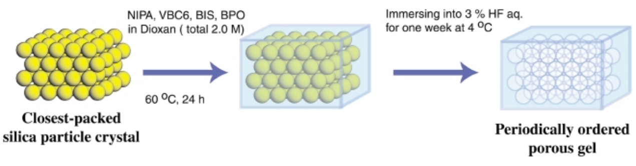
“The structural color” of periodically ordered porous gels can be well described by combining Bragg’s law with Snell’s law.[3] The spectral position of the peak of the reflection spectra, λ_{max}, can be found from:

$$\lambda_{max} = 1.633(D/m)(d/d_0)(n_a^2 - \sin^2\theta)^{1/2} \quad (1)$$

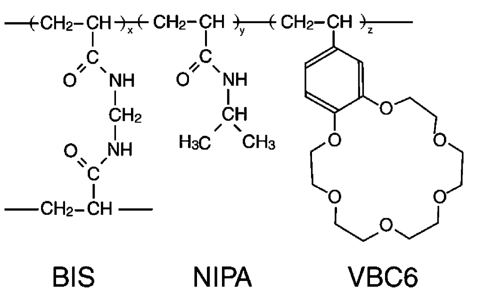
where D is the sphere diameter of the silica colloidal particle, m is the order of Bragg diffraction, (d/d_0) is the degree of swelling of the gel (d and d_0 denote the diameters of the gel in the equilibrium state at a certain condition and in the reference state, respectively), n_a is the average refractive index of the porous gel at a certain condition, and θ is the angle of incidence. The swelling ratio can be estimated by monitoring the diameter of a cylindrical gel prepared in a glass capillary having a certain inside diameter. In this case, d_0 is the inside diameter of the capillary. The average refractive index is given by $(\Sigma_i n_i^2\phi_i)^{1/2}$, where n_i and ϕ_i are the refractive index and the volume fraction of the i-component respectively. Since the change in n_a is negligible for thermo-sensitive porous gels composed of *N*-isopropylacrylamide (NIPA) when the volume of the porous gel is varied, λ_{max} of the porous gel made from a closest-packing colloidal crystal composed of a certain size of silica colloidal particle is attributed mainly to the swelling ratio for normal incidence (*i.e.*, $\theta = 0$).

Based on the above, it is technically possible to prepare a porous gel reflecting a specific color at a certain condition by controlling the amount of the monomer and the cross-linker in the pre-gel solution, because the swelling ratio of a gel at a certain condition can be changed by the components of the gel.[3c] Moreover, the swelling ratio can be controlled by the species and the amount of co-monomers for the gel.[4] To demonstrate the desired properties, we carefully selected the monomer species, their concentrations and the ratio, the concentration of cross-linker, and the diameter of silica particle in order to make a porous gel.

To prepare a gel which can change its swelling ratio depending on the concentration of a certain ionic species, we used the crown derivative vinyl monomer, 4-vinylbenzo-18-crown-6 (VBC6) (Scheme 2) as a co-monomer. This type of crown ether can form a complex with a potassium ion and act as an ionic species, because the counter ion for the captured potassium ion, such as chlorinate ion, dissociates in aqueous media. Thus, the gel composed of NIPA and VBC6 increases its volume with the concentration of potassium ions, which is caused by the positive internal osmotic pressure of the counterions. First, the ion-sensitive and thermo-sensitive gels were prepared by free-radical polymerization as follows: NIPA (2.034 g), VBC6 (0.762 g), *N,N′*-methylenebisacrylamide (BIS) (0.102 g) as a cross-linker, and benzoylperoxide (BPO) (9.7 mg), the initiator, were dissolved in degassed and nitrogen-saturated 1,4-dioxan to a final volume of 10 ml. The polymerization was conducted at 60 °C for 24 h. The resulting gel was washed carefully with distilled water for 1 week. Measurement of the degree of swelling was carried out by monitoring the diameter of a cylindrical gel in aqueous solutions. The variation of the swelling ratio with the potassium ion concentration can be observed at lower temperatures (Fig. 1a,c). However, the addition of sodium ions does not affect the swelling ratio of the gel (Figs. 1b,c). This is because the logarithm of binding constants between 18-crown-6 derivatives and potassium ions in aqueous solution is about 2, while those between 18-crown-6 derivatives and sodium ions are < 1.[5]



Scheme 1 Preparation of a periodically ordered interconnecting porous gel using a closest-packing silica colloidal crystal as a template.



Scheme 2 Chemical structure of Poly(NIPA-*co*-VBC6) gel.

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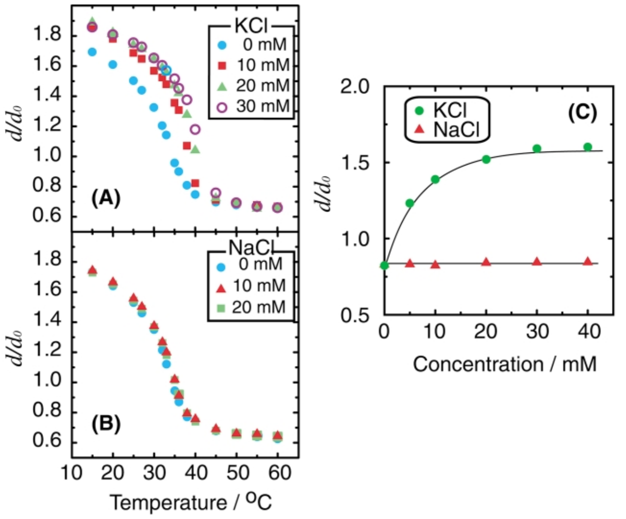

Fig. 1 Degree of swelling of poly(NIPA-*co*-VBC6) gel (total monomer conc. is 2 M, NIPA : VBC6 = 9 : 1, BIS 67 mM) as a function of temperature in aqueous solution containing various concentrations of NaCl (A), and KCl (B). (C) Degree of swelling of poly(NIPA-*co*-VBC6) gel as a function of salt concentration at 36 °C.

Subsequently, the periodically ordered porous gel created by a templating method using a closest-packing colloidal crystal as a template was prepared by using the same recipe as the bulk gel. The closest-packing colloidal crystal was fabricated by silica sphere particles of 210 nm in diameter. The growth of the crystal has already been reported.[3] The reflection spectra were obtained by means of an Ocean Optics USB2000 fiber optic spectrometer. The temperature in the measurements was controlled using a circulating water temperature control system.

Fig. 2 shows the photographs of the NIPA-VBC6 porous gel at different temperatures in water. The change in the structural color of the gel can be observed when the water temperature is changed. The temperature range where we can observe a visible color by the naked eye is from about 20 °C to 40 °C in pure water. Since this gel increases its volume and the λ_{max} of the reflection spectrum changes to a higher wavelength with the increase in potassium ion concentration, we selected 36 °C to observe the change in λ_{max} of the reflection spectrum with the change in the ion concentrations.

We could observe the change in λ_{max} to the higher wavelength in the visible region when the potassium ion concentration was increased at 36 °C (Fig. 3,4). On the other hand, the change in λ_{max} was not observed for the NaCl aqueous solution. A visible indicator for the specific ion can be constructed by this simple and precise method. In this way, it is possible to create tailor-made visible indicators not only for other cationic ions but also for some organic species. Similar systems composed of non-closest packing colloidal crystals immobilized by polymer gels for sensing some chemicals have been reported by Asher's group.[6] However, our system is easier to make than their systems. Furthermore, the time to reach swelling equilibrium for the porous gels is shorter.[3b,d] These points are advantageous in creating a useful system that will perform as a sensor or an indicator.

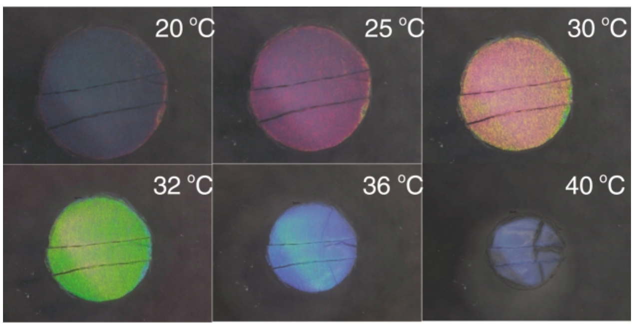

Fig. 2 Photographs of porous poly(NIPA-*co*-VBC6) gel at various temperatures in water.

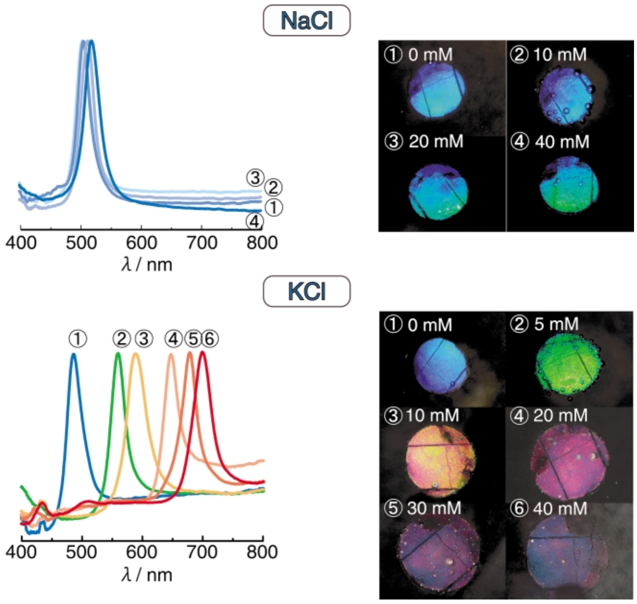

Fig. 3 Reflection spectra and photographs of periodically ordered interconnecting porous gels at 36 °C.

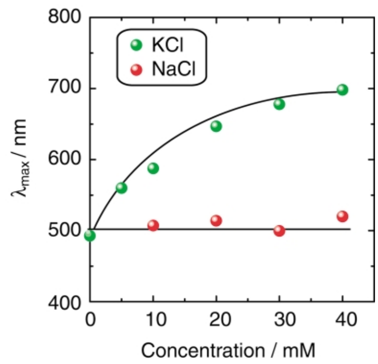

Fig. 4 Ionic concentration dependence of λ_{max} on the reflection spectra.

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