



Preparation of colorimetric hydrogel beads for hydrofluoric acid detection



Chaemyeong Lee, Sang-Yup Lee *

Department of Chemical and Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea

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ABSTRACT

Colorimetric HF-sensitive hydrogel beads were prepared using alginate hydrogel as a host matrix and a pyrocatechol violet (PV)–titanium(IV) bis(ammonium lactato)dihydroxide (TALH) complex as a HF-sensing dye. The PV–TALH complex dye was released into a HF solution from the host matrices and turned the transparent HF solution yellow. From the results of control experiments, this yellow color was exclusively observed when the beads were exposed to HF. The color change allowed the detection of HF with the naked eye. Optimal conditions for the preparation of the HF-sensitive hydrogel were determined with consideration of the swelling behavior of the alginate hydrogel beads.

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Introduction

Hydrofluoric acid (HF) is classified as a code 4 health hazard according to the U.S. National Fire Protection Association (NFPA) 704 Hazard Identification ratings system; as such, it requires special care for handling and disposal. HF is a highly corrosive inorganic acid used in the semiconductor industry for etching and cleaning purposes, and its usage has increased due to growing need in the cleaning of ceramic appliances [1]. This increasing usage of HF is accompanied by an elevated risk of HF exposure to the public and the environment. Regarding its toxicity, HF may chemically burn the skin and penetrate it to damage organs and bones; thus, it represents a threat to public health [2,3]. In addition to its high corrosiveness and toxicity, the insensitivity of HF in an olfactory or visual sense increases the difficulty of HF safety control [4,5]. Thus, the development of simple and economic HF detection (or sensing) methods is of utmost importance for HF safety control.

Colorimetric monitoring of HF using a HF-sensitive dye is the simplest method of visual detection. In contrast to other electrochemical or spectroscopic methods [6,7], visual monitoring of the color change is advantageous as a cheap detection method since it does not require any costly equipment and enables

intuitive recognition of the target substance with the naked eye. However, only a small number of studies have been reported for the visible detection of HF. For example, a block copolymer was developed for a visible HF-gas sensor, which required complicated synthesis and fabrication processes to exhibit HF selectivity [8]. Recently, we reported a pyrocatechol violet (PV)–titanium(IV) bis(ammonium lactato)dihydroxide (TALH) complex dye that displays a selective color change in the presence of HF (Fig. 1a) [9]. PV is a water-soluble photometric triphenylmethane reagent whose ionization state is sensitive to pH [10,11]. Changes in its ionization state cause shifts in its visible light absorption, which results in a noticeable color change of PV. TALH is a titanium alkoxide with lactate ligands that is commercially available and easily coordinates with PV. When the PV–TALH complex dye is exposed to HF, TALH dissociates from the PV–TALH complex, and then PV protonation occurs leading to a color change [9]. The cleavage of TALH from coordinated PV by HF is the key mechanism of the selectivity of the PV–TALH complex. This enables the discernment of HF from other common acids. Although the PV–TALH complex dye was sensitive to HF, with considerable selectivity over other acids, manipulation of the dye was not easy because it exists as an aqueous solution. To overcome this hurdle in manipulation, we entrapped the PV–TALH solution in a hydrogel (Fig. 1b). Hydrogel could be fabricated into a variety of shapes, such as beads and thin films [12]. The dye entrapped in the alginate hydrogel could be released in a controlled manner according to the properties of the hydrogel host matrix [13].

* Corresponding author. Tel.: +82 2 2123 5758; fax: +82 2 312 6401.
E-mail address: leessy@yonsei.ac.kr (S.-Y. Lee).

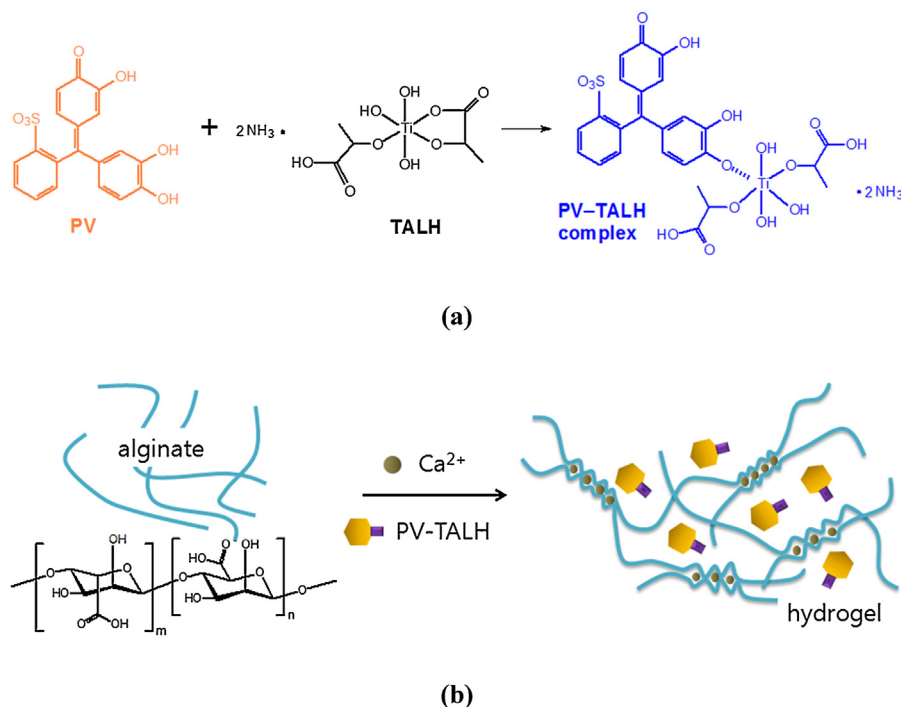


Fig. 1. Chemical structure of PV–TALH complex and illustration of HF-detecting alginate hydrogel beads. (a) Chemical structures of PV, TALH, and PV–TALH complex dye [9]. (b) Scheme of the preparation of alginate hydrogel with entrapped PV–TALH complexes.

In this study, we prepared PV–TALH hydrogel beads with a diameter of ~ 4 mm and examined their sensitivity and selectivity to HF. Characterization of the PV–TALH hydrogel beads was carried out, along with investigations of their microstructures and swelling behaviors. By entrapping the PV–TALH dye solution in hydrogel beads, the dye solution can be handled with ease, and facile screening of HF in acid solutions was achieved.

Experimental

Chemicals

Pyrocatechol violet (analytical grade) and titanium(IV) bis(ammonium lactato)dihydroxide solution (TALH, 50% in water) were purchased from Sigma–Aldrich. Sodium alginate (Wako Pure Chemical Industry, Japan), a hydrogelator, was purified by 1-day dialysis against deionized water to remove sodium ions and other artifacts using a dialysis bag (MWCO = 25 kDa). The dialyzed alginate was freeze-dried to obtain white alginate powder. The purified alginate was kept dry before preparation of the hydrogel. Acids were purchased from local vendors and diluted to the target concentrations with deionized water (*Note*: HF should be handled with care. Proper safety wear should be used and experiments should be performed in a certified ventilation hood).

Preparation of PV–TALH hydrogel and detection test

PV was dissolved in deionized water to a concentration of 1 mM and then mixed with as-received TALH solution (50% in water) in a volumetric ratio of 1:0.01 (approximate 1:20 in molar ratio) to generate a PV–TALH complex dye solution. The prepared dye solution was mixed further with 1 wt% (1 g alginate per 100 ml of water) alginate solution in a volumetric ratio of 3:7. The mixture solution of the dye and hydrogelator was dropped into a 1 M calcium chloride (CaCl_2) solution to generate elastic PV–TALH hydrogel beads. A syringe equipped with a micro-needle

(i.d. = 200 μm) was used to drop the mixture solution in the CaCl_2 solution using a syringe pump (model 781200, KD Scientific, Co.) at a volumetric flow rate of 100 $\mu\text{l}/\text{min}$. The calcium ions cross-linked with the alginate molecules via ionic binding to generate an elastic hydrogel [14]. The hydrogel beads were collected and washed with deionized water to remove the remaining CaCl_2 salt on the surface. The microstructures of the prepared hydrogel beads were investigated by optical and field-emission scanning electron microscopy (FE-SEM, S-800, Hitachi, 20 kV). The prepared hydrogel beads were immersed in the acid solutions, and the color of each acid solution was monitored. For the swelling tests, the hydrogel beads were collected by picking them up from the acid solutions using a polyethylene tweezer. The remaining acid solution on the beads was soaked with a tissue paper before weighting the hydrogel beads. After weighting, the beads were re-immersed in the acid solutions to proceed the swelling test. Same procedures were carried out for the swelling test of HF solution in a certified ventilation hood. Spectroscopic analyses of the color changes were performed using a UV–vis spectrometer (S3100, Scinco) in the visible light range of 400–700 nm.

Results and discussion

Uniform PV–TALH hydrogel beads with an average diameter of ~ 4 mm were prepared by dropping the hydrogel mixture solution into CaCl_2 solution. By ionic bridging of Ca^{2+} ions [14,15], alginates in the mixture solution were cross-linked to form elastic hydrogels containing the PV–TALH dye. Photographs and the average size of the prepared PV–TALH hydrogel beads are shown in Fig. 2. Because of the entrapped PV–TALH dye, the HF-sensitive hydrogel beads were dark blue in color. For the purpose of comparison, other hydrogel beads were prepared in the presence of PV and in the absence of dye. The beads were yellow in the presence of PV dye, and were transparent without any dye. The discernible blue color of the hydrogel beads clearly indicates the entrapment of PV–TALH dye in the hydrogel. The dark blue color of the PV–TALH complex

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