Notes

Incorporation of Graphene Oxide to pH-Responsive Hydrogel for Rapid Adsorption-Desorption of Nanoparticles on Patterned Hydrogel Surface

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Introduction

Polymer scientists have focused on smart hydrogels that can undergo reversible, three-dimensional, large-scale physical or chemical changes in response to small external changes in environmental conditions, such as temperature,¹ pH,² light,³ magnetic or electric field,⁴ ionic strength and biological molecules.⁵ Most pH-responsive polymers are polyelectrolytes with weak acidic or basic groups in their structure, which either accept or release protons in response to changes in environmental pH. Responsive hydrogel networks consisting of polyacrylic acid, polymethacrylic acid (PMAA), and poly(ethylene glycol) (PEG) are common pH-sensitive carriers.^{6,7}

Despite great interest on stimuli-responsive hydrogels for the exploitation of their useful and advanced attributes, such as serving as drug or gene carriers with triggered release properties, one major limitation of bulk hydrogels for potential applications as stimuli-sensitive hydrogels in detection and sensing systems is the diffusion rate-limited transduction of signals. More effective applications of such hydrogels require fast response to external stimuli. Thus, to achieve this response, the bulk stimuli-sensitive hydrogel is reduced to small particles because the response rate is inversely proportional to the square of the characteristic dimension of the hydrogel.⁸ Consequently, the preparation of nano- or micro-sized hydrogel particles⁹ and the fabrication of stimuli-responsive hydrogels with patterned films have become very important for the potential applications of such materials.¹⁰

Besides volume change of pH-responsive hydrogels, hydropho-

bic interaction on the hydrogel surface is accompanied by pH change because of the alteration in hydrophobic interaction of the hydrogel surface caused by the degree of protonation of the acid group. As one of the universally weak interactions in nature, hydrophobic interaction can be observed in smart hydrogel surfaces. Therefore, novel smart surfaces can be designed by utilizing weak hydrophobic interactions to reversibly adsorb and desorb target particles.

Graphene oxide (GO) and GO-based nanocomposites have received significant attention because they demonstrate exceptional performance in numerous aspects, such as their conductive, mechanical, thermal and biocompatible properties.¹¹ However, only a few investigations about GO-based composite hydrogels have been reported.¹² Given the high specific surface area and abundant hydrophilic groups on the GO surface,¹³ GO is a good candidate for fabricating novel adsorption-desorption hydrogels with significantly increased applications.

In this study, we prepared a new composite pH-responsive hydrogel that is highly sensitive to the adsorption-desorption of nanoparticles by incorporating GO into the PMAA hydrogel grafted with PEG. For rapid response in the adsorption and desorption to pH stimuli, the hydrogel was fabricated to a patterned surface film. The morphological structure of the patterned hydrogel surface and the adsorption-desorption of Ag nanoparticles were greatly altered by the environmental pH variations.

Experimental

Figure 1 shows the overall experimental scheme for the fabrication of patterned hydrogel film using honeycomb-patterned polystyrene film as template. For the fabrication of GO-incorporating hydrogel with patterned surface, preparation of chemically modified GO nanoparticles was conducted for the homogeneously soluble GO nanoparticles into the ethanol/water solution. GO nanoparticles were first prepared by chemical oxidation of graphite powder following a modified Hummers method.¹⁴ For chemical modification of GO, the GO nanoparticles were treated by PEG. For the PEGylation process, 5 mL GO aqueous solution was diluted to obtain 2 mg/mL concentration, and then bath sonicated for 1 h to obtain a clear solution. NaOH (1.2 g) and chloroacetic acid (1.0 g) were added into the 10 mL GO suspension (~2 mg/mL) and bath sonicated for 1 h to 3 h to convert the -OH groups to -COOH by the conjugation of acetic acid moieties, which were named GO-COOH. The obtained GO-COOH solution was neutralized and purified by rinsing and filtration. GO-COOH suspension was diluted with water to obtain an optical density of 0.4 at 808 nm. 6-Armed PEG-amine (2 mg/mL) was added into the GO-COOH suspension, which was then sonicated for 5 min for the preparation of PEG-GO.¹⁵

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Figure 1. Schematic diagram for the fabrication of patterned GO-incorporated hydrogel surface film using the honeycomb-patterned PS film as a template.

For the fabrication of GO-incorporating hydrogel into patterned surface, photo-polymerization on the honeycomb-patterned polystyrene (PS) thin film using as template was done.¹⁶ MAA (0.43 g, 0.05 M) and PEGMMA (2.50 g, 0.05 M) were dissolved in ethanol/water solution (50:50 volume ratio) as monomer solution. The crosslinking agent of tetraethylene glycol dimethacrylate (TEGDMA) (0.25 g) and the initiator 1-hydroxycyclohexyl phenyl ketone (Irgacure 184) (1.46 g) were added into monomer solution with 0.75 mol% and 0.5 wt% total monomer, respectively. Subsequently, 0.8 mL PEG-GO solution was added into 4 mL monomer solution for pre-gel solution. The PS template on the Petri dish was placed in a vacuum chamber, and then 4 mL pre-gel solution containing monomer solution and PEG-GO was poured on the Petri dish to fabricate a convex-patterned hydrogel film. After removing the air in the vacuum chamber with a vacuum pump for 1 min, the chamber was filled with nitrogen. The mold was then exposed to UV light (Hamamatsu Co. L8252A) for 5 min on the template. The patterned hydrogel film was prepared by peeling the film from the PS template and then rinsing with deionized water several times.

Results and Discussion

Figure 2 shows the result for the characterization of synthesized GO and PEG-GO. Figure 2(a) shows the UV-vis absorption spectra of GO and PEG-GO exhibiting one broad band with a maximum at 232 nm and a shoulder at 300 nm, which originate from the π - π^* transition of C=C and n - π^* transition of C=O, C-O-C or O-O groups, respectively. Figure 2(b) shows the FTIR spectral peaks obtained by GO and PEG-GO, respectively. The peaks of GO show characteristic bands given in previously reported papers.¹⁷ The IR peaks of PEG-GO showed at 1650 cm^{-1} characteristic C=O stretching mode of the carboxylic acid group. The bands due to C-O

Figure 2. Characterization of the synthesized GO and PEG-GO. (a) UV-vis absorption spectra, (b) FTIR spectra, and (c) SEM image of GO and PEG-GO in the powder state.

stretching mode were merged in the very broad envelope centered on 1414 and 1007 cm^{-1} arising from C-O, C-O-C stretches and C-O-H bends vibrations of PEG after composition with GO. Figure 2(c) shows the SEM images of GO and PEG-GO in the powder state. The images of GO shows the solid crystalline particles as the form of layered structures that is the typical structure of GO powder.¹⁸ However, the image of PEG-GO shows needle like structures due to the polymer of GO attached to the surface of GO.

Figure 3(a) and (b) show the typical SEM images (by COXEM CX-100s) of the patterned hydrogel films obtained without

Figure 3. Typical SEM images of (a) PMAA-PEG hydrogel film and (b) GO-incorporated composite hydrogel film. The left, right, and bottom show the surface, the cross-sectional image, and the SEM-EDS analysis results, respectively. (c) Typical SEM image of honeycomb-patterned PS film used as template.

and with GO incorporation, respectively. The left shows the surface image, the right one shows the cross-sectional image, and the bottom part shows the SEM-EDS analysis. The SEM images for the patterned hydrogel film exhibits regularly ordered convex and hexagonal structure, indicating that the experimental method used in this study is effective and facile for preparing micro-patterned hydrogel film. No significant difference was found in the obtained SEM image of the two hydrogel surfaces regardless of GO incorporation. However, the SEM-EDS image showed significant difference between the two hydrogel films. The peaks indicating C and O were

Figure 4. Typical SEM images showing the morphology change of the patterned hydrogel surface by pH variation in (a) PMAA-PEG hydrogel and (b) GO-incorporated hydrogel after 10 min of soaking in the buffer solutions at pH 4 and 9. The inset figure in (b) shows cross sectional image.

significantly increased by the incorporation of GO, indicating that GO was incorporated in the PMAA-PEG hydrogel. Figure 3(c) shows a typical SEM image for the honeycomb-patterned PS film used as template in fabricating the patterned hydrogel films.

Figure 4 shows typical SEM images for the surface morphology of the patterned hydrogel film altered by environmental pH variation. The image was obtained after 10 min of soaking in buffer solutions at pH 4 and 9 and immediately frozen by soaking in liquid nitrogen and lyophilized for 24 h. The image shows that the hydrogel surface morphology is sensitive to environmental pH variations by the GO-incorporation similarly with the pH-responsive hydrogel surface synthesized by PAA without incorporation of GO introduced in our previous report.¹⁹ The highly ordered hexagonal patterns of the hydrogel films changed into squeezed state after soaking in pH 4 buffer solution. Meanwhile, after soaking at pH 9 buffer solution, the patterned hydrogel surface show highly swollen morphology, indicating the deformed or irregularly patterned structures. However, the changes by the pH variations were more remarkable in the GO-incorporated hydrogel surface as shown in Figure 4(b) comparing to change obtained by without GO incorporation as shown in Figure 4(a). This result can be attributed to the addition of GO, which stimulates the change in hydrophilic state of hydrogel surface caused by the additional change of the remained carboxyl group ($-\text{COO}^-/-\text{COOH}$) and hydroxyl groups ($-\text{O}^-/-\text{OH}$) to facilitate good interfacial interaction between GO with composite hydrogel surface in aqueous solution in spite of PEG treatment.

Figure 5(a) the adsorptivity of the two hydrogel surfaces of with and without incorporation of GO obtained by separate beakers with pH 4 buffer solution containing 0.01 M Ag nanoparticles. Ag nanoparticles were prepared by reduc-

Figure 5. (a) Adsorptivity of Ag nanoparticles on the patterned hydrogel surfaces at pH 4 buffer solutions. (b) Release of Ag nanoparticles with time from the patterned hydrogel surfaces at pH 9 buffer solution.

ing AgNO_3 . The procedure for Ag metallization was introduced in our previous report.¹⁹

The change in the concentration of Ag nanoparticles was measured using a flowing UV-visible detector (Hitachi L-7400) by placing the patterned hydrogel films ($1.5 \text{ cm} \times 1.5 \text{ cm} \times 1.0 \text{ mm}$) into the solution. The wavelength of absorbance was fixed at 450 nm, which corresponds to the characteristic band of the Ag nanoparticles.^{19,20} As shown in the figure, the concentration of Ag nanoparticles in the buffer solution decreased with time due to the hydrophobic interaction of the hydrogel film. However, adsorptivity of the GO-incorporating film was significantly higher than that of pure PMAA-PEG hydrogel film without incorporation of GO as shown in the figure, indicating that the GO-incorporating hydrogel surface is more efficient than pure polymer hydrogel surface in the adsorption of Ag nanoparticles at low pH.

Figure 5(b) also shows the desorptivity of Ag nanoparticles from the patterned hydrogel surfaces. For the release experiment, hydrogel surface adsorbed by the Ag nanoparticles was soaked in different beaker containing pH 9 buffer solution without Ag nanoparticles. The releasing rate of the GO-incorporated hydrogel film was also higher than that of the pure polymer hydrogel film as shown in the figure. The higher releasing rate in the GO-incorporated composite might be due to the high surface area of GO inducing uniform adhesion of Ag nanoparticles on the hydrogel surface with low density during adsorption process. And additional ionic repulsion force induced by the functional groups of GO, such as GO-COO^- and GO-O^- , can accelerate the release of Ag nanoparticles from the GO-incorporated hydrogel surface.

Conclusions

A pH-responsive hydrogel with rapid response time in adsorption-desorption of nanoparticles on the hydrogel surface was prepared by incorporating GO in the grafted PMAA-PEG hydrogel. For effective applications of the hydrogel requiring rapid response to external pH change, the hydrogel was fabricated with a patterned surface film. Both the adsorptivity at low pH and desorptivity at high pH buffer solution were greatly enhanced by the incorporation of GO into the polymer hydrogel, possibly due to high surface area and strong hydrophobic interaction of the hydrogel surface facilitating good interfacial interactions between GOs in the composite hydrogel surface in the aqueous solution.

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