

HYDROGEL AS A MINI REACTOR FOR FERROCENIUM NANOPARTICLES

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ABSTRACT

A simple method to produce ferrocenium nanoparticles (FcNPs) based on pH induced using hydrogel systems as a mini reactor is described. Hydrogels were prepared using *Acryl Amide* (AM), *N, N' methylenebisacrylamide* (MBA) as cross-linking agent, *Potassium Persulfate* (KPS) as the initiator and also *Tetramethylethylenediamine* (TEMED) as a gelling agent. In order to prepare the nanoparticles, two different approaches were used. First, the FcNPs were prepared in-situ and secondly the hydrogel was immersed into the Ferrocenium solution at different concentrations. These nanoparticles were characterized by Fourier Thermal Infrared (FTIR), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The analytical results show the hydrogel systems are able to act as a mini reactor for FcNPs.

Key words: ferrocenium, hydrogels, mini reactor, nanoparticles

INTRODUCTION

Hydrogels as three-dimensional hydrophilic polymeric network can provide unique environments for the preparation and protection of metal nanoparticles. The hydrogels are three-dimensional, water swollen, crosslinked, hydrophilic polymer chains makes them especially suitable. The polymer chains in the hydrogel networks have functional groups such as $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{CONH}_2$, $-\text{OH}$ and $-\text{NH}_2$ that render their hydrophilic character. Some of these chemical functional groups such as $-\text{SO}_3$ and $-\text{COO}^-$ in the hydrogel network can be formed as negative charges in aqueous environments and absorb metal ions via electrostatic interactions. Taking advantages of these characteristics of hydrogel networks, various metal nanoparticles or nanocluster can be prepared in situ by mixed ferrocenium into the preparation or immersed template with aqueous solution of ferrocenium iron.

Ferrocene/ferrocenium is well-known, electrochemically reversible redox couple. Ferrocene remains one of the most important and intensely studied organometallic compounds, but the ease of functionalisation of ferrocene, its stability to air and water have studies as well as employment in many diverse applications (Bean *et al.*, 2010).

The hydrogel template approach is based on the unique properties of physical gels that can undergo sol-gel phase transition upon changes in environmental conditions. The phase reversible hydrogels, however are in generally too weak to be treated as a solid material. It was unexpectedly found that gelatin hydrogels could be made to possess various properties necessary for microfabrication of nanoparticle in large quantities. Recently, microfabrication methods have been used to make nanoparticle with monodisperse size distribution. The existing methods utilize solid templates for the making particles and the collection of individual particle after preparation has not been easy. The size of the particle can be adjusted from 300 nm to 5 nm, providing flexibility in controlling the size in drug delivery formulations.

The gelation property of the hydrogel was investigated by using methods such as transmission electron microscopy, field-emission scanning electron microscopy and fourier transform infrared spectroscopy. Present of sunlight and air, ferrocenium iron were reduced by potassium group of gelatin agent. The conditions of preparations of hydrogel, the incorporation of potassium persulfate and the kinetics under conditions have been evaluated. Transparent, opaque or elastic gel were prepared depending on the amount of acrylamine (AM) and the crosslinking agent, *N,N*-methylenebisacrylamide (MBA). The amount of kalium persulfate (KPS) that could be incorporated per gram of transparent gel was a function of the amount of polymer initiator *N,N,N,N*-tetramethylene diamine (TEMED) used per gram of gel. Additionally, hydrogels can be used for the removal of toxic metal ion from aquatic media. Hydrogel are soft and versatile materials, and are biocompatible, which used in many applications in biomedical fields as an active agent (drug, protein and gene) delivery vehicle, as a template for tissue engineering, wound

dressing materials and artificial organs and as actuator responding to various stimuli. (Sahiner *et al.*,2010).

METHODOLOGY

Hydrogel were prepared using *Acryl Amide* (AM), *N, N'* *methylenebisacrylamide* (MBA) as cross-linking agent, *Potassium Persulfate* (KPS) as the initiator and also *Tetramethylethylenediamine* (TEMED) as a gelling agent, the preparation takes 2 different methods that is the steps taken were differentiated. From this research we would want to show that Ferrocenium iron can be used as the initiator for the hydrogel. The first method used KPS and TEMED as the initiator and gelling agent while the second method used Ferrocenium. In this research, different approaches were used to introduce the ferrocenium into the hydrogel where one was immersed in Ferrocenium while other is prepared in-situ. The nanoparticle in the hydrogel were characterized by Fourier Thermal Infrared (FTIR), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

AM hydrogels were prepared by using acrylamide (AM) as monomer, N,N-methylenebisacrylamide as cross-linker (MBA), N,N,N,N-tetramethylethylenediamine (TEMED) as an accelerator and potassium persulfate (KPS) as redox initiator. DI water was used throughout the experiments.

Hydrogel Synthesis: AM hydrogel were prepared via radical polymerization in the presence of redox initiator. Briefly, 1.0g AM was mixed with MBA 0.1g in 2ml DI water. About 0.1g KPS was dissolved in 1ml of DI water. One ml aqueous initiator (KPS) solution was added to the hydrogel precursor. One drop of TEMED was dropped. The polymerization and crosslinking reaction was allowed to proceed for 10 minutes to complete the reaction at ambient temperature. The hydrogel were immersed in water for one days and the gel was swollen. The amount of water absorbent was determined.

Hydrogel as template for Ferrocenium nanoparticle: For in situ preparation of Ferrocenium nanoparticle during formation of gel, the following method was employed, 50ml 0.01M aqueous solution of ferrocenium was prepared from 36% 11.7M HCl and 0.12g Ferrocene $C_{10}H_{10}Fe$. DI water was used to dissolve the monomer, crosslinker, and initiator. About 1.0g AM, 0.1g MBA, 0.1g KPS were dissolved in 3ml DI water and 2ml of ferrocenium was mixed. In a few second, after adding the ferrocenium, the gel was formed. The blue color has changed to green and then yellow. The gel was oxidized after a few minutes.

For absorption of ferrocenium into hydrogel, briefly, 0.4g AM, 0.008g MBA, 0.12g KPS were dissolved in 4ml DI water and 2 drops TEMED dropped in the preparation of hydrogel. The hydrogel was absorbed ferrocenium iron in one day completely, where it was immersed into the solution.

Characterization: Fourier transform infrared spectroscopy (FTIR): The spectroscopic analyses of samples were carried out using a Fourier transform infrared spectrometer. Spectra in the wavenumber range of $4000-400\text{cm}^{-1}$ were collected with a resolution of 2cm^{-1} . The specimen were vacuum dried and then prepared by the KBr-disk method. **Scanning electron microscopy (SEM):** The dried hydrogel samples were fractured after immersing them in liquid nitrogen for purpose of analyzing the internal morphologies of the samples. The samples were ferrocenium iron has mixed during hydrogel preparation, and a Field Emission Scanning Electron Microscope was used for the observation of the cross section of the samples. The surface morphologies of ferrocenium iron were observed.

RESULTS AND DISCUSSIONS

In Situ Formation and Characterisation of Ferrocenium Particles: In Situ Ferrocenium nanoparticle syntheses were carried out. A schematic representation of ferrocenium particle synthesis in AM hydrogel network is depicted in Figure 1, with corresponding digital camera images. As can be seen, the formation of ferrocenium nanoparticle, within 7 minutes all the available sites are assumed to be occupied with ferrocenium ions. The blue color formed, and changed to green and then yellow which were oxidized. Exothermic reaction was occurred. DI water was added to dissolve the monomer, cross-linker and initiator where remove/excess unbound ferrocenium ions. Hydrogel-Ferrocenium networks were treated with ferrocenium ion to replace TEMED as gelatin agent and generate immediately ferrocenium nanoparticle.

Hydrogel immersed in Ferrocenium: In the second method, the gel was immersed in the ferrocenium was observed. The absorption of ferrocenium has been observed. The schematic

ferrocenium nanoparticle syntheses outside the hydrogel network has been observed, in Figure 2 with corresponding digital camera images.



Figure 1. Ferrocenium nanoparticle

Table 1.

AM (g)	MBA (g)	Fc ⁺ Cl ⁻ (ml)	KPS (g)	DI water (ml)
1.0 g	0.1 g	2 ml	0.1 g	3 ml



Figure 2. Hydrogel was immersed in ferrocenium ion

After formation of hydrogel, the gel was immersed in Ferrocenium ion (Fc⁺ Cl⁻) for a one day. About 1.8 ml of ferrocenium ion (Fc⁺ Cl⁻) was absorbed into hydrogel. The gel was changes to colorless after immersed in water.

Table 2

AM (g)	MBA (g)	KPS (g)	TEMED	DI water (ml)	Fc ⁺ Cl ⁻ (ml)
0.4 g	0.008 g	0.12 g	2 drops	4 ml	1.8 ml

CONCLUSIONS

We prepared two methods of hydrogel as a template for ferrocenium nanoparticle, first method by in situ radical polymerization and second method absorption of ferrocenium into hydrogel have successfully done. The method presented here is novel in the metal nanoparticle can easily be prepared at room temperature, compared to P-NIPAM that sensitive to temperature. Acrylamide is toxic that should used hand glove to protect skin. Other material used in the hydrogel preparation help to reduced its toxicity, even there are some particle are not dissolved during formation of gel. The hydrogel system established here is flexible and can swell and deswell in the presence and absence of water. The blue color from ferrocenium iron was oxidized to yellow, but after immersed in the tap water the yellow turns to colorless. The surface of ferrocenium nanoparticle were characterized by Fourier Thermal Infrared (FTIR), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

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