



# Tunable chitosan hydrogels for adsorption: Property control by biobased modifiers

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## ABSTRACT

A sustainable strategy to fabricate chitosan-based composite hydrogels with tunable properties and controllable adsorption capacity of trace pharmaceuticals was demonstrated. Two biobased modifiers were utilized to tune the properties, nano-graphene oxide (nGO) derived from chitosan via microwave-assisted carbonization and oxidation, and genipin as the crosslinking agent. An increase in genipin content facilitated an increase in the degree of crosslinking as shown by improved storage modulus and decreased swelling ratio. Increasing nGO content changed the surface microtopography of the hydrogel which correlated with the surface wettability. nGO also catalyzed the genipin-crosslinking reaction. The hydrogel was further shown to be an effective adsorbent for a common anti-inflammatory drug, diclofenac sodium (DCF), with the removal efficiency ranging from 91 to 100% after 48 h. DCF adsorption efficiency could be tuned through simple alteration of nGO and genipin concentration, which provides promising potential for this environmental-friendly adsorbent in removal of DCF from pharmaceutical waste water.

## 1. Introduction

Hydrogels are three-dimensional polymeric networks exhibiting the ability to swell and absorb large amounts of water within the structures (Peppas, Bures, Leobandung, & Ichikawa, 2000). Among numerous macromolecules capable of forming hydrogels, polysaccharides, e.g. chitosan (Konwar, Gogoi, Majumdar, & Chowdhury, 2015), starch (Zhu, Ma, Wang, & Zhang, 2015), cellulose (Abe & Yano, 2011), and alginate (Mohammed, Grishkewich, Waeijen, Berry, & Tam, 2016) are endowed with competitive advantages such as wide-available, low-cost and renewable nature.

Chitosan (CS) as a well-known linear polysaccharide of N-deacetylated chitin can be extracted in massive quantities from the exoskeleton of crustaceans. Due to its eco-friendly properties such as non-toxicity, antibacterial function, controllable biodegradability and good biocompatibility (Khan, Islam, Sarwar, Gull, & Jamil, 2016), CS has been widely used for wound dressing (Wang, Zhu, Xue, & Wu, 2012), drug delivery (Muhsin et al., 2014), food packaging (Dutta, Tripathi, Mehrotra, & Dutta, 2009), tissue engineering (Jana, Florczyk, Leung, & Zhang, 2012) and other applications. Moreover, CS has attracted significant interest in the waste water treatment, due to the presence of the primary amine and hydroxyl groups on the CS chains, which can serve as reaction sites for entrapping various metal ions and organic dyes (Chen, Chen, Bai, & Li, 2013; Li et al., 2016; Yu and Wang et al., 2017)

through various secondary interactions such as chelation, hydrogen bonding and electrostatic interactions. CS can form hydrogels either through physical or chemical crosslinking of the polymer chains. Compared with the physical crosslinking strategy, covalent crosslinking is superior in promoting mechanical strength and providing controllable physiological stability (Racine, Texier, & Auzély-Velty, 2017). Genipin (GP) as a natural crosslinking agent, extracted from the fruit of *Gardenia jasminoides*, can at trace amounts spontaneously react with polymers containing primary amine groups such as chitosan, gelatin and collagen and upon reaction the dark blue pigment is formed (Djerassi, Eisenbraun, Finnegan, Gilbert, & Djerassi, 1960). Compared with the commonly used crosslinking agent glutaraldehyde, GP has good biocompatibility with 10000 times lower cytotoxicity (Sung, Huang, Huang, & Tsai, 1999) and 5000 times higher cell proliferating rate (Yuan et al., 2007). It was also reported that genipin-crosslinked products demonstrated slower degradation rate than those crosslinked with glutaraldehyde (Mi, Tan, Liang, Huang, & Sung, 2001; Mi, Shyu, & Peng, 2005). These findings inspired us to utilize genipin as a green modifier to produce novel functional hydrogels with major interest in the environmental domains.

Carbon additives derived from biopolymers and waste products (Hassanzadeh, Aminlashgari, & Hakkarainen, 2014; Hassanzadeh, Aminlashgari, & Hakkarainen, 2015; Wu & Hakkarainen, 2014) have also been shown to be effective biobased property enhancers in

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biopolymer and bioplastic composites (Feng, Simeone, Odelius, & Hakkarainen, 2017; Xu, Xie, Li, & Hakkarainen, 2017). Carbon nanospheres (CN) can be produced by mild microwave-assisted carbonization of biopolymers and CN can be subsequently transformed into nanographene oxide (nGO) via a simple oxidation route (Adolfsson, Hassanzadeh, & Hakkarainen, 2015; Wu, Xu, & Hakkarainen, 2016). Compared with conventional two dimensional (2D) graphene oxide (GO), the bio-derived nGO is considered as GO with all the lateral dimensions in nanoscale (below 100 nm), and with a higher amount of oxygenated functionalities (Xu et al., 2016). To date, a number of chitosan/GO composite materials in the form of films, hydrogels and beads have been explored in fundamental to applied research. Good compatibility between the chitosan matrix and GO sheets caused by strong secondary interactions provides better load transfer in the composite system compared to pure chitosan material, which in general yields improved mechanical performance (Han, Yan, Chen, & Li, 2011; Yang, Tu, Li, Shang, & Tao, 2010; Zhang et al., 2017). Chitosan/GO composites also demonstrated good adsorption abilities towards dyes (Gul et al., 2016; Wang et al., 2015), heavy metals (Ge & Ma, 2015; Yu and Wang et al., 2017) and organic compounds (Yu and Shi et al., 2017). Triggered by these findings, exploring the effect of smaller-size and bio-derived nGO in the chitosan-based composite system is of great interest.

Previously we have synthesized chitosan-based nGO and utilized it to fabricate fully biobased CS composite hydrogels with genipin as the crosslinking agent (Feng et al., 2017). The synthesized hydrogel demonstrated effective adsorption ability towards the common anti-inflammatory drug diclofenac sodium (DCF). Herein, we hypothesized that the properties of the chitosan composite hydrogel could be tuned and controlled by using different feed ratios of chitosan-based nGO and genipin as the biobased modifiers. Via regulating the composition of nGO and genipin, hydrogel properties such as wettability, swelling behavior, and rheological performance were targeted to be controlled. The optimal approach to reach the highest DCF adsorption capacity was also explored. The effect of nGO and GP on the structure-property tunability is developed in depth and the interaction behind them is elaborated. These tunable CS composite hydrogels are anticipated to provide promise for pharmaceutical waste purification.

## 2. Experimental

### 2.1. Materials

Medium molecular weight Chitosan (CS) with following characteristics: number-average molecular weight ( $M_n$ ) 119 000 g/mol, weight-average molecular weight ( $M_w$ ) 566 000 g/mol, and molecular weight distribution (MWD) 4.8 as determined by SEC, viscosity-average molecular weight ( $M_v$ ) 300 000 g/mol as determined by viscometer (Supplementary information Figs. S1, S2 and Table S1) and degree of deacetylation ca. 77%, as determined by  $^1\text{H}$  NMR (Supplementary information Fig. S3) was purchased from Sigma Aldrich. Diclofenac sodium (DCF, 99%), nitric acid ( $\text{HNO}_3$ , 70%) and sulfuric acid ( $\text{H}_2\text{SO}_4$ , 95%–98%) were also purchased from Sigma Aldrich. Genipin (GP,  $\geq 98\%$ ) was purchased from Linchuan Zhixin Bio-Tech. Acetic acid ( $\text{CH}_3\text{CO}_2\text{H}$ ,  $\geq 99.5\%$ ) was provided by Acros Organics. Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , 96%) was obtained from VWR Chemicals. All chemicals were used as received.

### 2.2. Synthesis of nGO from chitosan

Chitosan-based nGO was prepared according to our previous work (Feng et al., 2017). The average particle size was 80–90 nm, as measured statistically from transmission (TEM) and scanning (SEM) electron microscopy images, and 100 nm as determined by dynamic light scattering (Feng et al., 2017). Briefly, six cylinder shaped TFM (Teflon Fluor Modified) vessels were prepared with 2 g chitosan and 20 mL of

sulfuric acid solution (0.1 mg/mL) in each. The hydrothermal carbonization process was carried out under Milestone flexiWAVE microwave irradiation with maximum power of 1200 W. The irradiation power is adjusted automatically to keep the programmed temperature. The temperature was increased to 200 °C at a RAMP-time 20 min and then kept isothermally at 200 °C for 2 h. Black solid carbon nanospheres (CN) were obtained and filtrated through a Büchner funnel and dried in vacuum at room temperature for 3 days. nGO was produced by oxidation of the CN in nitric acid (10:1 w/v) under sonication for 30 min and subsequent heating at 90 °C for 60 min in an oil bath. 150 mL of deionized water was added to cool down the solution and to stop the oxidation process. Purified nGO, with a dark brown colour, was obtained after vacuum distillation to remove solvent and a freeze-drying process.

### 2.3. Preparation of the hydrogels

CS solution (1% w/v) was prepared by dissolving a given amount of CS in an acetic acid solution (2.5% v/v) and stirred overnight. GP was dissolved in ethanol (60% v/v) and nGO suspensions were prepared by adding different amounts of nGO (4, 10, 20 mg) into deionized water under sonication for 10 min. Then CS, GP and nGO solutions were mixed together by magnetic stirring for 20 min and the mixed solutions were poured into DUROPLAN® petri dishes (50 mm in diameter and 20 mm in height) covered with parafilm. The mixed solutions were incubated under 37 °C for 48 h. All prepared hydrogels with different compositions and the corresponding control samples which were subjected to the same process, are listed in Table 1.

### 2.4. Fourier transform infrared spectroscopy (FTIR) analysis of the hydrogels

To verify the crosslinking reaction in the hydrogel systems as well as to obtain information concerning the interactions between nGO, GP and CS matrix, FTIR spectra of neat CS, Control 1(CS), pure nGO, and a series of hydrogels with different compositions were recorded by a PerkinElmer Spotlight 400 FTIR spectrometer equipped with an attenuated total reflectance (ATR) crystal accessory, within a range from 4000  $\text{cm}^{-1}$  to 600  $\text{cm}^{-1}$ . The resolution was set to be 4  $\text{cm}^{-1}$ .

### 2.5. Morphological characterization by SEM

To examine the interior structure and surface morphology changes with different compositions of nGO and GP, the cross sections of a series of lyophilized hydrogel samples were studied by FE-SEM (Hitachi S-4800). The samples were freeze-dried for three days, then a slice was

**Table 1**  
Composition of the prepared hydrogels and control samples.

Sample Denomination	CS [mg/mL]	GP [mg/mL]	nGO [mg/mL]
GP2/nGO0	10	2	0
GP2/nGO2	10	2	2
GP2/nGO5	10	2	5
GP2/nGO10	10	2	10
GP5/nGO0	10	5	0
GP5/nGO2	10	5	2
GP5/nGO5	10	5	5
GP5/nGO10	10	5	10
GP10/nGO0	10	10	0
GP10/nGO2	10	10	2
GP10/nGO5	10	10	5
GP10/nGO10	10	10	10
Control 1 (CS)*	10	0	0
Control 2 (CS10 + nGO10/no GP)*	10	0	10
Control 3 (GP10 + nGO2/no CS)*	0	10	2
Control 4 (GP10 + nGO10/no CS)*	0	10	10

Note: \* represents the control sample.

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