

## Environment-Sensitive Carbon Nanotube/Polymer Composite Microhydrogels Synthesized via a Microfluidic Reactor

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**ABSTRACT:** Multiwalled carbon nanotubes (MWCNTs)/poly(*N*-isopropylacrylamide-*co*-acrylic acid) composite microhydrogels are simply synthesized with controllable size distribution via a microfluidic reactor system. Monomers (*N*-isopropylacrylamide and acrylic acid) are rapidly copolymerized (about 3 s) with the embedding of nanoscaled inorganic materials (MWCNTs and hectorites) in microfluidic channels. MWCNTs/hectorites act as “molecular heater” and inorganic crosslinkers in this hydrogel system. As a result, microminiaturization, multifunctionalization, and modification of traditional polymer hydrogels are realized simultaneously. Fourier transform infrared spectroscopy is used to confirm polymerization and environment-sensitive tests are done as well. The resultant microgels exhibit dual near-infrared and pH response with good reversibility, indicating their potential applications in microreactor fields. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

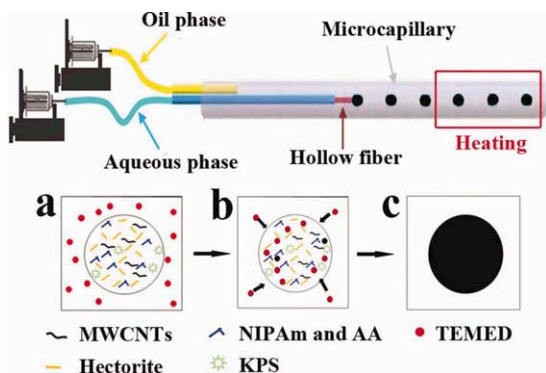
Polymeric hydrogels, known as soft smart or intelligent materials, can exhibit a volume phase transition under external stimuli, such as pH,<sup>1</sup> light,<sup>2</sup> magnetic field,<sup>3</sup> and temperature.<sup>4</sup> Many potential applications such as biotechnological devices<sup>5</sup> and drug delivery systems<sup>6</sup> stem from the environment-responsive properties of hydrogels. For example, poly(*N*-isopropylacrylamide) (PNIPAm) shows a lower critical solution temperature (LCST) in water with a phase transition point in the physiologically relevant range at about 32°C, which was used as switchable cell culture substrates reported by Schmidt et al.<sup>7</sup> recently. The copolymers of PNIPAm and polyacrylic acid was developed as a new sharply pH- and temperature-responsive hydrogel system by Garbern et al.<sup>8</sup> reported recently. In addition, interest in incorporating carbon-based materials (carbon nanotubes, graphene oxide [GO], and graphene) into hydrogel matrices has grown.

As the typical sp<sup>2</sup> carbon nanomaterials, carbon nanotubes, and graphene have high aspect ratios and unique mechanical, thermal, and electrical properties that are potentially useful in many applications.<sup>9,10</sup> Fujigaya et al.<sup>11</sup> embedded carbon nanotubes in PNIPAm as phase transition triggers under the near-infrared

(NIR) laser light irradiation. Our group has reported the functionalization of PNIPAm using magnetically-functionalized graphene sheets to explore the application fields of hydrogels.<sup>12</sup> GO is a precursor of graphene-based materials with similar one-atom thickness but with many oxygenated defects, which are rather suitable for covalent functionalization of hydrogel such as the GO interpenetrating P(NIPAm-*co*-AA) hydrogels reported by Sun et al.<sup>13</sup>

Though some of the above mentioned up to date works report the synthesis of micro hydrogels, there is still a lack of simple controllable synthesis strategy of carbon embedded microgels. As the microfluidic technology has been extensively developed in the last decade,<sup>14–16</sup> microfluidic reactors supply a route to realize the size control and shape control, microminiaturization, and rapid synthesis of carbon/polymer composite microgels.

In this article, we present a simple method to prepare multiwalled carbon nanotubes (MWCNTs)/P(NIPAm-*co*-AA) microgels with controllable size distribution via a microfluidic reactor. Both the NIR-laser-responsive and pH-responsive behaviors of the as-prepared microgels are investigated. In this microgel system, MWCNTs serve as an effective “molecular heater” around the NIR region, which makes the microgel a strong candidate



**Figure 1.** Sketch of the microfluidic system. Inset a–c: polymerization process of the microgels. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

for the light-driven switch applied in microreactors. Our approach combines microminiaturization, multifunctionalization, and modification of traditional polymer hydrogels. We believe that this approach opens up novel ways for polymer research.

## EXPERIMENTAL

### Materials

MWCNTs (length 5  $\mu\text{m}$ ; o.d. 50–90 nm; purity: 95–98%) were purchased from Shenzhen Nanotech Port (Shenzhen, China). Hectorite “Laponite XLG” (Rockwood:  $[\text{Mg}_{5.34}\text{Li}_{0.66}\text{Si}_8\text{O}_{20}(\text{OH})_4]\text{Na}_{0.66}$ , layer size =  $\Phi 20\text{--}30\text{ nm} \times 1\text{ nm}$ , cation exchange capacity = 140 mequiv/100 g) having negatively charges on surfaces and positively charges on edges was used. NIPAm (purity: 99%) was purchased from J&K Chemical. The other chemicals, such as nitric acid ( $\text{HNO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ),  $N,N,N',N'$ -tetramethyldiamine (TEMED), and potassium persulfate (KPS) were analytical grade and acquired from Sinopharm Chemical Reagent.

### Modification of MWCNTs

0.15 g of MWCNTs was dispersed into 17 mL of concentrated  $\text{H}_2\text{SO}_4$  and 35 mL of concentrated  $\text{HNO}_3$  at  $100^\circ\text{C}$  for 24 h. Then the mixture was diluted with distilled water and rinsed for several times until the pH value reached neutral. The resulting MWCNTs were separated by centrifugation and dried in an oven at  $60^\circ\text{C}$  for subsequent use.

### Synthesis of Bulk Hydrogels

P(NIPAm-co-AA) hydrogels and MWCNTs/P(NIPAm-co-AA) hydrogels were prepared by simple mixture and solution polymerization. The solution compositions are as follows:  $\text{H}_2\text{O}$ /NIPAm monomer/AA monomer/hectorite (and MWCNTs)/TEMED/KPS = 2 mL : 0.2 g : 14 mg : 40 mg (and 24 mg) : 24  $\mu\text{L}$  : 0.03 g, according to Sun et al.<sup>13</sup> and Liu et al.<sup>17</sup> *In situ* free radical polymerization was achieved by transferring the final solution from the ice bath into the water bath ( $5\text{--}50^\circ\text{C}$ ). Throughout the experiment, oxygen was excluded from the system.

### Synthesis of Microgels

MWCNTs/P(NIPAm-co-AA) microgels were prepared in a microfluidic reactor (see Figure 1). NIPAm monomer (2 g), AA

monomer (0.14 g), hectorite (0.4 g), MWCNTs (0.24 g), and KPS (0.3 g) were dissolved in deionized water (20 mL) as the aqueous phase solution. TEMED (2 mL) were dispersed in soybean (20 mL) as the oil phase solution. Oxygen was excluded from those solutions. Two solutions were encased in two glass syringes separately and injected in microcapillaries (1000  $\mu\text{m}$  diameter, made of polytetrafluoroethylene, without any further inner surface treatment) by two syringe push pumps. Aqueous drops were generate in the oil phase solution and the heated to  $40^\circ\text{C}$  in an oil bath for a short time (about 3 s) to gain polymerization.

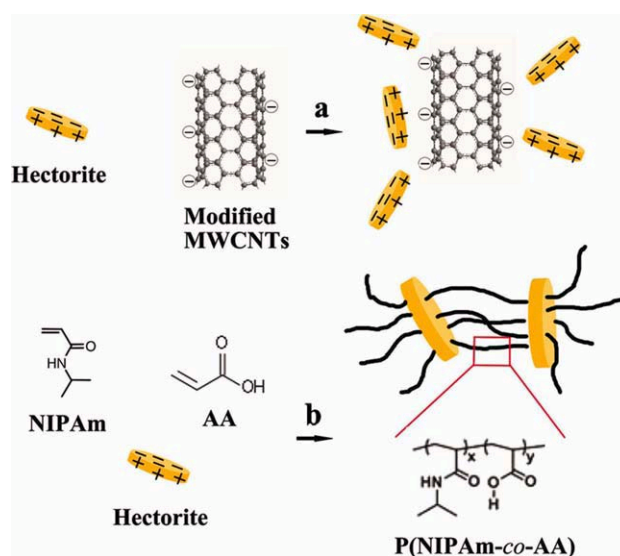
### Characterization and Measurements

Fourier transform infrared (FTIR) spectra were recorded on Nicolet NEXUS-670 spectrometer with KBr pellets in the  $4000\text{--}800\text{ cm}^{-1}$  region.

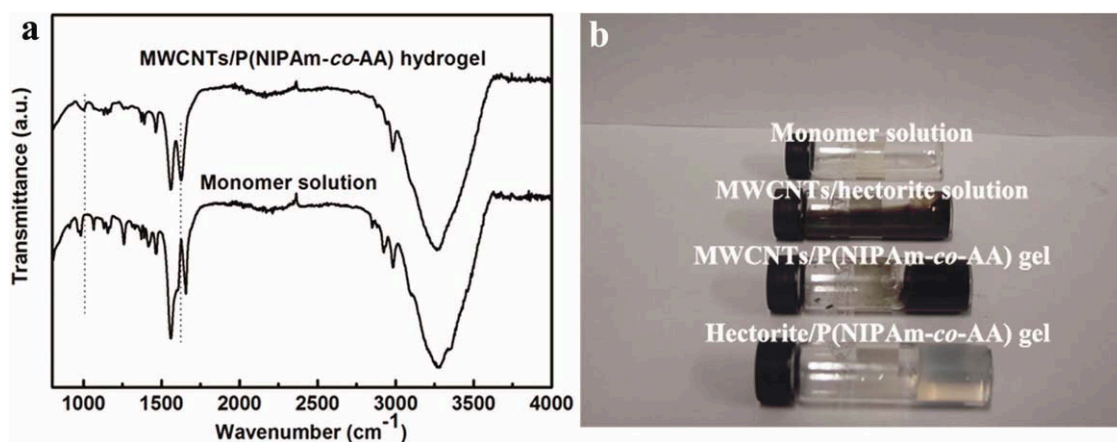
Microscopic images of the as-prepared microgels were monitored by a CCD video camera (Caikang, XPS-550C) and captured by a computer equipped with a video capture card. The gels were placed in a microcapillary (1000  $\mu\text{m}$  diameter) at room temperature. A 1064 nm laser beam from continuous wave laser was focused on the gels. The effect of the pH was verified by adding appropriate amount of NaOH or HCl solutions in the microcapillary. Photographs of the gels were taken by a CCD video camera (Canon, PowerShot G10). Diameters of the gels were measured from the photographs.

## RESULTS AND DISCUSSION

MWCNTs/polymer composite microhydrogels were prepared in a microfluidic system. As shown in Figure 1, two different solutions were injected in microcapillaries by two syringe push pumps, then aqueous drops were generated in the oil phase and gained polymerization after a short time heating treatment [Figure 1(a–c)]. In Figure 2 it is shown that the organic/inorganic network structure is built by initiating polymerization of



**Figure 2.** Schematic representation of the organic/inorganic network in the copolymer hydrogel. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



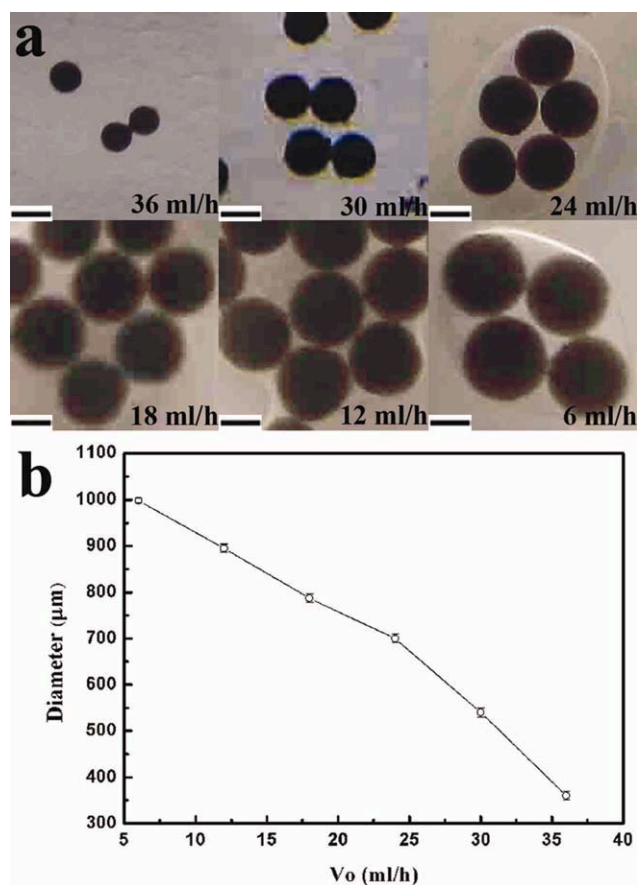
**Figure 3.** a: FTIR spectrum of the as-prepared MWCNTs/P(NIPAm-co-AA) microgel and monomer solution; b: the photograph of the bulk hydrogels and the products without monomers or crosslinkers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

P(NIPAm-co-AA) from the MWCNTs/hectorites surface: first (process a), water dispersible hectorite discs (surface and edges are negatively charged and positively charged, respectively) adsorb to the modified MWCNTs surface (negatively charged) through an electrostatic attraction, they are dispersed in water after ultrasound treatment, and then (process b), NIPAm monomers and AA monomers copolymerize in the microfluidic system with a uniform dispersion of MWCNTs/hectorites, in which process hectorite is regarded as a kind of large inorganic crosslinker and polymer chains are effectively crosslinked by hectorite discs.<sup>18</sup> The network structure of bulk hydrogels is the same as that of the microgels. This structure is expected to be applicable to other polymer materials. For comparison, hectorites/P(NIPAm-co-AA) gels without MWCNTs were also crosslinked following the same procedure. The resultant composite hydrogels and microgels were obtained by washing with acetone and water.

The evidence for the successful crosslinking reaction can be seen in Figure 3. As shown in the FTIR spectrum in Figure 3(a), a peak shift of amide I can be observed from  $1656\text{ cm}^{-1}$  attributed to carboxyl groups of AA monomers to  $1626\text{ cm}^{-1}$  attributed to ester groups of the resultant MWCNTs/P(NIPAm-co-AA) gel. The peak at  $1463\text{ cm}^{-1}$  is attributed to C—N stretching of the NIPAm unit. A peak can be observed at  $1001\text{ cm}^{-1}$  in the gel spectra, corresponding to the Si—O stretching of clay. The photograph of bulk hydrogels and the products without monomers or crosslinkers is shown in Figure 3(b). All samples underwent the same reaction process. Hydrogels were well formed using MWCNTs/hectorites or hectorites as crosslinkers, in contrast, the crosslinker solution and monomer solution without crosslinkers failed to form a hydrogel, indicating the successful crosslinking reaction in MWCNTs/P(NIPAm-co-AA) gels.

Figure 4(a) shows microscopic images of the as-prepared microgels with different sizes. It is found that their size could be effectively tuned by controlling the push speed of the aqueous phase solution ( $V_a$ ) and oil phase solution ( $V_o$ ). As shown in Figure 4(a), when  $V_a$  was set at  $1.8\text{ mL/h}$ , by altering  $V_o$  from 6 to 36 mL/h the diameter of the obtained microgels varied from

1000 to about  $360\text{ }\mu\text{m}$  accordingly. In addition, microgels prepared under the same  $V_o$  show uniform size and monodisperse in water. The diameter of the microgels prepared under different  $V_o$  values are shown in Figure 4(b). The diameter- $V_o$  curve shows an approximately linear relation between the diameter



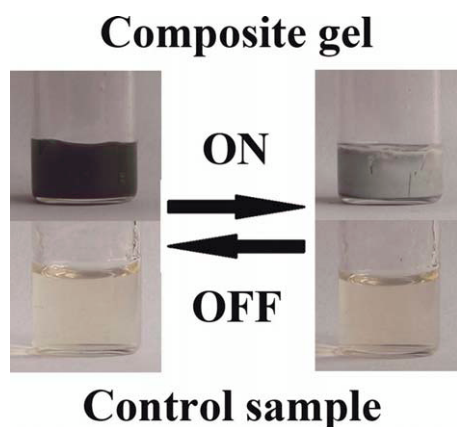
**Figure 4.** a: microscopic images of microgels prepared under different  $V_o$  values, scale bar is  $450\text{ }\mu\text{m}$ ; b: diameter- $V_o$  curve of the as-prepared samples. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

and  $V_0$  value. The above results indicate the high size controllability of the microfluidic system.

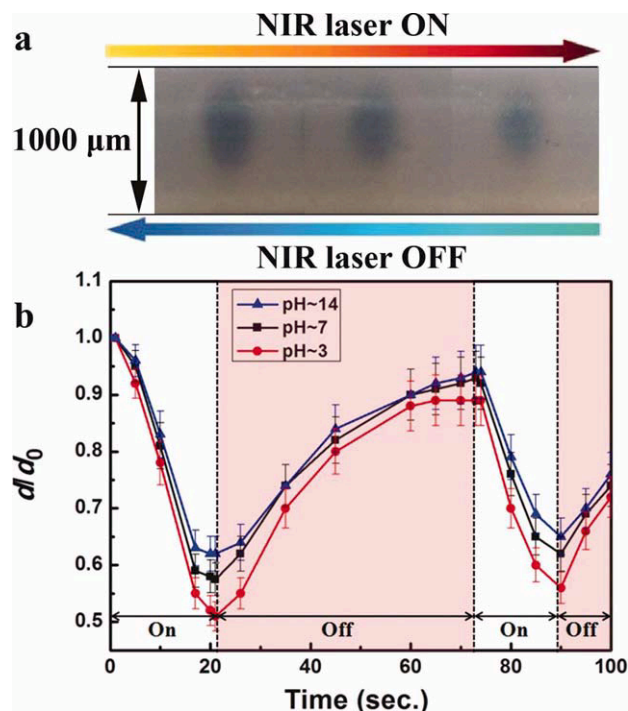
NIR laser irradiation experiments for both bulk gels and microgels were carried out. In Figure 5, the bulk composite gel sample show clear phenomena that upon irradiation with NIR light centered at 1064 nm (500 mW) phase transition occurs and hydrogel shrinks within 3 min, which is reversible and circularly upon ON/OFF NIR laser irradiations. Meanwhile, the control sample without MWCNTs exhibits no response to the NIR light. The observed results could be attributed to the photothermal conversion effect of the MWCNTs. It has been reported that carbon nanomaterials generate heat when exposed to the NIR laser,<sup>10,19</sup> also we have confirmed that the temperature of carbon-embedded PNIPAM gels rises when exposed to the NIR laser.<sup>20</sup> So in this work, MWCNTs are identified as an effective “molecular heater” around the NIR region.

The NIR- and pH-responsibility of the as-prepared MWCNTs/P(NIPAm-co-AA) microgels were also investigated. Same as the bulk hydrogels, composite microgels exhibit a strong response to the NIR laser irradiation. As shown in Figure 6(a), the MWCNTs/P(NIPAm-co-AA) microgel shrunk and formed a gel with a smaller diameter after about 10 s treatment of the NIR light. This process is completely reversible upon room temperature environment without the NIR laser irradiation. Moreover, no noteworthy degeneration of the shrinking/swelling property of the sample was observed after 100 cycle operation, considering the previous works' results,<sup>11,20</sup> we believe that more rounds of the volume change cycles can be repeated. The resultant microgels are expected to be used as NIR-driven switch devices that would be widely applied in microfluidic technology.

Furthermore, as shown in Figure 6(b), it is clear that the as-prepared MWCNTs/P(NIPAm-co-AA) microgels are pH sensitive: as pH value decreases, microgels shrink more during the same treatment duration, in other words, the NIR-response speed increases. In addition, it is notable that the smaller microgels shrink the harder they swell back to initial volume. It is reported that carboxyl groups would form stronger hydrogen



**Figure 5.** Photographs of the as-prepared MWCNTs/polymer composite hydrogels (top) and the control sample without MWCNTs (bottom) upon the NIR laser irradiation treatment (ON and OFF). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** a: photographs of shrunk MWCNTs/P(NIPAm-co-AA) microgel prepared in the microcapillary (1000  $\mu\text{m}$  diameter) on the ON/OFF NIR laser irradiation; b: NIR laser-driven size change of the microgel at different pH values, the  $d/d_0$  values of the gel are plotted as a function of time, where  $d_0$  and  $d$  denote the diameters of the initial gel and shrunken gel, respectively. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

bonds with themselves than amide groups, the decrease of pH value would cause the ionization of carboxyl groups, which reduces the number of their hydrogen bonds resulting in a lower volume phase transition temperature (or LCST).<sup>13</sup> The pH-responsive behavior of the MWCNTs/P(NIPAm-co-AA) microgels would explore their potential applications in microfluidic fields, for instance, they could be used to detect the pH level of the surrounding liquid by investigating their NIR-response speed, also their different NIR-responsive volume change rates in different pH environments lead to the application in controlling flow rate in a microfluidic system.

## CONCLUSIONS

A facile method for the controllable synthesis of MWCNTs/P(NIPAm-co-AA) microgels was demonstrated. MWCNTs acted as an effective “molecular heater” to raise temperature of the composite. Both NIR-laser-driven volume phase transition and pH-responsive behaviors of the microgel were realized, making it a candidate for the environment-driven switch which could be applied in microreactors.

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