

# Highly selective iodide-responsive gel–sol state transition in supramolecular hydrogels†

Jiang-Shan Shen, Dong-Hua Li, Qing-Guo Cai and Yun-Bao Jiang\*

Received 5th May 2009, Accepted 10th June 2009

First published as an Advance Article on the web 8th July 2009

DOI: 10.1039/b908755a

We demonstrate for the first time a highly selective anion-responsive reversible gel–sol state transition in a supramolecular hydrogel of Ag(I)-glutathione (GSH) coordination polymers, which allows for facile and selective visual recognition of I<sup>−</sup> *via* naked eyes even in a strongly colored and/or fluorescent background. Such a strategy overcomes the drawback of spectral interferences which are often encountered in conventional colorimetric and fluorimetric means. It was rationalized that I<sup>−</sup> functioned as a depolymerizing agent for the Ag(I)-GSH supramolecular hydrogels. A feasible quantitative assay for I<sup>−</sup> was established that afforded satisfactory results for simulated wastewater samples. We believe that this strategy can in principle be applicable to other species by following a smart gel–sol state transition in designed supramolecular hydrogel.

## 1. Introduction

Anions especially halides play important roles in both environment and life sciences. For example, iodide (I<sup>−</sup>) can induce depolymerization of actin filaments and the corresponding transition from a gel–like state to a sol state, possibly by influencing the hydration shell that is thought to surround and stabilize the actin filaments polymer.<sup>1</sup> Therefore, developing selective and feasible detection strategies for anions are undoubtedly crucial. Actually, anion recognitions have indeed received much attention during past decades.<sup>2</sup> However, only few investigations involve I<sup>−</sup> recognition, and most of which were conducted by colorimetric and fluorimetric methods.<sup>3</sup> Although colorimetric and fluorimetric means are able to offer ingenious strategies for anion sensing,<sup>2,4</sup> feasible and highly selective recognition for anions is still demanded and remains challenging because these spectrophotometric methods often suffer from serious spectral interferences in colored and/or fluorescent backgrounds. Supramolecular hydrogels of low-molecular-weight gelators, formed by three-dimensional and elastic networks that encapsulate a large amount of water to have a solid-like appearance, have been shown to undergo a gel–sol and/or a sol–gel state transition when triggered by external stimuli such as pH,<sup>5</sup> heat,<sup>6</sup> light,<sup>7</sup> host–guest interaction<sup>8</sup> and even biologically relevant molecules.<sup>9</sup> Such stimulus-responsive gels, called “smart” or “intelligent” gels, have recently been extensively investigated due to their potential applications in for example controlled drug delivery and release,<sup>10</sup> and pollutant capture and removal.<sup>11</sup> In terms of employing anions as a stimulus, however, only a few reports are known that involve anion-

responsive gel–sol state transition in supramolecular organogels.<sup>12</sup> In most of these cases anions were suggested to be an inhibitor to the formation of supramolecular organogels. Recently, several anion-responsive supramolecular hydrogels have been reported. These hydrogels either showed response unselectively toward a variety of anions<sup>13</sup> or served as the support and matrix for sensing.<sup>14</sup> To the best of our knowledge, highly selective anion-responsive reversible gel–sol state transition in supramolecular hydrogels has not been achieved so far.

It is known that thiols react with Au(III) or Ag(I) to form Au(I)-SR or Ag(I)-SR coordination polymers.<sup>15</sup> The gelation of Au(I)-glutathione (GSH) or Ag(I)-GSH coordination polymers could be realized under certain pH.<sup>16</sup> Here we report a highly selective recognition platform for I<sup>−</sup> based on anion-responsive gel–sol state transition in supramolecular hydrogels of Ag(I)-GSH coordination polymers. Transparent, homogeneous, and stable Ag(I)-GSH supramolecular hydrogels could be facilely obtained by a newly developed acid volatilizing manner which allows pH to undergo a slow decrease with no need for stirring. These hydrogels demonstrate intriguing photoluminescence (PL) and circular dichroism (CD) signals which are probably related to argentophilicity.<sup>17,18</sup> I<sup>−</sup> was found capable of triggering the hydrogels to perform a macroscopic gel–sol state transition, whereas other anions such as F<sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>−</sup> hardly led to any observable change in the gel state. Furthermore, reversible sol–gel state transition could be performed by adding 1 eq. Ag(I) into the resulting sol solution (Scheme 1). Such an intriguing feature offers a highly selective visual recognition of I<sup>−</sup> by naked eyes. It is able to overcome the drawbacks of traditional spectrophotometric means in a colored and/or fluorescent background which often results in troublesome spectral interferences.

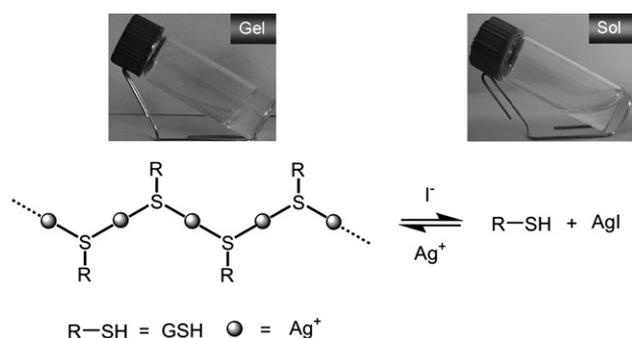
## 2. Experimental

### Materials

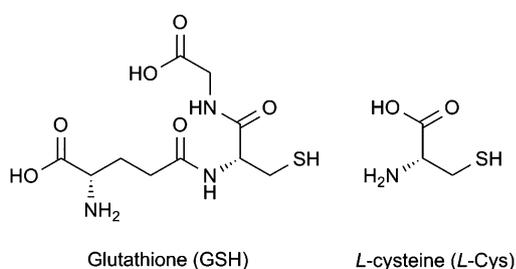
Glutathione (GSH, > 98%), L-cysteine (L-Cys, > 99%), and AgNO<sub>3</sub> (> 99.8%) were purchased from Sangon (Shanghai,

Department of Chemistry, College of Chemistry and Chemical Engineering, The MOE Key Laboratory of Analytical Sciences, Xiamen University, Xiamen, 361005, China. E-mail: ybjiang@xmu.edu.cn; Fax: +86 592-218-5662; Tel: +86 592-218-5662

† Electronic supplementary information (ESI) available: Other characterizations of the supramolecular hydrogels, photographs of hydrogels under room and UV light and in the presence of anions, PL and CD spectra of hydrogels, and possible mechanism of the hydrogel formation. See DOI: 10.1039/b908755a



**Scheme 1** Illustration of reversible gel-sol state transition of supramolecular hydrogel of Ag(I)-GSH coordination polymers triggered by alternately adding  $I^-$  into hydrogel and Ag(I) into the resulting sol solution.



**Scheme 2** Molecular structures of GSH and L-Cys.

China). Other chemicals (AR) were obtained from Guoyao (Shanghai, China) without further purification before use. Molecular structures of GSH and L-Cys are given in Scheme 2.

### Characterization of Ag(I)-GSH supramolecular hydrogel

PL spectra were taken on a Hitachi F-4500 fluorescence spectrophotometer using excitation and emission slits of 5 nm and 10 nm, respectively. CD spectra were measured on a JASCO-810 CD spectrophotometer. Infrared (IR) spectra were measured by using a Nicolet AVATAR FT-IR 360 IR spectrophotometer. Scanning electron microscopy (SEM) experiments were performed on LEO1530 working at an accelerating voltage of 20 kV. Dynamic light scattering data were obtained from ZetaPALS zeta potential analyzer.

### Preparation of supramolecular hydrogel with varying Ag(I)-GSH content

1 equivalent of  $AgNO_3$  and 1 equivalent of GSH were respectively dissolved in pure water of a certain volume. Two solutions were mixed, leading to systems with Ag(I)-GSH content by weight of 0.2%, 0.3%, 0.4%, 0.5%, and 1%. pH of these systems were adjusted to 6.0 by using 0.1 M NaOH solution that the systems gradually became clear and transparent. The homogeneous and transparent solutions (1 mL) were then put in a sealed container in which 5 mL glacial acetic acid was placed. It takes *ca.* 5–6 h for the solution to transform completely into homogeneous, transparent, and stable hydrogel.

### Response of Ag(I)-GSH supramolecular hydrogel toward anions

Varying amounts of anion were respectively added into the hydrogel containing 0.5% Ag(I)-GSH (wt). The volume of added anion solution was kept to less than 100  $\mu L$ . The hydrogels then stood at room temperature for 1 h after which a macroscopic morphology change in the gel was observed and recorded by digital camera.

Reversed sol-gel state transition could be observed by adding 1 eq. Ag(I) into the resulting sol solution after re-standing in the sealed container placing 5 mL glacial acetic acid for *ca.* 5–6 h.

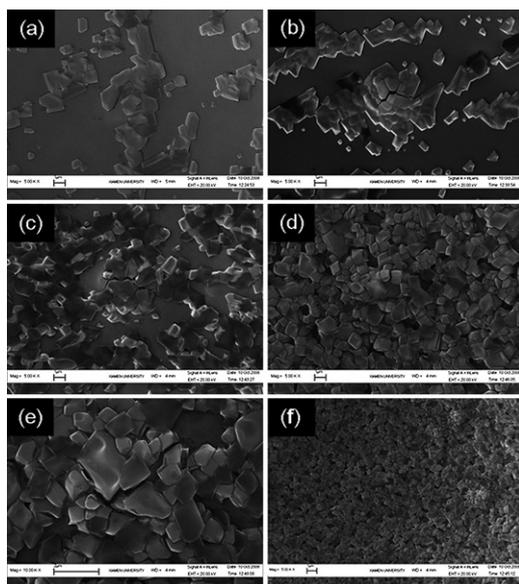
The ratio of the final apparent-weight of the sol solution to the initial apparent-weight of the gel ( $W_{sol}/W_{gel}$ ) was obtained by means of weighing. The resulting sol solutions could be easily and feasibly isolated. The linear relationship between  $W_{sol}/W_{gel}$  and  $I^-$  amounts could be built for quantitative assay. The employed hydrogel contained 0.5% Ag(I)-GSH (wt).

$1.0 \times 10^{-3}$  M fluorescein dye was employed in the 0.5% Ag(I)-GSH (wt) system to show the gelation and the reversible gel-sol and sol-gel state transition response toward  $I^-$  and Ag(I) in the colored and/or fluorescent background, respectively. The experiments were similarly conducted by following the above-mentioned procedures. The macroscopic morphology change in the hydrogels was similarly observed and recorded.

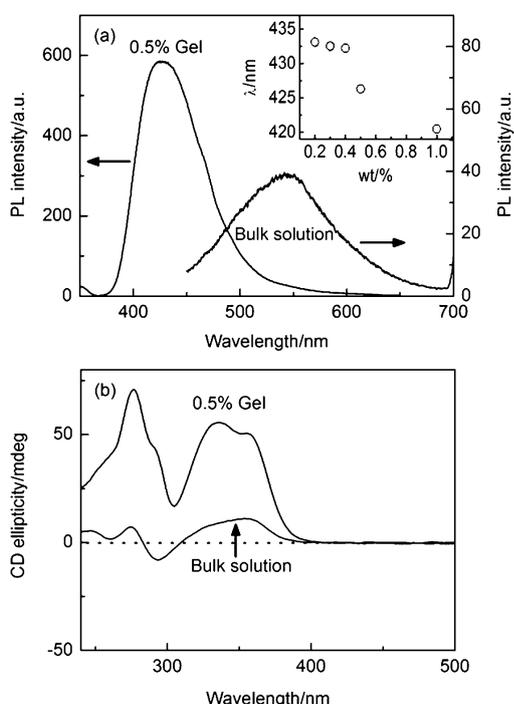
## 3. Results and discussion

Two crucial factors affecting the formation of Ag(I)-GSH supramolecular hydrogel were examined, one of which is pH and the other is Ag(I)-GSH content. We have recently observed that at spectral measurement concentration of 75  $\mu M$ , absorption, CD, and PL spectral signals of Ag(I)-GSH bulk solution, which resulted probably from ligand-to-metal charge transfer transitions that mixed with metal-centered (ds/dp) states modified by metallophilic interaction (LMMCT),<sup>17,18</sup> can be switched on and off *via* altering pH.<sup>17</sup> It has previously been shown that the gel state of Ag(I)-GSH supramolecular coordination polymer appeared at pH of 2–5.<sup>16b</sup> We noted that direct addition of acid into Ag(I)-GSH solution could hardly form transparent, homogeneous, and stable hydrogels. Reason might be that in this manner stirring is required and consequently the solution pH undergoes a rapid decrease. Volatile acids such as acetic acid (HAc) were therefore expected to allow a slow decrease in pH with no need for stirring. HAc was introduced into Ag(I)-GSH solution in a sealed environment, by a newly developed volatilizing method. On the basis of the tilting tube method, we found that it took 5–6 h to form transparent, homogeneous, and stable Ag(I)-GSH supramolecular hydrogels.<sup>19</sup> SEM images of the dried hydrogels show that the hydrogels contain well defined three-dimensional nanosized or even microsized structures of brick-like aggregates (Fig. 1).

Regarding to the effect of Ag(I)-GSH content, we found that gelation could still be observed at Ag(I)-GSH content as low as 0.2% by weight, which can be taken as the minimum gelator concentration (MGC). Five hydrogels with increasing Ag(I)-GSH content are shown in Fig. S1. All these hydrogels are luminescent, with maximum emission wavelength varying from 433 nm to 421 nm (Fig. 2a and Fig. S2 in ESI<sup>†</sup>). The weak blue-light emitted by the hydrogels under UV-light can be observed by



**Fig. 1** SEM images of xerogels containing Ag(I)-GSH of 0.2% (a), 0.3% (b), 0.4% (c), 0.5% (d,e), and 1.0% (f) by weight. Scale bar for (a–d) is 1  $\mu\text{m}$  and for (e,f) is 2  $\mu\text{m}$ .



**Fig. 2** PL (a) and CD (b) spectra of hydrogel and of bulk solution (75  $\mu\text{M}$  Ag(I)-GSH, pH 3.8<sup>17</sup>).  $\lambda_{\text{ex}} = 350$  nm. Inset in (a) shows plot of maximum emission wavelength of the hydrogel versus Ag(I)-GSH content (wt).

naked eyes (Fig. S1b). Compared with emission of the bulk solution (75  $\mu\text{M}$  Ag(I)-GSH, pH 3.8) with a maximum of 545 nm,<sup>17</sup> PL of these hydrogels are dramatically blue-shifted. The observed blue shift in the emission with increasing Ag(I)-GSH content (Fig. 2a inset) is tentatively attributed to the rigidochromic effect.<sup>20</sup> CD spectra of the hydrogels (Fig. 2b and

Fig. S3, ESI<sup>†</sup>), however, are somewhat similar to that of the bulk solution.<sup>17</sup> The CD spectra demonstrate positive Cotton effect despite of their complexity. PL and CD signals of the hydrogels are probably related to LMMCT transition due to argentophilicity.<sup>17,18</sup> In this regard, it is noteworthy that the bulk solution (75  $\mu\text{M}$ ) or the resulting sol solution (0.2–1% Ag(I)-GSH by weight) does hardly show any CD and PL signals at neutral and basic pH since under such pH conditions the argentophilicity is turned off.<sup>17</sup> The metallophilic attraction hence appeared to be an important driving force for the gel formation. It should be pointed out that, only one case of switchable photoluminescent organogel of coinage metallophilic interaction origin has yet been observed,<sup>21</sup> whereas optical active supramolecular organogel or hydrogel of metallophilicity origin has not been demonstrated so far.

Gelation of Ag(I)-GSH under varying ionic strength was investigated. It was found that the gel formation was independent of the ionic strength maintained by NaNO<sub>3</sub> and NaCl (Table 1). Stable hydrogels could be obtained in the presence of strong electrolytes over a wide concentration range, although at high concentration the hydrogel was somewhat translucent. Temperature effect experiments showed that the original gel state remained essentially unchanged under a sealed environment from room temperature to 90 °C. This indicates that the hydrogels are unusually thermostable. Taking together all these observations, synergistic interactions involving metallophilic attraction,<sup>17</sup> hydrogen bonding and/or electrostatic interaction<sup>22</sup> are suggested to be responsible for the gelation (Fig. S4, ESI<sup>†</sup>).

Another SH-containing biomolecule of similar structure, *L*-cysteine (*L*-Cys, Scheme 2), was employed to examine the feasibility of the formation of supramolecular hydrogels. No obvious gelation, however, was observed at a series of Ag(I)-*L*-Cys content (wt) and pH. This indicates that the bulky molecular structure of GSH compared to *L*-Cys as the ligand plays a critical role in the gelation. This is probably because that GSH residues in the polymeric backbone provide enough space for water molecules to be trapped between the self-assembled 2D sheets of Ag(I)-thiolates, leading to the formation of stable hydrogels in the case of Ag(I)-GSH.

Response of the hydrogel toward a number of anions F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> was followed in a hydrogel containing 0.5% Ag(I)-GSH (wt). Upon addition of 1 eq. I<sup>-</sup> into the hydrogel, the gel was found to be transformed into a slightly yellow fluidic solution after 1 h. In contrast, the hydrogel remains in its original

**Table 1** Ionic strength effect on hydrogel formation from Ag(I)-GSH sol solution<sup>a</sup>

Electrolyte	Conc./mM	Results
NaNO <sub>3</sub>	5	Gel
NaNO <sub>3</sub>	10	Gel
NaNO <sub>3</sub>	100	Gel
NaNO <sub>3</sub>	500	Gel <sup>b</sup>
NaCl	50	Gel
NaCl	200	Gel
NaCl	500	Gel <sup>b</sup>
NaCl	1000	Gel <sup>b</sup>

<sup>a</sup> The employed sol solution contained 0.5% Ag(I)-GSH (wt). <sup>b</sup> The gel state was somewhat translucent.

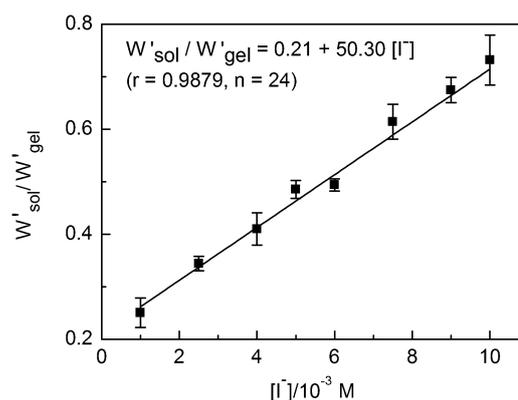
gel state upon addition of 1 eq. of the tested other anions  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $H_2PO_4^-$  (Fig. S5a, ESI†). Note that the stability constants of  $AgXs$  ( $X = F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $I^-$ ) are  $2.09$ ,  $1.05 \times 10^{10}$ ,  $1.35 \times 10^{11}$ , and  $1.08 \times 10^{16} M^{-1}$ , respectively,<sup>23</sup> whereas those of the  $Ag(I)$  thiolates are at  $10^{13} M^{-1}$  order of magnitude<sup>24</sup> and  $AgH_2PO_4$  is water soluble. Because of a stronger complexation ability of only  $X = I^-$  towards  $Ag(I)$  than that of  $-SR$ , it is reasonable to attribute the  $I^-$ -triggered gel-sol state transition to the displacement by  $I^-$  of  $-SR$  component in the coordination polymeric backbone that results in the depolymerization of  $Ag(I)$ -GSH polymeric structures and the release of entrapped water (Scheme 1). It was found that, even mixed for 24 h with 1 eq. of the tested other anions  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $H_2PO_4^-$ , the original gel state remained essentially unchanged. This means that the possible kinetic processes would not lead to gel-sol state transition. The counter cation effect was also examined, which revealed that the gel-sol state transition was independent of the counter cation (Table 2). This offers a further support for the assumption of the depolymerization caused by  $I^-$ . Response to  $I^-$  of varying concentration was then monitored, from which it was found that 0.25, 0.5, and 0.75 eq.  $I^-$  could induce partial transformation of the hydrogel into sol, and 1 eq.  $I^-$  was enough to trigger a full gel-sol transition (Fig. S5b, ESI†). More importantly, the resulting sol state could return to the homogeneous gel state again upon addition of 1 eq.  $Ag(I)$  (Scheme 1). Such a reversible gel-sol state transition can be repeated at least three times by alternately adding  $I^-$  into the hydrogel and  $Ag(I)$  into the resulting sol solution. This allows for a visual semi-quantitative assay for  $I^-$  by naked eyes.

A quantitative analysis of  $I^-$  was further conducted by using sol/gel weight. This was realized by plotting the ratio of final apparent-weight of the sol solution to initial apparent-weight of the gel ( $W'_{sol}/W'_{gel}$ ) versus  $I^-$  concentration. A linear correlation of  $W'_{sol}/W'_{gel} = 0.21 + 50.30 [I^-]$  ( $r = 0.9879$ ) was obtained (Fig. 3). The limit of detection for  $I^-$  was estimated to be  $4.23 \times 10^{-4} M$  ( $3\sigma/k$ ,  $n = 11$ ) with a relative standard deviation (RSD) of 0.71%. This quantitative method provides a well supplement to the semiquantitative naked-eye viewing. It should be noted that the released water molecules actually functioned as the signal reporter which offered a signaling

**Table 2** Results of state change of the hydrogel upon addition of 1 eq. anions with different counter cation<sup>a</sup>

Cation	Anion	State
$Na^+$	$F^-$	Gel
$K^+$	$F^-$	Gel
$Ca^{2+}$	$F^-$	Gel
$Na^+$	$Cl^-$	Gel
$K^+$	$Cl^-$	Gel
$Mg^{2+}$	$Cl^-$	Gel
$Ca^{2+}$	$Cl^-$	Gel
$Na^+$	$Br^-$	Gel
$K^+$	$Br^-$	Gel
$Ca^{2+}$	$Br^-$	Gel
$Na^+$	$I^-$	Sol
$K^+$	$I^-$	Sol
$Na^+$	$H_2PO_4^-$	Gel
$K^+$	$H_2PO_4^-$	Gel

<sup>a</sup> The employed hydrogels contained 0.5%  $Ag(I)$ -GSH (wt).

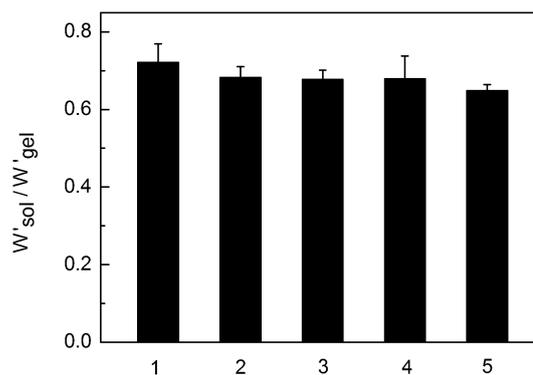


**Fig. 3** Linear relationship with  $I^-$  concentration of apparent-weight ratio of the final sol solution to initial hydrogel. The employed hydrogel contained 0.5%  $Ag(I)$ -GSH (wt).

amplification, since the weight of released water is *ca.* 660 times that of the introduced  $I^-$  in the case of 0.5%  $Ag(I)$ -GSH hydrogel.

The excellent selectivity for  $I^-$  was further demonstrated by the observation that the gel-sol state transition response to  $I^-$  was unaffected by the presence of tested other anions  $F^-$ ,  $Cl^-$ ,  $Br^-$ , and  $H_2PO_4^-$  (Fig. 4). This result confirms that the gel-sol state transition response is highly selective for  $I^-$ .

In order to demonstrate the advantage of this highly selective anion-triggered gel-sol state transition, a colored and fluorescent dye was employed as the anion-responding background. It was found that the  $Ag(I)$ -GSH supramolecular hydrogel could form in the presence of colored fluorescein with strong fluorescence. Yet the macroscopic gel-sol state transition upon addition of  $I^-$  can still be easily identified by naked eyes (Fig. S6, ESI†). This allows for an easy recognition of  $I^-$  and successfully avoids the interference of colored and fluorescent background. Reversible gel-sol state transition could similarly be conducted (Fig. S6, ESI†). To show the sensing potential of this strategy in practical application, it was applied to the determination of  $I^-$  in simulated wastewater samples. The iodide amounts measured by this strategy agreed well with those added, with satisfactory RSDs (Table 3).



**Fig. 4** Ratio of apparent-weight ratio of the final sol solution to initial hydrogel toward  $I^-$  ( $1.0 \times 10^{-2} M$ ) in the absence (1) and presence (2–5) of equimolar another anion. The mean value and standard deviation were obtained from three measurements. 1:  $I^-$  only; 2:  $I^- + F^-$ ; 3:  $I^- + Cl^-$ ; 4:  $I^- + Br^-$ ; 5:  $I^- + H_2PO_4^-$ . The employed hydrogel contained 0.5%  $Ag(I)$ -GSH (wt).

**Table 3** Determination of iodide in simulated wastewater samples containing  $1.0 \times 10^{-3}$  M fluorescein<sup>a</sup>

I <sup>-</sup> added / $10^{-3}$ M	I <sup>-</sup> found / $10^{-3}$ M <sup>b</sup>	RSD /%	Recovery /%
6.00	5.96	3.90	99.3
8.00	7.89	3.27	98.6

<sup>a</sup> The employed hydrogel contained 0.5% Ag(I)-GSH (wt). <sup>b</sup> Mean value of three measurements.

## 4. Conclusions

In summary, we showed for the first time a highly selective recognition of anions based on gel–sol state transition of supramolecular hydrogels. Transparent, homogeneous, and stable supramolecular hydrogels of Ag(I)-GSH coordination polymers could be facily obtained in an acid volatilizing manner. It was found that I<sup>-</sup> was able to trigger gel–sol state transition of the Ag(I)-GSH supramolecular hydrogel, whereas the tested other anions F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> could not. Large difference of the stability constant of AgI from those of the other AgXs (X = F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and -SR) is considered responsible for the high selectivity towards I<sup>-</sup> that results in depolymerization of Ag(I)-GSH supramolecular hydrogels. Alternately adding I<sup>-</sup> into the hydrogel and Ag(I) into the resulting sol solution led to reversible gel–sol and sol–gel state transition that could be repeated for at least three times. Similar state transitions were also successfully performed under a colored and highly fluorescent background. The highly selective recognition of I<sup>-</sup> can therefore be easily realized by means of naked-eye viewing, with no need of instrumental assistance. This overcomes the drawback of spectral interferences which are often encountered in conventional colorimetric and fluorimetric means. A feasible quantitative assay for I<sup>-</sup> was further shown and successfully applied to the simulated wastewater samples. The released water molecules in the gel–sol state transition process actually acted as the signal reporter in this strategy, which differs from the conventional gravimetric method in that the weight of released water is ca 660 times that of the introduced I<sup>-</sup>. The operative principle reported here is expected to be applicable for extended uses to other species following a smart gel–sol state transition in designed supramolecular hydrogels.<sup>8,9</sup> In addition, the intriguing PL and CD properties may enable Ag(I)-GSH supramolecular hydrogels to be developed as switchable chiral and photoluminescent devices.

## Acknowledgements

This work has been supported by the NSF of China (Grants Nos. 20675069, 20835005, and J0630429). Thanks are due to Mr. Jun Zheng of the Department of Chemistry, Xiamen University for his generous help in SEM experiments.

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