Effect of pH on Swelling Ratio and Fluorescence of Quantum Dots (QDs) Hydrogel ($CuInS_2/ZnS$ Hydrogel)

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ABSTRACT

Quantum dots (QDs) are semiconductor materials possessing a distinct electrical order and physical dimensions that are less than the excitation of the Bohr radius. The innovative combination of hydrogel and QDs has many applications in critical areas like the environment and health. In the biosensor application, QDs hydrogel can be used as active sensors by changing the fluorescence properties when reacting with analytes or by conjugating antibodies to the dot surface to act as passive label probes. This study aims to study the effect of pH on the fluorescence and swelling ratio of $CuInS_2/ZnS$ hydrogel. $CuINS_2/ZnS$ hydrogel is synthesized by sonication a mixture of QDs ($CuInS_2/ZnS$), N-(3-aminopropyl) methacrylate, polyethylene glycol methacrylate, methylene bis acrylamide, and ammonium persulfate solution for 5 min with amplitude of 20 kHz. $CuInS_2/ZnS$ acts as QDs, while N-(3-aminopropyl) methacrylate, polyethylene glycol methacrylate, methylene bis acrylamide, and ammonium persulfate act as hydrogel synthesizing components. The QDs hydrogel was then immersed in water with varying pH to observe the effect of pH on fluorescence and swelling ratio. The results show that increasing pH will reduce the swelling ratio and increase the fluorescence strength. $CuInS_2/ZnS$ hydrogel has a maximum swelling ratio at a pH of 5 and provides strong fluorescence at pH 7, 9, and 11. The result also revealed that $CuInS_2/ZnS$ hydrogel has sufficient fluorescence and swelling ratio characteristic at the pH level of the biological fluid of the human body, namely 7.35-7.45; this suggests the biological application of $CuInS_2/ZnS$ hydrogel such as for drug delivery and biosensing.

1. Introduction

Hydrogel is a macro-molecular material that has cross-linked tissue which when exposed to water forms a three-dimensional macromolecule tissue. It is capable of absorbing water exceeding its weight or volume and capable of releasing water based on external stimulation [1]. Some important applications of this hydrogel are in mechanisms for the controlled delivery of drugs, as heavy metal ion removals, as a material for lensing in tissue engineering, contact lens production, as sensors, and as super-capacitors [2], [3]. In biomedical fields, hydrogel is used to store bio-macromolecules such as proteins and DNA [4]. The development towards the application of hydrogel is also applied as a fever-reducing plaster [5].

Meanwhile, quantum dots (QDs) are semiconductor materials possessing a distinct electrical order and physical dimensions less than the excitation of the Bohr radius. The Bohr radius is the distance in an electron–hole exciton [6]. Its value is 5.29×10^{-11} m [7]. The period of II or III–V

elements from the periodic system are typically used to synthesize the QDs. QDs have potential applications in the fields of biology, nano-diagnostics, bio-imaging, drug delivery, and photodynamic therapy [8], [9]. QDs are frequently utilized in fluorescence detection because of their exceptional photoluminescence characteristics, strong water solubility, and good biocompatibility. The fluorescence quantum yield (QY) of QDs is a critical factor in determining their photoluminescence characteristics. Quantum yield is defined as the relationship between photon emission and absorption [10].

$CuInS_2$/ZnS is one of the QDs that has a 1.45 eV belt gap and has low stability, efficiency, toxicity, and spectrum in the red spectrum range to close to the visible light spectrum ranging from 600 to 1100 nm [11]–[14]. Adding Zn^{2+} or ZnS to the core of the QDs will improve the fluorescent performance of the semiconductor QDs. Deng et al. [15] indicate that an increase in the Zn in the AISe QDs system will lead to the blue spectrum at photoluminescent emission, which increases the quantum yield (QY) by 50%. Separately, Deng also observed the optical characteristics of the AISe QDs after the addition of the ZnS by hot injection process, the quantum yield of AISe QDs can reach 40% with emissions in the range of 700-820 nm. So this emission range makes QDs applicable for biological purposes [12].

The innovative combination of hydrogel and QDs has a broad range of applications in critical areas like the environment, health, and energy. QDs hydrogel has been applied as a biosensor and in the waste processing industry. Fluorescent QDs hydrogel has successfully identified several heavy metal ions such as Pb^{2+} [16], [17], Fe^{3+} [18]–[22], Cu^{2+} [19], [21], [23], Cr^{6+} [24], Ag^{+} [25] and Hg^{2+} [26]. Several types of QDs have been combined with hydrogel such as CdS, graphene-Fe3O4, ZnO, and CdSe ZnS [17], [26]. By immobilizing the QDs in a hydrogel matrix, sample conditions that produce analyte-independent effects are reduced and on-site detection of heavy metal ions is made possible [26]. However, no research has observed the potential of semiconductor $CuInS_2$/ZnS hydrogel. Therefore, this study examines the initial potential of $CuInS_2$/ZnS hydrogel in particular the influence of pH on the fluorescence of hydrogel, and studies the swelling ratio of $CuInS_2$/ZnS hydrogel to water. From this research it is expected that $CuInS_2$/ZnS hydrogel with excellent swelling and fluorescent performance will be obtained at specified pH, thus enabling its application in the biosensor and waste processing industry.

2. Research Methodology

2.1. Materials

Copper acetate (CuAc, 99.995% purity Sigma Aldrich, USA), Zinc stearate (ZS, purity 90%, Sigma Aldrich, USA), 1-dodecanethiol (DDT, 97% purity Sigma Aldrich, USA), 1-octadecene (ODE, 90% purity Sigma Aldrich, USA), Indium acetates (InAc) (99% purity Alfa-Aesar, USA), Zinc chloride (99% purity Riedel-deHaen AG Germany), Poly (ethylene glycol) methacrylate (PEGMA, Mn~360 and Mn~526), N, N-dimethyl formamide (99.8% purity, Sigma Aldrich, USA), N'-methylene bis acrylamide (98% purity Sigma Aldrich, USA), and ammonium persulfate (99% purity Sigma Aldrich, USA), N-(3-aminopropyl) metacrilamide hydrochloride (99% purity Polysciences), all organic solvents obtained from EM-Sciences, and Zinc ethylxanthate (ZE) is synthesized following a method used by Mintcheva et al [27].

2.2. Procedures

1) Preparation $CuInS_2$/ZnS QDs Solution

The preparation of $CuInS_2$/ZnS QDs followed existing literature guidelines [13]. Shortly, a mixture of 0.17517 g $In(Ac)_3$, 0.0245 g $Cu(Ac)_2$, 2.5 mL ODE, and 2.5 ml DDT was agitated at 40 ℃ for 1 h while purged in a nitrogen atmosphere. Next, the mixture underwent moderate heating, reaching 240 ℃ to ensure the nucleation process, which gave the solution a reddish-orange color. Then, another mixture in the form of 0.1 mL DMF, 0.031 g ZE in 1 mL toluene, and 0.504 g ZS in 3 mL ODE, was immediately added to the mixture to make the shell of core. After the addition was complete, this mixture was cooled to 30 ℃ and centrifuged for 20 min at 6000 rpm. Next, the supernatant was thrown away. The precipitate was dispersed in 10 ml chloroform under sonication and precipitated by adding a methanol/acetone (1:1) and the $CuInS_2$/ZnS QDs formed was precipitated by centrifugation at 6000 rpm for 10 min. The Series of $CuInS_2$/ZnS QDs synthesis apparatus is shown in Fig. 1.

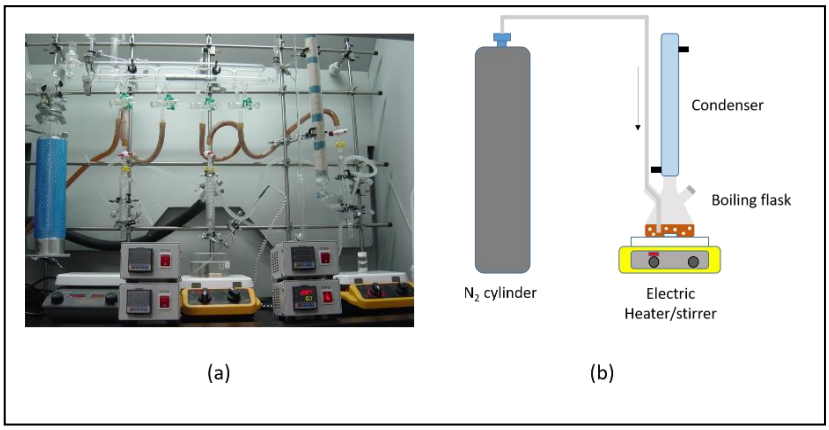

Fig. 1.$CuInS_2$/ZnS (QDs) synthesis apparatus, a) the photograph of the core synthesis apparatus, b) the series of the core-shell synthesis apparatus

2) Synthesis $CuInS_2$/ZnS Hydrogel

$CuInS_2$/ZnS hydrogel was synthesized by mixing and sonicating a solution of 40 mg N-(3-aminopropyl) methacrylate/100 µL water, 10 mL polyethylene glycol methacrylate, 3 mg methylene bis acrylamide/100 µL water, 3 mg ammonium persulfate/100 µL water and 0.5 ml $CuInS_2$/ZnS (QDs). After 5 min of sonication at an amplitude of 20 kHz, the solution became a hydrogel. This immobilized $CuInS_2$/ZnS hydrogel system exhibits unique luminescence characteristics for semiconductor QDs nanocrystals. To determine the effect of pH on the $CuInS_2$/ZnS hydrogel, the hydrogel was immersed in a solution with pH variations of 1, 3, 5, 7, 9, 11, and 13 for one and five days, with NaOH and HCl as pH control levels. Fig. 2 shows the sonication process of $CuInS_2$/ZnS hydrogel synthesis using Ultrasonic Homogenizer Mixer Sonicator 125 W. Next, the $CuInS_2$/ZnS hydrogel was irradiated using a UV lamp to observe fluorescence characteristics.

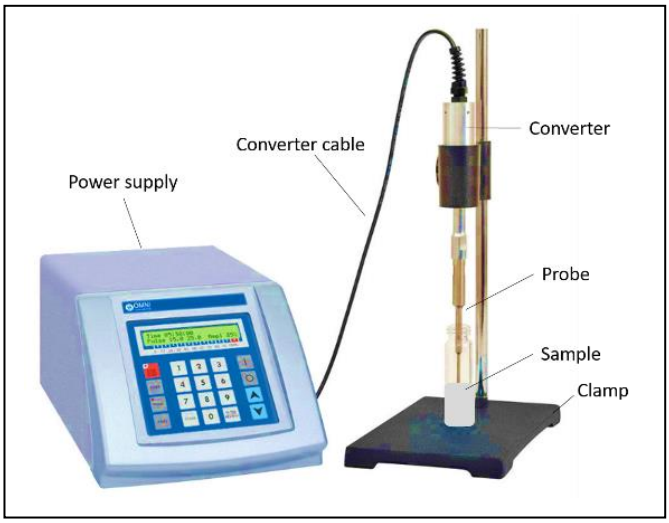

Fig. 2. Sonication process of $CuInS_2$/ZnS hydrogel synthesis

3) Swelling Ratio Calculation

The swelling behavior of hydrogel is their most interesting feature. Hydrogels begin to absorb fluid when they come into contact with solutions, which causes them to swell. The following equation applies to hydrogel's swelling ratio (*Sr*):

$$Sr = \frac{Ws - Wi}{Wi} \times 100 \quad (1)$$

Where *Wi* is the hydrogel's initial weight before submersion in water, and *Ws* is the weight of the swollen hydrogel [28].

3. Results and Discussion

The manufacture of $CuInS_2$/ZnS hydrogel is carried out in two stages. The first stage is the $CuInS_2$/ZnS (QDs) solution synthesis stage, and the second stage is the $CuInS_2$/ZnS hydrogel synthesis. The first stage of synthesis was carried out using Copper acetate (CuAc), Indium acetates (InAc), Zinc stearate (ZS), 1-dodecanethiol (DDT), 1-octadecene (ODE). Copper acetate (CuAc) is a source of Cu, Indium acetates (InAc) is a source of In, while 1-dodecanethiol (DDT) is a solvent and source of S. Cu, In, and S (CIS) are the core of QDs. The CIS QDs satisfy the needs of down-conversion materials with their adjustable emission wavelengths, increased stoke shifts, low toxicity, and affordable price [29]. ZnS (which is made from zinc stearate (ZS) and Zinc ethyl xanthate (ZE)) coating of the CIS core structure is required to enhance its stability and fluorescence characteristics [29], [30]. DMF acts as an organic solvent. Meanwhile, a polyvalent metal salt solution (ZnCl2) is used to form $-(COO)_{ns,}$ which is then used to produce a second cross-linking effect on the gel [31]. The polyvalent salts act as coordination centers in hydrogels that can enhance the mechanical characteristics of hydrogels [32].

The main materials in the second stage are polyethylene N-(3-aminopropyl) methacrylate (AMP), glycol methacrylate (PEGMA), methylene bis acrylamide (MAA), and ammonium persulfate (AP). These monomers are used in the radical copolymerization process that created the QDs hydrogel, which is also characterized by ionic coordination, micro crystallinity, and hydrophobic association [32]. AMP is the main material for hydrogel fabrication. To improve the hydrogel's hydrophilicity and water retention, MAA monomer was added. PEGMA monomers were added to enhance their mechanical performance through the synergistic strengthening impact of ionic coordination (IC) and hydrophobic association (HA) [32] and also act as coating material that can reduce nanoparticle aggregation [33]. AP monomer acts as an initiator agent. The addition of chloroform and acetone aims to purify the QDs [29]. Heating at a temperature of 240 °C is carried out to ensure that the nucleation process of the core and the growth of the shell occurs completely [29].

3.1. Effect of pH on Swelling Ratio

The swelling properties of the hydrogel are their most intriguing characteristic. The swelling mechanism is a critical component in the biological uses of hydrogel. Since biological fluid makes up the majority of the human body, the hydrogel's capacity to expand and release the drug is a crucial characteristic for drug delivery applications [2]. Estimating the swelling ratio can be done using several hydrogel characteristics. A hydrogel's type of porosity is one of its key parameters. Hydrogel pores facilitate cellular ingrowth, vascularization, and nutrition transfer. When pore size is increased, angiogenesis in the hydrogel is more efficient, resulting in faster swelling kinetics and better absorbent qualities than in non-porous hydrogel [34].

Table 1 shows that increasing the pH from 1 to 5 increases the weight of the hydrogel, for pH above 5 the weight of hydrogel tends to decrease. The reason for the decreasing weight of hydrogel is that hydrogels are three-dimensional macromolecule networks. The hydrogel contains N-(3-aminopropyl) methacrylate, which is aminoalkyl methacrylate derivative monomers with double bonds and tertiary amino or quaternary ammonium (cationic) groups in the molecule. The polymer's tertiary amine side chains become protonated at a specific temperature when the pH drops into the acidic zone, raising the network's charge density. The network's internal osmotic pressure rises sharply in tandem with the concurrent rise in mobile counterion content, causing swelling transitions that have been observed. On the other hand, if the hydrogels were submerged in the alkaline solution, the internal osmotic pressure decreased, causing the hydrogels to shrink [35][36]. This result is by the study conducted by Ali et al. [36], which examines swelling behavior, mechanical properties, and network parameters of pH- and temperature-sensitive hydrogels of poly((2-dimethyl amino) ethyl methacrylate-co-butyl methacrylate). This study shows a decrease in the swelling ratio as the pH increases from 3 to 9. This result is different from the study conducted by Xiongfei et al. [32] and Sudarsan et al. [37], which uses sodium alginate and acrylic acid as the main materials for making hydrogel. The use of sodium alginate will cause an increase in the swelling ratio along with increasing pH. This hydrogel contains abundant –COO– (from sodium alginate) and –COOH (from Acrylic acid) groups. In alkaline environments, the -COOH groups can be reversibly converted to negative -COO– groups, while in acidic media, the -COO– groups can be reversibly converted back to -COOH groups. The hydrogel's –COOH groups decreased and its negative –COO– groups

increased upon immersion in the alkaline solution. This resulted in a weakening of the hydrogen bonds between the –COOH and –OH/–NH2 groups as well as an increase in the repulsive force between the polymer chains due to an electrostatic repulsive interaction between the negative –COO– groups. The swelling ratio increased as a result of the increased repulsive force between the polymer chains, which created more space in the hydrogel network and allowed more water to enter the hydrogels [32]. So, the pH value has a significant impact on how quickly the hydrogel network relaxes. As a result, the pH value and the hydrogel's resistance are related to the pace at which free ions migrate throughout the network [32]. Fig. 3 shows the hydrogel swelling data and its interpolation curve at varying pH. The maximum swelling occurs at a pH of 5. Fig. 3 shows that increasing pH can prevent hydrogel formation. The interpolation curve shows that the optimum swelling ratio exists at the pH level of the biological fluid of the human body namely 7.35-7.45 [38], this suggests the application of QDs hydrogel for drug delivery. In the waste processing industry, the swollen hydrogel provides a more porous matrix than the shrunken hydrogel. Via passive diffusion, ions, and small molecules can enter the hydrogels through their porous matrix. In the matrix, functional molecules that are the same size as or greater than the pore size can be physically immobilized. On-site detection of the heavy metal ions is made possible by immobilizing the QDs in a hydrogel matrix [26], [39].

Table 1. Effect of pH on the weight of $CuInS_2$/ZnS hydrogel

	pH						
	1	***3***	***5***	***7***	***9***	***11***	***13***
(Botol + gel= P) (mg)	14.8	14.97	14.86	14.86	15.09	14.79	14.88
Water, 200 ml	16.76	16.94	16.83	16.83	17.08	16.78	16.87
(P + water= Q) (mg)	15.118	15.22	15.22	15.109	15.448	15.107	15.097
Q-P (mg)	0.318	0.25	0.36	0.249	0.358	0.317	0.217

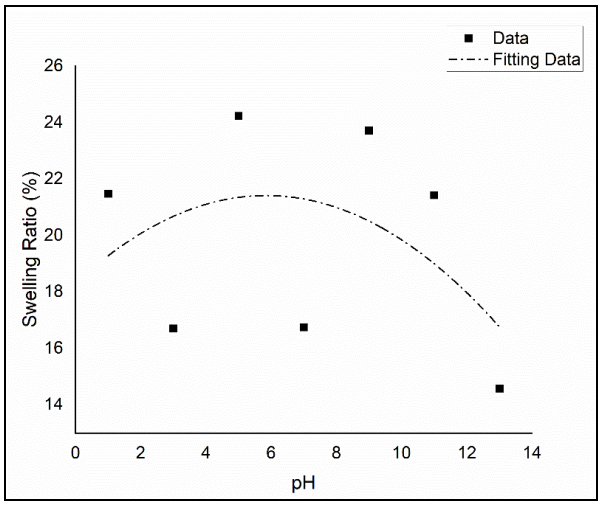

Fig. 3. Swelling ratio of $CuInS_2$/ZnS hydrogel at different pH levels

3.2. Effect of pH on Fluorescence Properties

Hydrogel fluorescent characteristics are attractive because of their enormous potential for biological imaging [40], biosensing [41], [42], and biological monitoring [43]. QDs are regarded as the perfect materials for generating fluorescent light because of their unique electrochemical characteristics, two-photon excitation, and adjustable emission wavelength [20]. Fig. 4 shows the photographs of the $CuInS_2$/ZnS (QDs) solution observed under daylight and under UV radiation. The $CuInS_2$/ZnS (QDs) present red fluorescence under UV radiation. This indicates that $CuInS_2$/ZnS QDs spectrum exists in the red spectrum range that is close to the visible light spectrum ranging from 600 to 1100 nm [11]–[14].

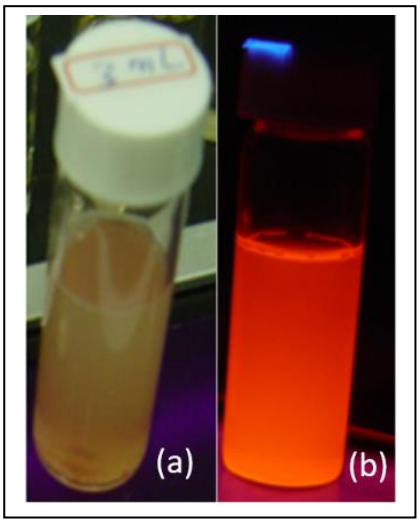

Fig. 4. The photographs of $CuInS_2/ZnS$ (QDs), a) observed under daylight and b) observed under UV radiation

The photographs of $CuInS_2/ZnS$ hydrogel and their fluorescent characteristic are presented in Fig. 5a-d. Fig. 5a and d show that the $CuInS_2/ZnS$ hydrogel experienced swelling after 1 day of immersing. Meanwhile, Fig. 5b reveals that the $CuInS_2/ZnS$ hydrogel leads to the red spectrum of photoluminescent emission at the overall pH range. Photoluminescence emission in Fig. 5c, after 5 days of immersing, presents a blue spectrum at pH of 1, 3, 5, and 13, and presents red spectrum at pH of 7, 9, and 11. The results show that immersing the $CuInS_2/ZnS$ QDs hydrogel for 5 days at pH 1, 3, 5, and 13 changes the color spectrum from red to blue. This emission spectrum makes $CuInS_2/ZnS$ hydrogel applicable for biological purposes [12]. The gel fluorescence at pH 1, 3, and 13 appeared very weak before absorbing water. After absorbing water (after 5 days), the gel fluorescence showed the same results. Even gels with a pH of 5 look weak. However, the QDs gel at pH 7, 9, and 11 showed strong fluorescence, especially at pH 11 which looks very strong. This result is different from the study conducted by Wang et al. [44], which uses glutathione as the main material in QDs synthesis. The results of this study show that optimum fluorescence occurs at pH 3, whereas in our study optimum fluorescence occurs at pH 11. This probably occurs because glutathione is an anionic group of the tripeptide, whereas in our study we used amino alkyl methacrylate which is a cationic group. The unique characteristic of QDs hydrogel is had strong fluorescence at a pH level of 7, in the range of the biological fluid of the human body (7.35-7.45), shows the suitability of the application of QDs hydrogel as a biosensor. QDs hydrogel can be used as active sensors by changing their fluorescence properties when reacting with analytes, or by conjugating antibodies to the dot surface to act as passive label probes. The idea is that light is absorbed by this QD hydrogel at a certain wavelength (excitation) and emitted at a different, higher wavelength (emission). For example, fluorophore-coupled particular antibodies or proteins are introduced into the cell to visualize the target molecule. After that, the specimen is exposed to light at the excitation wavelength and seen via a filter that only lets light that indicates the presence of the structure of interest pass through [45].

This research is limited to analyzing the characteristics of QDs hydrogel based on pH parameters only, other parameters such as temperature and time are still open to research. Likewise, the synthesis of QDs with different core and shell structures, and the using of different hydrogel materials is a new opportunity.

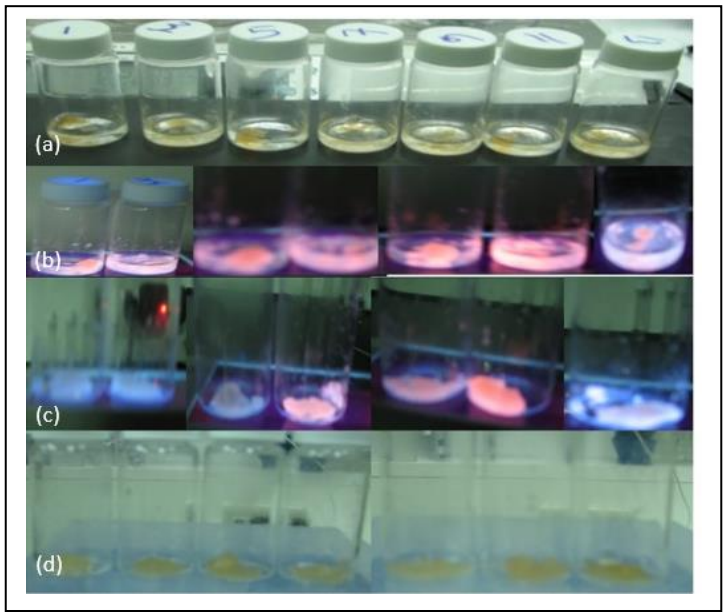

Fig. 5. The photographs of $CuInS_2$/ZnS hydrogel a) QDs hydrogel appearance under daylight b) QDs hydrogel appearance under UV lamp radiation c) QDs hydrogel appearance under UV lamp radiation after 5 days immersed in water d) QDs hydrogel appearance under daylight after 1 day immersed in water

4. Conclusion

$CuInS_2$/ZnS hydrogel has important applications in biosensors and waste processing industries. Swelling ratio and fluorescence are important characteristics of QDs hydrogel. In the waste processing industry, the swollen hydrogel provides a more porous matrix than the shrunken hydrogel. The porous matrix of the hydrogels allows the heavy metal to penetrate the hydrogels via passive diffusion and immobilize the matrix. Hence, on-site heavy metal ion detection is made possible by the QDs hydrogel. In the biosensor application, QDs hydrogel can be used as active sensors by changing their fluorescence properties when reacting with analytes, or by conjugating antibodies to the dot surface to act as passive label probes. The results show that pH affects the swelling ratio and fluorescence of $CuInS_2$/ZnS hydrogel. The increase of pH from 1 to 5 increases the swelling ratio of the hydrogel, for pH above 5 the hydrogel tends to shrink. $CuInS_2$/ZnS QDs hydrogel has a maximum swelling ratio at a pH of 5 and provides a red spectrum at the initial state and strong fluorescence at pH of 7, 9, and 11. The result also revealed that $CuInS_2$/ZnS hydrogel has sufficient fluorescence and swelling ratio characteristic at the pH level of the biological fluid of the human body namely 7.35-7.45, this suggests the biological application of $CuInS_2$/ZnS hydrogel such as for drug delivery and biosensing.

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