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REVIEW

Photoresponsive Smart Hydrogels and Their Versatile Applications

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Stimuli responsive hydrogels are emerging as smart materials due to their tunable chemical and physical properties in response to various stimuli like pH, temperature, chemicals, pressure, electrical or light. Photoresponsive hydrogels are more attractive for versatile applications as their properties can be manipulated *via* contact free fine tuning of wavelength and intensity of light. If designed properly photoresponsive hydrogels could also have inherent biocompatibility. Their smart responsiveness along with biocompatibility have made them suitable for applications in versatile fields starting from drug delivery, cell-culture to surface modification and soft-robotics. In this review article, basic mechanisms responsible for photo-responsiveness in hydrogels along with their potential applications are discussed.

Keywords: Photoresponsive hydrogels, Photo-thermal, Photo cleavage, Photo dimerization, Actuators, Soft robots, Drug delivery.

INTRODUCTION

Hydrogels are the three dimensional networks that can immobilize large amounts of water. They can be made of conventional synthetic polymeric gelator molecules as well as supramolecular hydrogels can be formed by self-assembly of low molecular weight gelators in water. Low molecular weight hydrogelator molecules can entrap water in their supramolecular network arising from several non-covalent interactions like hydrogen bonding, π-π stacking and electrostatic and van der Waals interactions among the gelator molecules. On the other hand, polymer molecules forms hydrogel network by two ways. One is by covalent crosslinking produced by chemical reactions between polymer chains and other is formation of polymer network through non-covalent interactions among polymer chains. Now a days stimuli-responsive smart hydrogels are emerging as smart materials due to their responses toward various internal or external triggers, such as temperature, pH, light, electric or magnetic fields and the presence of enzymes or ion concentrations [1-6]. Among these stimuli, light is particularly desirable due to their contact-free application, easy availability, tunable intrinsic properties like wavelength and intensity.

The photo-responsiveness of hydrogel can be achieved by inclusion of photochromic fluorophore within the gel network. In 1968, Irie & Kungwatchakun [7] developed photosensitive hydrogels by incorporating photosensitive triphenylmethane leucocyanide and leucohydroxide groups in polyacrylamide gels network. But these gels were not efficient enough to show reversible phase change. In 1990, Mamada *et al.* [8] developed photoresponsive transitions of gels for the first time by incorporating *bis*(4-(dimethylamino)phenyl)(4-vinylpheny1)methyl leucocyanide into *N*-isopropylacrylamide (PNIPAAm) gels the polymer network. Thereafter lots of research works have been done to develop new and effective photo-responsive hydrogels for their promising applications in drug delivery, development of extracellular matrices, development of soft actuator as well as robotics and self-healing materials [9], photodynamic therapy [10], smart energy storage systems [11], ocular therapy [12]. There are very few examples of low molecular weight photoresponsive hydrogels [13,14], however, the gel-sol transition takes longer time. Although there are few reports of low molecular weight hydrogelators comprising of asymmetric *bis*-dendritic molecules which shows rapid sol-gel transition [15], polymeric photo-responsive hydrogels are more popular due to their wide range of applications. Polymeric photosensitive hydrogels contain a polymeric network and a photochromic moiety, which follows chemical or physical transformations in response to optical signals. Majorly used light sources are ultraviolet (UV), visible light and near-infrared (NIR) light. For external use any light can be used but for application in living systems, NIR responsive hydrogels are more advantageous due to their less toxicity and deep penetrating power. In this review, we will discuss the design of reported photosensitive hydrogels with mechanism of responsiveness and their potential applications.

Mechanism of photoresponsiveness: Any kind photoresponsive materials generally exist in two states and there is always equilibrium in between these two states.

$$X \underset{h\nu_2/\Delta}{\overset{h\nu_1}{\rightleftharpoons}} Y$$

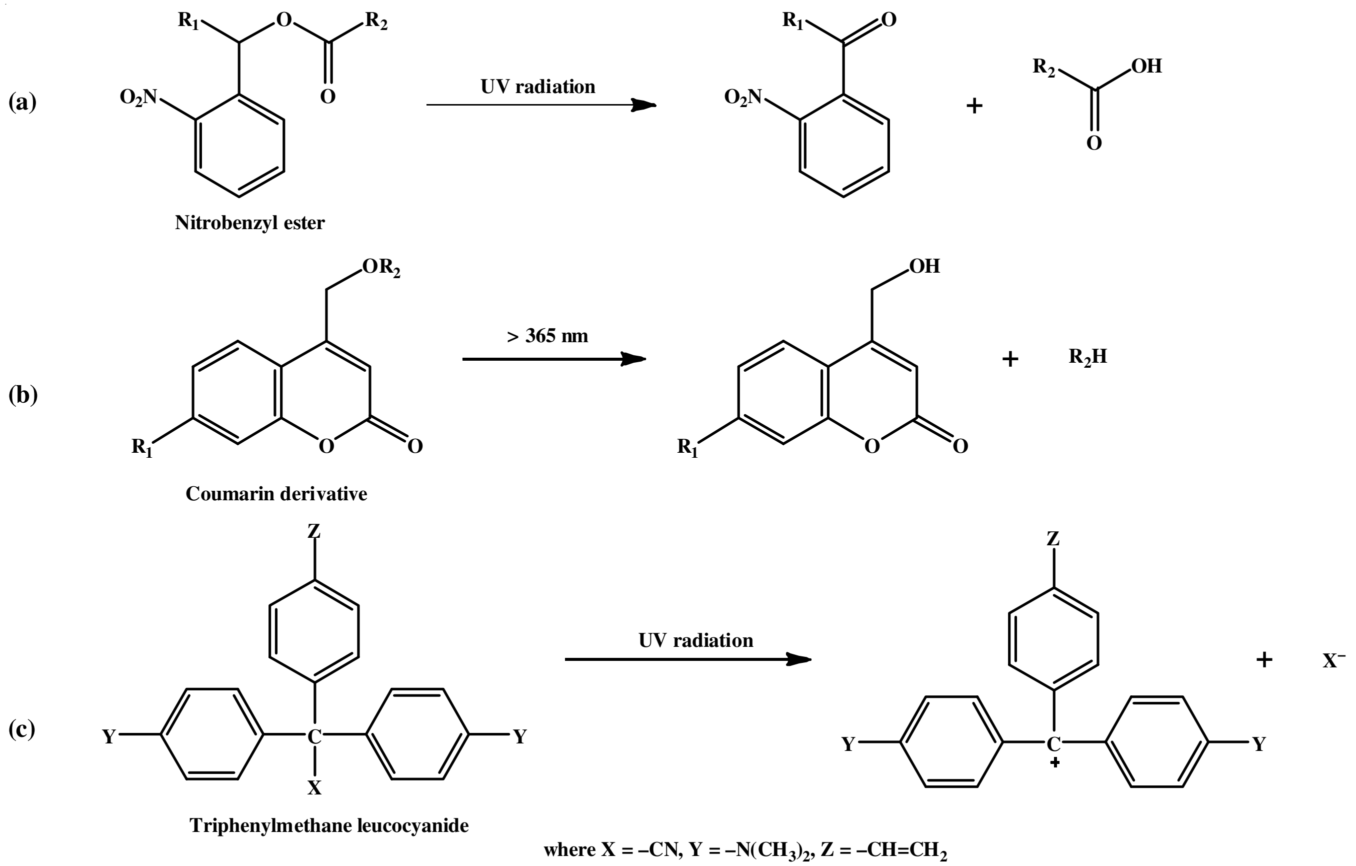
Thermodynamically stable X is converted to Y in presence of light and Y can further be converted to X again by photochemically or thermally. Upon light irradiation, the internal chemical structure or configuration changes resulting in deformation of hydrogel network. This sensitivity toward light can be introduced by incorporating photosensitive molecules into hydrogels and can induce phase transition by three major mechanisms.

Inducing photo-thermal effect: In this mechanism, the photo-sensitive molecules incorporated in a thermosensitive hydrogel can absorb light as external exposure and convert the light energy to heat energy. This heat energy increases the temperature of hydrogel and results in volume phase transition as host hydrogel is thermos-responsive but it is very difficult to control extent of deformation. This photothermal changes must be reversible in nature so that when the light source is removed the gel will be restructured again as temperature of the gel is reduced. This type of hydrogels is known as photo-thermal hydrogel.

Xing *et al.* [16] used light absorbing gold nanoparticle to prepare photo-thermal collagen-gold hybrid hydrogel. The temperature of hydrogel increases up to 40 ºC upon 1.5 min of laser irradiation. This collagen-based hydrogel was used as an injectable local drug delivery gel to enhance the antitumor efficacy. Zheng *et al.* [17] incorporated photothermal Cs_xWO_3 nanorods in polyacrylamide network during cross-linking. Upon 980 nm laser irradiation in NIR region, the hydrogel can be heated upto 45 ºC. Suzuki & Tanaka [18] introduced copper chlorophyllin salts into temperature-responsive N-isopropylacrylamide (NIPAM) gel to develop photothermal hydrogel.

Photo-cleavage: Photo-cleavage of photo-sensitive groups can also deform the network structure of hydrogel. Incorporation of photocleavable groups like nitrobenzyl estser and coumarin into the backbone of hydrogelator molecules can make photo responsive hydrogel [19]. In this context, *o*-nitrobenzyl group based photolabile linkers are widely used to get photodegradable hydrogels [20,21]. The *o*-nitrobenzyl ester has found to have photolysis into carboxylic acid and *o*-nitrosobenzyladehyde when exposed to 260 nm light (Fig. 1a). If it is substituted with electron donating group like 4,5-dimethoxy *o*-nitrobenzyl moieties 350 nm, photoirradiation is required for photodegradation.

Coumarin derivatives are also becoming popular as photosensitive moiety in the formation of responsive smart gels due



where $X = –CN$, $Y = –N(CH_3)_2$, $Z = –CH=CH_2$

Fig. 1. Photosensitive functional groups utilized for the design of photoresponsive hydrogels using photocleavage mechanism

to their biocompatibility, fast cleavage rates in biologically relevant range [21-24]. They produce biologically inert byproducts after photodegradation (Fig. 1b). Zhu *et al.* [25] have reported a wide range of coumarin derivatives which shows excellent absorption in blue-green region (430 and 515 nm). Anseth *et al.* [26] developed coumarin-based photodegradable hydrogel using copper-catalyzed click chemistry, which showed rapid photodegradation and rapid reverse gelation. Feng *et al.* [27] developed photoresponsive coumarin-based isonicotinic acid containing dual physically crosslinked (DPC) hydrogel, which can be applicable for photoresponsive drug release.

In some instances, photo-sensitive groups dissociate into additional charge or dipoles in the gel network, which creates an imbalance in osmotic field resulting in the sol formation. Triphenylmethane leucocyanide groups containing acrylamide gels have shown volume expansion upon ultraviolet irradiation [7] (Fig. 1c). The expanded gel shrank to its initial size in dark, since triphenylmethane leuco-derivatives can produce ions upon photoirradiation reversibly. The electrostatic force of repulsion between these ions can produce conformational changes in polymer causing reversible destruction in gel network.

Photo-dimerization: Cycloaddition is a well-known pericyclic reaction which can be applied to develop photo-responsive materials as reaction can be achieved at a particular wavelength of light can also be reversed by choosing proper wavelength or by applying heat. Leblanc *et al.* [28] have synthesized PEG-anthracene based hydrogel by [4+4] cycloaddition at 365 nm within 1 min and then upon irradiation at 254 nm the properties of gel changed significantly (Fig. 2). In another work, Haslinger *et al.* [29] synthesized coumarin containing poly(2-oxazoline) (POx) hydrogel (Fig. 3) by photoinduced crosslinking. Coumarin is incorporated in the gelator molecule as pendant, which undergo [2+2] cycloaddition reaction under UV light irradiation and resulted in formation of hydrogel.

Photoisomerization: The groups that can undergo reversible isomerization under a particular wavelength of light can be incorporated into hydrogelator molecule to get photoresponsive hydrogel. There are two most popular groups under this

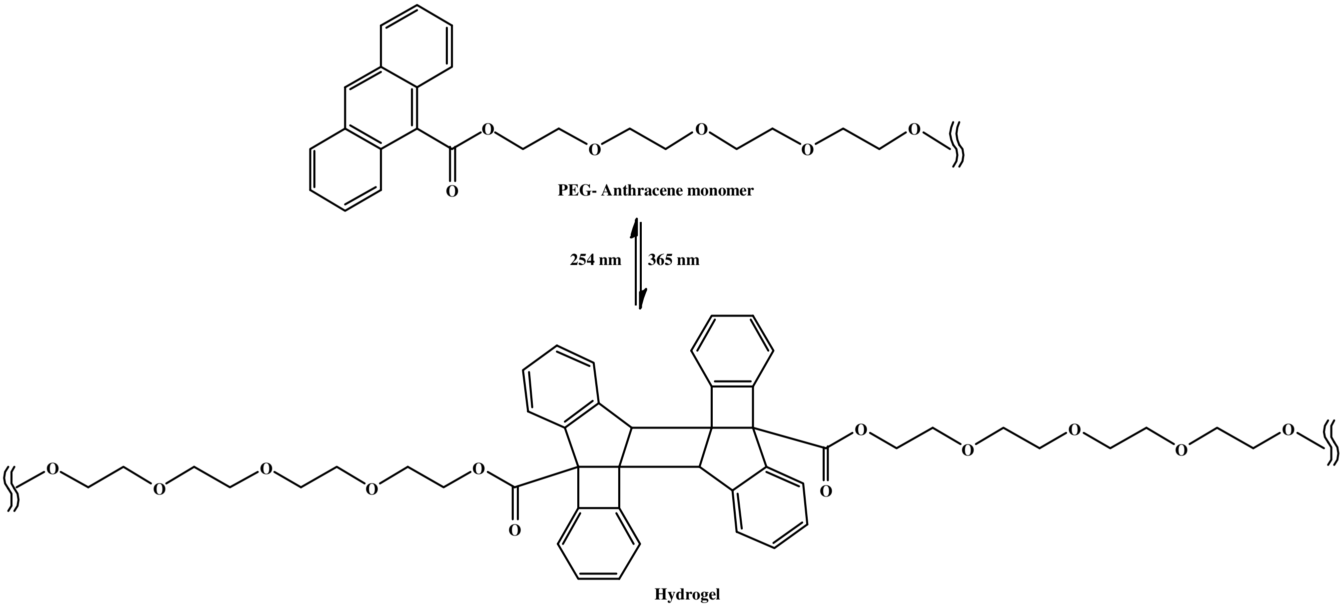


Fig. 2. Formation of hydrogel by [4+4] cycloaddition reaction of anthracene containing PEG monomer

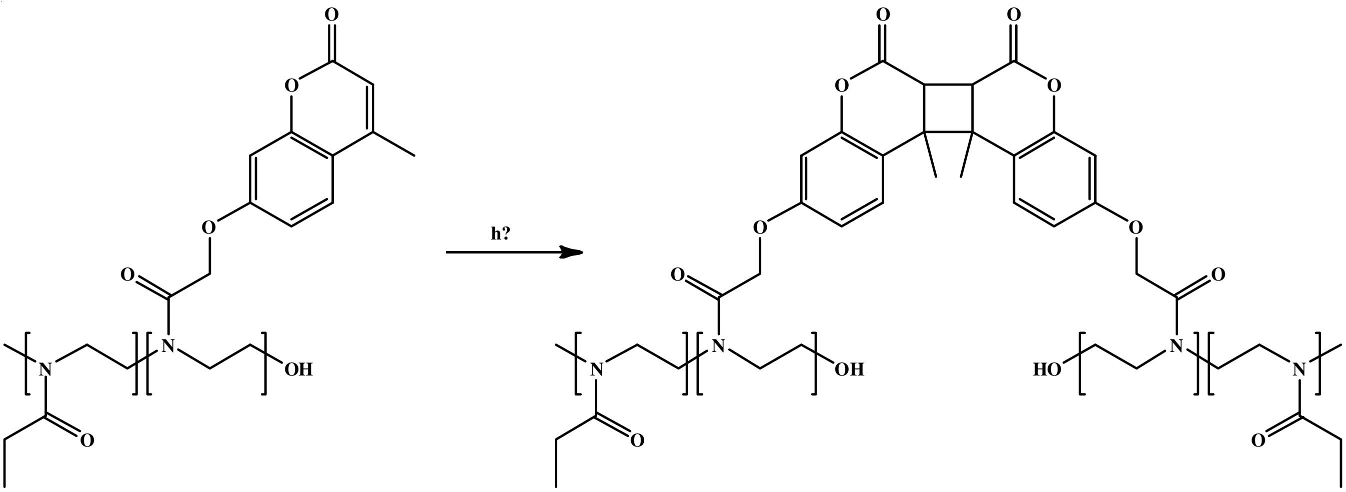


Fig. 3. Formation of hydrogel by [2+2] cycloaddition reaction of coumarin incorporated in poly(2-oxazoline) (Pox)

category are azobenzene and spiropyran. *trans*-Azobenzene isomerizes to *cis*- form upon UV-irradiation and reversibly changes to again trans for on visible light irradiation or heating. Schneider *et al.* [30] utilized this property of azobenzene to get photosensitive low molecular weight peptide hydrogel. The trans azobenzene-containing cyclic dipeptide PAP-DKP-Lys 2,5-diketopiperazine produced hydrogel, which disintegrated upon UV light exposure at 365 nm as azobenzene moiety undergoes isomerization to *cis* form (Fig. 4). The sol is again returned to gel form when irradiated with blue light (460 nm). This gel can entrap dsDNA or doxorubicin and release them upon photo-irradiation.

Azobenzene can also form supramolecular complexes with cyclodextrin. Stability of these complexes depend on *cis*- or *trans*- form of azobenzene. Many research groups utilized cyclodextrin-azobenzene host-guest complexes to develop photo-responsive hydrogels [31-34]. Spiropyran is another popular unit to induce photo-responsiveness as its two isomers are hugely different. Upon the UV irradiation at 365 nm or in acidic environment less hydrophilic close ring of spiropyran isomerises into more hydrophilic open chain merocyanine isomer, which can reversibly change into spiropyran with close ring structure again after visible light exposure or heating (Fig. 5) [35].

According to Diamond *et al.* [36] when benzospiropyran is incorporated in poly(NIPAM) hydrogel gel in very dilute acidic medium it opens up to protonated merocyanine forming an yellow gel. When this gel is exposed to white light protonated merocyanine again forms benzospiropyran and releases proton there resulting in decrease in hydrophilicity. Thus, the gel will shrink by expelling water. Several others groups [37-41] have applied photoisomerization of spiropyran to develop photo-responsive hydrogels for various applications.

Applications of photo-responsive hydrogels

Wound healing: Skin is the natural protector of internal organs of living systems. When this protector is wounded microbes attack through this ruptured site causing more severe wounds and infections. Wound healing materials must protect the wounded site from further injury as well as help in healing process of body. Biocompatible hydrogels can maintain the cellular atmosphere at wounded site so they are considered to be applicable for wound healing. Smart hydrogels are emerging as advanced wound healing materials due to their adjustable properties according to wound environments, high-tension durability and less painful dressing changes [42]. Smart materials helps in different stages of wound healing like hemostatis, reducing inflammation and infection and finally cell proliferation. In 2019, Cai *et al.* [43] reported Cu nanoparticles incorporated in hydrogel derived from polymerization of *N*,*N*-*bis*(acryloyl)cystamine and methacrylate modified gelatin,

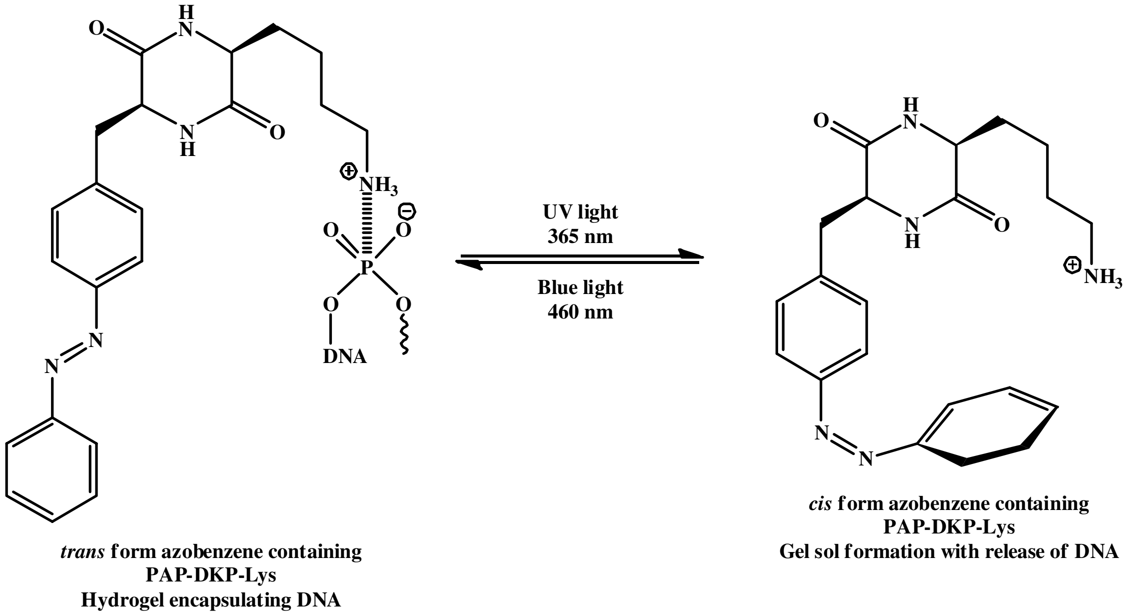


Fig. 4. Formation of photo-responsive hydrogel by *cis-trans* isomerization of azobenzene in PAP-DKP-Lys cyclic peptide

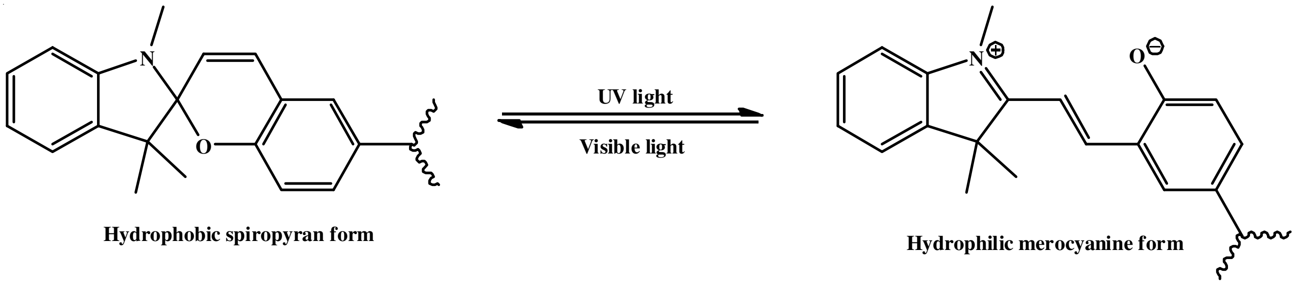


Fig. 5. Isomerization of spiropyran

which shows photothermal effect at wounded site upon NIR laser irradiation at 808 nm. Copper nanoparticles can absorb strongly in NIR region resulting in local heating in affected area where gel is applied, which can kill the pathogens by increasing temperature. This photo-thermal hydrogel has shown profound antibacterial efficacy against both Gram-positive and Gram-negative bacteria. They have also checked wound healing efficiency *in vivo* in Sprague-Dawley rats with wounded area infected with *S. aureus*. The wounded site is filled with hydrogel and exposed to 808 nm irradiation for 10 min. The temperature of the hydrogel filled site was increased from 25 to 49.8 ºC, which was sufficient to kill the bacteria. After 8 days of treatment wound area was sufficiently reduced and increase in numbers of collagen fibrils and connective tissues were found. After 14 days almost complete wound healing was observed compared to control group. Guo *et al.* [44] developed QCS-CD-AD/GO4, supramolecular hydrogel by mixing quaternized chitosan-graft-cyclodextrin (QCS-CD) and quaternized chitosan-graft-adamantane (QCS-AD) and then adding 0.4 wt.% of GO (reduced graphene oxide). This hydrogel shows photo thermal effect due to presence reduced graphene oxide. Wound dressing prepared from this polymer also have similar conductance as skin which facilitated the wound healing process. This supramolecular hydrogel was not only detrimental for both Gram-positive and Gram-negative bacteria but also it can kill multidrug resistant type of *Staphylococcus aureus*. They have reported that this hydrogel dressing has shown even better performance than conventional Tegaderm™ film in a mouse model with full-thickness skin defect. Same group also used doxycycline loaded hyaluronic acid-graft-dopamine hydrogel embedded with reduced graphine oxide (HA-DA/rGO3/Doxy) to treat full-thickness skin defect in a mouse. HA-DA/rGO3 has excellent cell proliferation and tissue adhesion ability as well as antioxidant property. The gel has shown antibacterial activity due to photothermal effect upon irradiation at 808 nm. The antibacterial activity even enhanced as doxycycline; the second-generation antibiotic can be slowly released at wounded site from the hydrogel matrix [45].

Zhan *et al.* [46] synthesized a hemostatic bioadhesive (HAD) from the reaction of hemocoagulase (HC), gelatin methacryloyl (GelMA), photo-initiator TEA and photosensitizer Eosin- Y. The visible light (430 to 530 nm) induced crosslinking of HAD produced gel in applied bleeding wound and stopped bleeding. It can ensure coagulation within a minute even in case of deep wounds with 2-3 mm thickness. They have also proved the efficiency of hydrogel *in vivo* with mouse models having different types of injuries like severe liver injury, tail cutting injury, abdominal aorta injury. Other works have also been reported where photo-responsive hydrogels are utilized for wound healing [47-56] and even for internal wound healing [54,55].

Drug delivery system: Any kind of stimuli responsive drug delivery system is a better option compared to non-responsive one due to controlled drug release and reduction in side effects away from targeted site. In this context, photo-responsive drug delivery vehicles like hydrogels are of particular interest due to its easy contact-free control, high resolution and on-off mechanism. Ghani *et al.* [57] developed UV-triggered drug delivery systems comprising silicone and spiropyran as photo-sensitive unit. They were able to achieve *in vitro* UV responsive drug release upto 90-95% for the encapsulated drugs doxycycline, dopamine, levodopa (L-dopa), prednisone, curcumin. Luo *et al.* [58] prepared dendritic copolymer containing photosensitive coumarin moiety poly(ethylene glycol) (PEG), dendritic polylysine and redox sensitive unit which can self-assemble to form drug carrier. They have successfully applied paclitaxel drug loaded carrier for UV responsive targeted drug release at tumour site in mice model. Anseth *et al.* [59] developed photosensitive host/guest complex hydrogel using photo responsive azobenzene derivative as guest and a β-cyclodextrin as host. When irradiated with UV light azobenzene isomerizes to *cis*-form and gel-degraded resulting release of a model drug fluorophore containing short peptide. Protein based photo responsive hydrogels are attractive alternative to synthetic hydrogel due to higher biocompatibility, easier regulation of protein structure and function. In this context, Sun *et al.* [60] synthesized photoresponsive protein-based hydrogels by copolymerizing C-terminal adenosyl cobalamin binding domain (CarHC) proteins, where the adenosyl cobalamin (AdoB12) acts as photoreceptor. Green (522 nm) light exposure led to rapid gel degradation resulting in the rapid release of encapsulated cargo like protein and live cells. Although there are plenty of examples of UV light-responsive hydrogels when we are concerned about drug release these hydrogels are not that much applicable as UV light can damage living cells. For application in living systems, NIR light is more useful due to deep penetrating power with less toxicity. Cao *et al.* [61] developed an NIR-responsive hydrogel comprising low-melting-point agarose and PEGylated black phosphorous (BP) nanosheets. Upon irradiation with NIR at 808 nm for 5 min, the temperature of this photo-thermal hydrogel was increased causing melting down of hydrogel and release of the encapsulated drug doxorubicin. *In vivo* experiments in mice showed that when the gel was injected at tumour site and exposed to NIR irradiation it resulted in localized release of doxorubicin compared to free doxorubicin injection and thus minimized the side effects. The tumour size was significantly reduced with respect to control groups. Sun *et al.* [62] developed NIR responsive GelPV-DOX-DBNP hydrogel system comprising of fructose-based glycopolymer, photosensitizer perylene diimide zwitterionic polymer, anticancer drug doxorubicin and photothermal nanoparticles. This hydrogel is capable of NIR responsive drug release applicable for chemotherapy and photothermal therapy. *In vivo* study in tumour model mice had also proved the enhanced synergistic efficacy of chemotherapy and photothermal therapy.

Shen *et al.* [63] synthesized unique pseudo-polyrotaxanes type of NIR sensitive hydrogel comprising of PNPG-PEG (poly(N-phenylglycine)-poly(ethylene glycol)) composites and α-cyclodextrin. NIR-irradiation increased the temperature of the hydrogel and de-threading of Qα-CD from PEG chains occurred. This caused the degradation of gel resulting in release of encapsulated drug *cis*platin. Treatment with cisplatin [*cis*-diamminedichloroplatinum(II)] encapsulated PNPG-PEG/Qα-CD upon 1064 nm laser irradiation reduced the tumour growth more effectively than controls. The synergistic effect of NIR responsive drug release and photothermal effect have been utilized in cancer therapy by several groups [64-69].

Development of cell culture matrix: Hydrogel materials are being used for cell culture medium for long time. The photoresponsive hydrogels are more appropriate modification as they are dynamic in nature like living cell and their properties can be regulated by remote and contact free control. To create a proper cell environment 3D cellular matrix for growth is ideal [70]. One method is photocaging of biologically active groups which at suitable condition are photocleaved to expose the active sites helping in cell adhesion and growth. Lutolf *et al.* [71] developed a strategy of site-specific caging of adhesion protein and growth factors within photo sensitive PEG based hydrogel. Upon laser exposure, uncaging of bioactive materials produced micropatterning of desired extracellular matrix (ECM) proteins and growth factors on hydrogel matrix. The have applied this photoresponsive hydrogel matrix as 3D cell culture media for primary human mesenchymal stem cells. García *et al.* [72] developed cellular matrix comprising poly(ethylene glycol) diacrylate (PEGDA) hydrogels and photo cleavable 3-(4,5-dimethoxy-2-nitrophenyl)-2-butyl ester (DMNPB) unit. Upon 350-365 nm light exposure caged cyclic RGD peptide cyclo-(Asp-d-Phe-Lys-Arg-Gly) became open and active. This RGD peptide containing hydrogels played important role *in vivo* cell adhesion and reducing inflammation at the tissue-biomaterial interface. In another method, photoresponsive hydrogel based cellular matrix can be prepared by photo-polymerization of reactive groups like acrylates, methacrylates or acrylamides [73]. The gelation time is very fast which maintain the cell viability. This approach is widely used in 3D micropattern arrangement of biomolecules and cells achieved by photolithographic technique [74,75]. Levkin *et al.* [76] developed photodegradable hydrogel containing poly(ethylene glycol)methacrylate (PEGMA)-based gelatin-methacryloyl (GelMA) capable of cell photoencapsulation. This matrix can be used for 3D-cell culture for more than 14 days. Campo *et al.* [77] synthesized photodegradable poly(ethylene glycol) (PEG) hydrogels containing photocleavable nitrobenzyl triazole unit and tissue adhesive catechol moieties. This hydrogel has shown excellent tissue adhesion, cell viability and controlled release of cell after photodegradation. Thus, it can be successfully utilized in wound healing where tissue adherence is required for certain period and after that the matrix should be removed.

Surface modification: Light induced surface modification can be achieved by photo-responsive hydrogels. Along with chemical nature, surface roughness, porosity and topology are also important parameter, which controls the surface behaviour. Surface wettability is an important feature as it can help in developing self-cleaning surfaces [78,79]. Neckers *et al.* [80] invented dual responsive hydrogels comprising poly-NIPAAM as thermo-responsive backbone and spironaphthoxazines as photosensitive pendant. Spironaphthoxazine present as stable closed isomer in the polymers just like spiropyran. Upon UV irradiation, spironaphthoxazine isomerises to a charge separated polar form which diffusion of polar solvents like water into the polymer and increases the wettability compared to polymers in ambient condition.

Kanamori *et al.* [81] developed rewritable microrelief pattern on glass surface with photoresponsive hydrogel consists of thermoresponsive pNIPAAm backbone with an acrylated photresponsive spirobenzopyran chromophore. The thickness of the hydrogel coating reduced within 3 seconds of irradiation at 436 nm and within 8 min the thickness was decreased to half of initial thickness. In dark, spirobenzopyran remains in positively charged hydrophilic open ring isomer and upon irradiation with visible light it isomerises to closed ring isomer along with losing charge (Fig. 5). Hence, hydrophilicity of the surface is reduced and thickness also reduced. The swelling in dark and deswelling in 436 nm light is a reversible process. Thus, instant rewritable microrelief formation can be achieved. Recently, Chen *et al.* [82] invented a writable and reconfigurable conductive ink from supramolecular assembly of azobenzene complexes and MXene nanosheets. This ink has ability of reversible liquefication and solidification under UV-visible light exposure. Esteves *et al.* [83] presented the reversible surface changes of cotton fabric using photo-responsive spiropyran–NIPAAm hydrogel. The thickness of cotton fabric reversibly changes along with the hydrogel coating by absorbing and releasing water. During copolymerization, spiropyran takes proton from acrylic acid and isomerizes to hydrophilic merocyanine-H$^+$ and uptakes water so thickness increases. Upon irradiation with white light again hydrophobic spiropyran formed resulting in the release of water (Fig. 5) and reduction in the thickness of fabric. Liu *et al.* [84] synthesized photoresponsive poly[2-((4,5-dimethoxy-2-nitrobenzyl)oxy)-*N*-(2-(methacryloyloxy)ethyl)-*N*,*N*-dimethyl-2-oxoethan-1-aminium] (polyCBNA) hydrogel by integrating photoresponsive 4,5-dimethoxy-2-nitrobenzyl group. The gels also included cationic quaternary ammonium groups, which can show antimicrobial properties against attached organisms on the surface coated with this hydrogel and eventually develop surface with antifouling properties. Upon irradiation with UV light, the hydrogel photolyzed to zwitterionic antifouling state and get rid of the attached bacteria without allowing further bacterial attachment. So, this polyCBNA hydrogel can be applied to antimicrobial and antifouling surface.

Soft actuator: In modern research development of soft actuators using stimuli responsive hydrogels has gained immense interest due to their ability to mimic the functions of living system. Properties like biocompatibility, stability in aqueous environment, advanced design have made them applicable in various fields like medicine, microfluids, soft robotics [85,86]. Photo-responsive hydrogels can absorb and release water and thus swell and shrink in aqueous environment depending on light exposure. Thus, the photosensitivity of hydrogels can give rise to exceptional bending property, which is the prerequisite of a good actuators. There are majorly two methods of designing photo-responsive actuators. First one is incorporation photothermal materials into thermos-responsive hydrogel. So, when irradiated with required light temperature of gel bed changes, which results in significant amount of volume change causing bending. Another is utilizing photo-responsive isomerization or ionization of chromophores like azobenzene, spiropyran or diarylethene and many others. Although the second method suffers from slow response of the actuators [85].

Xiong *et al.* [86] designed soft actuators from hydrogel comprising photo-responsive Fe_3O_4 nanoparticles implanted thermo-responsive poly(*N*-isopropylacrylamide-acrylamide) hydrogel. These actuators have shown observable volume change and high bending angle of 107.8° upon green light irradiation. Different shaped actuators can be designed using this photoresponsive hydrogel for different purpose. As for example hydrogel actuator with a strip shape can be used to move tiny objects whereas boomerang-shape soft actuator can be used to control the movement of foams floating on water. Yoon *et al.* [87] prepared bilayer actuators by incorporating photothermal magnetite nanoparticles in poly(*N*-isopropylacrylamide)-graft-methylcellulose hydrogel. They were able to achieve programmable volume change by visible light exposure and extreme cooling. For increasing the rate of response, they have also developed comb-like hydrogel matrix actuator which showed very fast bending motion on light exposure as well as rapid recovery.

Considering the second method of actuator design, Diamond *et al.* [88] developed a bipedal hydrogel actuator using *N*-isopropylacrylamide-*co*-acrylated spiropyran-*co*-acrylic acid hydrogels. In gel due presence of acrylic acid spiropyran exists in more hydrophilic ($MC-H^+$) form causing absorption of water and expansion of hydrogel. White light exposure is responsible for loss of proton and isomerization to hydrophobic spiropyran again causing shrinkage of gel (Fig. 5). This reversible swelling and shrinkage have been applied to develop photo-responsive hydrogel walkers. Bipedal actuator made of this gel on a ratcheted surface can walk in a particular direction upon light regulation when emerged in water [89]. Gao *et al.* [90] fabricated a photosensitive bilayer hydrogel actuator with dual functions of fluorescence colour changes along with shape distortion. They have combined two different layers of NIR active graphene oxide/poly(N-isopropylacrylamide) (GO-PNIPAM) hydrogel and UV active fluorescent poly(acrylic acid [4-(1,2,2-triphenylvinyl)]benzyl ester/N-isopropylacrylamide) (TPE-PNIPAM) hydrogel layer tightly together using 5-cyclodextrin as host guest complex. Two responses can be achieved simultaneously or separately depending on light exposure. Zhao *et al.* [91] designed temperature and IR responsive bilayer hydrogel actuators applicable for molding and 3D printing. Two different layers are made of thermoresponsive poly N-isopropylacrylamide (PNIPAM) hydrogel and graphene oxide incorporated in poly N-isopropylacrylamide (PNIPAM) hydrogel. Graphene oxide introduced NIR sensitivity in the actuator. Sumaru *et al.* [92] developed photoresponsive multiple microvalves, opening of which can be regulated by photoirradiation locally. They have prepared microvalves using thermoresponsive poly(N-isopropylacrylamide) hydrogel. Then photosensitive spirobenzopyran chromophore was fabricated at required positions in the microvalves. Blue light irradiation for 18-30 s to the desired microvalve locally resulted in selective opening and these array of microvalves were fabricated on microchip.

Soft robots: Soft robotics has become a topic of interest due to their flexibility, biocompatibility and self-repairing ability. Photo-responsive hydrogel based soft robots are more advantageous because they can produce wireless, contact free, easily regulated movement. The response mechanism of these kind of soft robots are mainly based on photochemical and photothermal responses. The soft actuators should have sufficient mechanical integrity to be used in soft robotics so that they can be used for multiple cycles. Different types of soft robots have been designed and developed like walking robots, swimming robots, jumping robots, soft grippers, crawling robots, *etc*. [93]. Wang *et al.* [94] synthesized Janus PNIPAM/GO hydrogels [poly(N-isopropylacrylamide)/graphene oxide nanocomposite] with high mechanical strength and controllable photothermal response with IR irradiation. Their stimuli responsive bending/unbending property is ideal for the preparation of soft smart robot. PNIPAM/GO hydrogel strip was used as a soft gripper. The grabbing of an object can be obtained by one hydrogel strip in a circular shape or two hydrogel strips can be joined together with their T surfaces in front of each other. Upon IR irradiation, the bending of the strips can perform grip, retain and transfer the object. Ren *et al.* [95] also designed a gripper and transfer robot using movable cross shaped hydrogel. Inspired by peristaltic crawling of earthworm, Aida *et al.* [96] developed crawling actuator based soft robot which showed peristaltic crawling not only in a particular direction but also can reverse its movement. The hydrogel was prepared using a thermoresponsive polymer network poly(N-isopropylacrylamide), photothermal gold nanoparticles and 2D electrolytes titanate nanosheets (TiNS). They have prepared cylindrical shaped hydrogel in such a way TiNSs are co-facially oriented and orthogonal to the cylinder axis. When irradiated with light at a particular point it expands locally in large extent within a second and when irradiation is stopped it got shrank at that point. Thus, with the movement of irradiation spot in a particular direction gave rise to peristaltic crawling due to consecutive expansion and shrinkage and the direction of crawling can easily be reversed.

Recently, Kegel *et al.* [97] have developed microscopic (~ 100 µm) hydrogel crawlers capable of moving in aqueous environment. The soft robot is made of photothermal hydrogel containing photo responsive gold nanoparticles incorporated into thermoresponsive poly-*N*-isopropyl acrylamide hydrogels. The light responsive thermal expansion and shrinkage of hydrogel crawler changed the friction between crawler and substrate and produce crawling movement in a direction. Ihara *et al.* [98] designed and fabricated photo-responsive bidpedal walking hydrogel minirobot as well as swimming gel minirobot the depth of which can be controlled. Diamond *et al.* [89] regarding spiropyran based actuator can also be utilized in generation of soft walking robots. Inspired by gymnast's somersault move Wu *et al.* [99] designed and developed a soft jumping robot with photo-responsive rolled carbon nanotube/polymer bilayer composite soft gel actuator. This rolled tubular bilayer actuator had shown electricity and sunlight-responsive actuation with high efficiency.

Zang *et al.* [100] developed four different types of NIR responsive hydrogel based soft robots using poly(*N*-isopropylacrylamide) hydrogel and gold-decorated carbon nitride (Au/g-C_3N_4) nanoparticles. They have developed composite hydrogel actuators with opening and closing action, four-arm gripper robot that can grab, lift materials, paddle like actuators on a boat with propelling function and walking hydrogel actuator. Inspired by butterfly biomimetic soft robot has been made by Yuan *et al*. [101] using poly-*N*-isopropylacrylamide (PNIPAM) and multi-walled carbon nanotubes (MWCNTs) composite hydrogel. Upon visible light exposure the robot can move its wing periodically fly in upward direction. It can also fly over obstacles and carry small cargo during the upward flight.

Zao *et al.* [102] have developed light responsive high-speed and programmable underwater soft robots using thermo-responsive hydrogel crosslinked by disulfide bonds. In this case, they have utilized the exchange nature of disulphide bond resulting in thermally controlled chain conformation change which is different from popular of water diffusion mechanism. This special mechanism along with photothermal heating gave rise to light regulated high speed robots with diversified movements. Increased amount of research works in the field of photo-responsive hydrogel-based robotics clearly indicates the future prospect of soft robots.

Conclusion

Several research works have already proved the scope of photoresponsive hydrogels as efficient 3D scaffolds for drug delivery, cell culture, modified surface, self-healing materials as soft actuators and robotics. But their real-life applications need to overcome some drawbacks. The hydrogel must be designed in a way that its response should be fast, reversible and reproducible for many cycles. The quantum efficiency should be high for practical economic applications. Another major concern is biocompatibility of hydrogel scaffold as well as light used specially in biological applications. Lots of efforts are being dedicated to overcome the challenges and apply the photo-responsive hydrogels in our daily life apart from only laboratory.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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