Inorganic Nanocomposite Hydrogels: Present Knowledge and Future Challenge

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Abbreviation

(1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide	EDC
2-acrylamido-2-methylpropane sulfonic acid	AMPS
Acrylamide	AAm
Acrylic acid	AA
Carbon nanotube	CNT
Carboxy methyl cellulose	CMC
Cellulose nanocrystal	CNC
Cetyl trimethyl ammonium bromide	CTAB
Copolymer	co
Double network	DB
Ethylene glycol dimethacrylate	EGDMA
Graft	g
Graphene oxide	GO
Graphene	G
Hydroxyapatite	nHA
Hydroxyethoxyethyl metha-crylate	HEEMA
Hydroxyethyl methacrylate	HEMA
Interpenetrating polymer network	IPN
Lower critical solution temperature	LCST
Magnetic field	MF
Montmorillonite	MMT
N-(2-hydroxypropyl) methacrylamide	HPMA
N,N-dimethylacrylamide	DMA
Nanocomposite Hydrogel	NCH

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Nanocomposite	NC
Nanoparticle	NP
N-isopropyl acrylamide	NIPAm
Poly(acrylic acid)	PAA
Poly(dimethylacrylamide)	PDMA
Poly(ethylene glycol) acrylate	PEGA
Poly(ethylene glycol) diacrylate	PEGDA
Poly(ethylene glycol) dimethacrylate	PEGDMA
Poly(ethylene glycol)	PEG
Poly(ethylene oxide)	PEO
Poly(fluorine)	PF
Poly(methacrylic acid)	PMAA
Poly(methyl methacrylate)	PMMA
Poly(N-isopropyl acrylamide)	PNIPAm
Poly(N-vinyl-2-pyrrolidone)	PVP
Polyaniline	PAN
Polycarbonate	PC
Polyvinyl alcohol	PVA
Sodium acrylate	SA
Sodium n-dodecyl sulfate	SDS
Tetraethyl orthosilicate	TEOS
Vinyl acetate	VAc

1 Introduction

Hydrogels are hydrophilic physically or chemically crosslinked polymer networks, capable of absorbing and retaining the various amount of aqueous fluids [1, 2]. This crosslinked nature affects the components rheometrical properties, and consequently, results in a non-Newtonian behavior (viscoelastic or even pure elastic) of the dissolved polymeric chains [3]. This behavior promotes swelling properties of hydrogels making it a candidate for versatile applications, including biomedicine, electronic, separation and water treatment, etc. [1]. The crosslink and charge densities of the network are of the essential factors for tailoring the hydrogels properties for a special application. Hydrogels can be articulated in a variety of physical forms, including slabs, microparticles, nanoparticles, coatings, and films [4].

Wichterlie and Lim [5] first reported the synthesis of hydrogels with controlled properties, such as swell and shrinkage, over several orders of magnitude. This initial discovery provided the foundations for a generation of the *stimuli-responsive* biocompatible systems based on glycolmethacrylate, which could be in a porous state or modified by acrylamide fibers. Great progress has been made in synthesizing and developing new types of hydrogels to meet the desired controllable

properties and overcome material deficiencies. To be highly sensitive to stimuli, such as solvent composition, the ionic strength of solutes, pH, temperature, electric field, and light could provide fabrication of various types of stimuli-responsive hydrogels [6]. Despite the great properties, these soft materials suffer from poor mechanical properties. One of the most used and efficient approach to boost the mechanical properties of hydrogels is to use inorganic nanoparticles which have great strength in the hydrogel structure [7].

In this chapter, the classification and desired properties of general hydrogels will be introduced. Various methods of nanoparticle preparation have been summarized. Different methods of nanocomposite hydrogel preparation, considering the method of nanoparticle insertion into the hydrogel structure will be presented. In addition, the application of these nanocomposite hydrogels based on the employed nanoparticles will be explained. The nanocomposite hydrogels based on organic or polymeric nanoparticles are out of the scope of this chapter.

1.1 Classification of Hydrogels

Hydrogels are classified based on different features, including the source, the network electrical charge, crosslinking type, method of preparation, polymeric composition, and the configuration of polymer networks.

Considering the source, hydrogels can be classified into natural, semi-synthetic, and synthetic polymers. While natural polymers are highly biocompatible, they lack reliability and consistency, due to the inherent inconsistencies, which stems from their natural origin. On the other hand, synthetic polymers are highly reproducible materials with tunable chemical and physical properties. However, compared to natural biopolymers, they suffer from poor biocompatibility: cytotoxic or non-biocompatible monomers and organic solvents are often required during their processing. Emission of toxic by-products, i.e. unreacted monomers or products of hydrolysis, during their lifecycle is another important issue. The choice of using natural or synthetic materials for the production of hydrogels is dependent on the aspired properties and applications [8].

Natural polymer sources consist of several minerals and animal-based or plant-based materials, and the most common examples are starch, cellulose, collagen, alginate, elastin, gelatin, lignin, chitosan, and different gum silicates.

Synthetic hydrogels are prepared from various monomers, including hydroxyethyl methacrylate (HEMA), hydroxyethoxyethyl methacrylate (HEEMA), ethylene glycol dimethacrylate (EGDMA), N-vinyl-2-pyrrolidone (NVP), N-isopropyl acrylamide (NIPAAm), vinyl acetate (VAc), acrylic acid (AA), acrylamide (AAm), N-(2-hydroxypropyl) methacrylamide (HPMA), ethylene glycol (EG), PEG acrylate (PEGA), PEG methacrylate (PEGMA), PEG diacrylate (PEGDA), and PEG dimethacrylate (PEGDMA) [9].

Three different integrated parts of the hydrogel preparation include monomers, initiators, and crosslinkers [10]. Any technique, which causes crosslinking in

polymers, can be employed to produce a hydrogel. The free-radical crosslinking polymerization/copolymerization is one of the most common techniques employed to produce hydrogels. In this technique, the network is created by the reaction of hydrophilic monomers and multifunctional crosslinkers in the presence of radical initiators [11]. Water-soluble linear polymers of both natural and synthetic origins are crosslinked to form hydrogels in several ways [10]: (a) via chemical reactions (bulk or surface crosslinking [12–16]), (b) by employing ionizing radiation to generate main-chain free radicals and recombination to form crosslink junctions, and (c) via physical interactions, such as entanglements, electrostatics, and crystallite formation. In addition, various polymerization methods, including bulk, solution, graft, or emulsion polymerization, as well as inverse suspension polymerization can be used for gel preparation [11].

1.2 *Feature Characteristics of Hydrogels*

The desired properties of hydrogels and their corresponding factors have been summarized in Fig. 1. The feature properties of hydrogels include aqueous solution absorption capacity, absorbency rate, the extent of soluble fraction and residual monomers, biodegradability, and biocompatibility, and mechanical strength of the swollen gel [11]. The thermodynamics of swelling can reflect the influence of

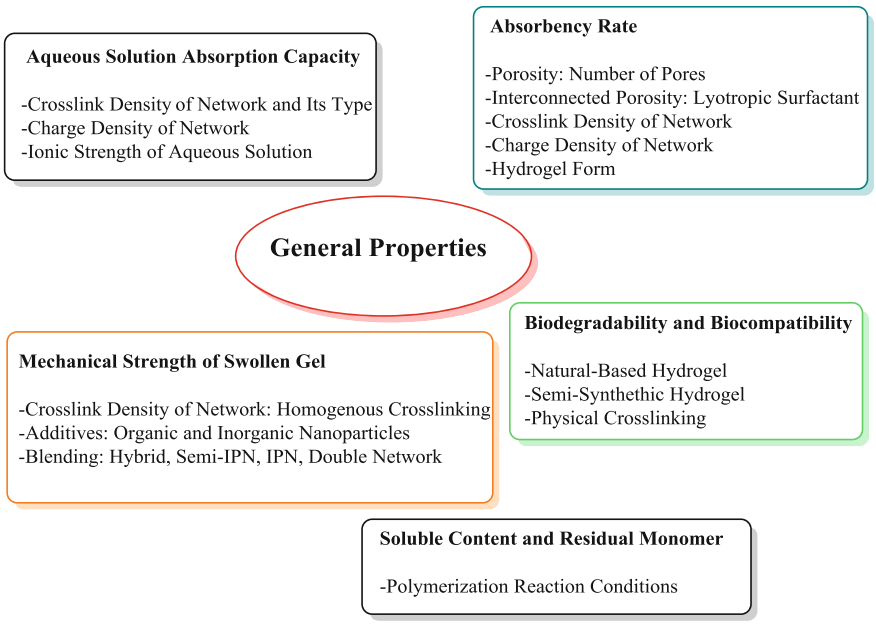

Fig. 1 Feature properties of hydrogels and their most effective parameters

crosslinking and the charge densities [17]. If the hydrogel is subjected to be used in biomedical and pharmaceutical applications, special attention must be paid to its swelling characteristics. In this case, detailed knowledge of swelling properties is essential, as the equilibrium degree of swelling affects several features of hydrogels, including its solute diffusion parameters, surface-dependent properties, optical properties as well as its mechanical properties [2].

Equilibrium swelling theory and the network characteristics of a single polymer network can be based on the contribution of mixing, network conformation (elastic), and ions. In terms of the free energy of the system, the total Gibbs free energy change (ΔG) upon swelling would be [17]:

$$\Delta G = \Delta G_{elastic} + \Delta G_{mix} + \Delta G_{ion} \quad (1)$$

Here, $\Delta G_{elastic}$ is the Gibbs free energy contribution of the elastic retractive forces (representing network crosslink density effect); ΔG_{mix} represents the thermodynamic compatibility of the polymer and the swelling agent (water), and ΔG_{ion} is the ionic contribution of poly (electrolyte) hydrogels (representing the network charge density effect) [17].

Differentiation of Eq. 1 with respect to the number of water molecules in the system, yields the chemical potential change of water, in terms of the elastic, mixing, and ion contributions during swelling of the gel [2].

$$\mu_1 - \mu_{1,0} = \Delta\mu_{elastic} + \Delta\mu_{mix} + \Delta\mu_{ion} \quad (2)$$

Here, μ_1 is the chemical potential of water within the gel and $\mu_{1,0}$ is the chemical potential of pure water. Equilibrium is reached when the chemical potentials of water inside and outside of the gel are equal. Therefore, the elastic, mixing and ion contributions to the chemical potential would balance at equilibrium. The chemical potential change upon mixing can be determined based on the Flory–Huggins theory [2, 18]. The elastic contribution of the crosslinked structure is usually described by the rubber elasticity theory and its variations [2]. The third contribution is taken as the ideal Donnan description for the ionic effect of polyelectrolytes [17]. This model has been illustrated in detail by Koetting et al. [19].

Even the *screening effect* of the ionic moieties, which is due to the high concentration of ions in an area next to the backbone that inhibits the ionization in polyelectrolytes, could influence the swelling ratio; often leads to the divergence between theory and practice [18, 20].

Swelling of polymer gels has adverse effects on its mechanical strength. Some hydrogels fracture under their own weight upon swelling. Inhomogeneity in hydrogels is often referred to as the inhomogeneous crosslinked density distribution of the gel. Inhomogeneity can decrease the hydrogels optical clarity, strength, ionization degree, electrostatic repulsion, and mobile counter ion number [21, 22].

On the other hand, several applications exist in which the hydrogels are required to sustain an external force in addition to their initial weight. *Tough hydrogels,* which reversibly deform to large extents without failure, are candidates for these

applications. The synthetic hydrogels are often brittle, while the biological tissues, such as muscles and tendons, are tough. These biological hydrogel materials offer a high swelling degree and low modulus, along with high extensibility and high toughness [23]. Recently, this combination of properties has been achieved with synthetic hydrogels [22].

Energy dissipation and high stretchability are the fundamental factors in the design of tough hydrogels [24]. So far, synthesis of different tough hydrogels have been introduced, including interpenetrating polymer network (IPN) and double network (DN) hydrogels, ionically crosslinked hydrogels, covalently and physically crosslinked nanocomposite hydrogels, slide ring hydrogels, tough tetra-PEG hydrogels, and dendritic polymer hydrogel adhesives [25].

2 Nanocomposite Hydrogels

Nanocomposite hydrogels are generally designed to promote the mechanical strength of the swollen state [7, 11]. They may also offer advanced properties such as stimuli-responsiveness [26] and self-healing [27]. Several nanoparticles have been employed in the production of nanocomposite hydrogels, including nanoparticles of inorganic ceramics, metal and metal oxides, polymer-based materials, active glass, and carbon-based nanomaterials.

2.1 Nanoparticles Preparation

Inspired by nature, the nanoscale design of polymeric materials, mainly in biomedical fields, has made great progress [28]. In this regard, nanoparticle size of compounds (0.1–100 nm), their surface area, and quantum tunnelling effects are the most important factors which confer special properties to the product [21]. Nanoparticles have been classified based on their nano dimension, source (mineral or synthetic), morphology (crystalline or amorphous), and chemistry (clays, metals, metal oxide, carbon-based, etc.). The nano-sized compartments could be arranged in one (layered, e.g. clays), two (fibrous, e.g. carbon nanotubes) or three (particulates, e.g. silica) dimensions [21].

The size of nanoparticles can strongly affect the nanocomposites properties. Moreover, the agglomeration of the nanoparticles in the suspension and their dispersion are other challenges in this field [28].

Several preparation methods have been introduced for preparation of nanoparticles: physical and chemical methods (based on chemical reaction), gas-phase, liquid-phase, and solid-phase methods (based on the state of the reaction system). Gas-phase methods include: (a) gas phase evaporation method, using heating, plasma, electron beam, and laser, (b) chemical vapour reaction, induced by heating, laser, and plasma, (c) chemical vapour condensation, and (d) sputtering methods [21].

Liquid-phase methods are the important nanoparticle preparation methods. They are based on precipitation, emulsion, hydrolysis, spray, pyrolysis, sol-gel, radiation chemical synthesis, oxidation-reduction, etc. while solid state reaction methods include milling, stripping, spark discharge, and thermal decomposition [21].

Clays, which are characterized by their crystal structure and their charge, are the most commonly used nanoparticles. The crystallinity of the clays is proportional to the composite mechanical properties. Kaolin, Serpentines, Micas ('Mica' is a generic term applied to a group of complex aluminosilicate), Chlorites and Vermiculites, Glauconite, Sepiolite, Palygorskite and Attapulgite, Bentonite, and Montmorillonite (MMT) are crystalline clays. Compared to Kaolins with uniform chemical composition, the smectites such as Bentonite and Montmorillonite have a wide range of composition and cation exchange properties [22]. Clay particles are often plate-shaped, in which the layers are *intercalated* by an intercalant (organic or inorganic material with the opposite charge of layers, e.g. onium salt), in order to induce spacing between layers (ionically induced distance is at least 1.5 nm). *Exfoliation* is another step to disperse individual platelets (an *intercalated layered*) in a polymer matrix with the distance above 8.8 nm [21].

There are some advantages and disadvantages of utilization of mineral and synthetic clays. The mineral clays are available, and can be produced by well-known technologies; whereas, the inconsistencies in composition, difficulties in the removal of amorphous clays, poor reproducibility, and the crystallographic defects which prevent total exfoliation, are of their disadvantages. On the other side, the synthetic clays, such as Laponite, would have controlled compositions and shapes, high aspect ratio, and reasonable reproducibility. The production of synthetic clays is a developing technology, resulting in a higher price for these nanoparticles than the mineral nanoparticle clays [23].

The formation of stable dispersions in the polymer matrix is even more important than the size of the nanoparticles; agglomeration of nanoparticles leads to inferior properties [29]. In order to avoid and control agglomeration in hydrogels, the in situ formation of nanoparticles (i.e. silver nanoparticles) is employed. The nanoparticles formed in this method are surrounded by the polymer matrix, and subsequently, the possibility of agglomeration is declined [30]. The in situ methods for preparation of nanoparticles, such as reduction of metal oxides, suffer from poor control over the nanoparticle properties. The risk of contamination by unconverted precursor material and/or by-products also exists in these methods [31]. Two-step preparation method has its own advantages. It is possible to optimize the synthesis conditions for each individual component (e.g. size and shape of the nanocrystals). However, the dispersion of nanoparticles by this method is a challenge and adversely affect the nanocomposite properties [31].

Modification and functionalization of nanoparticles are often employed to overcome the incompatibility of hard and soft phases of the composite hydrogels. The phase-separation is an inevitable phenomenon which occurs when compounds are incompatible. It also results in mechanical deficiency at the interfacial surface, due to the presence of losing uniform stress distribution. Therefore, various methods have been suggested to modify nanoparticles to promote the mechanical

properties. The nanoparticles could be modified by various functional groups [32, 33] such as amine [34], carboxylic acid [35], or silicone-based compounds [36].

2.2 Nanocomposite Hydrogel Preparation Methods

In general, the addition of filler compounds may be added to improve the mechanical strength of polymers. The high modulus of elasticity of the inorganic part improves the toughness of the polymer. Moreover, the nano-sized particles can significantly reform the properties, due to the scale of modification. Therefore, the combination of these two features is believed to improve mechanical properties [25] and also confer stimuli responsiveness to the hydrogels [37].

Based on the final application considered for the nanoparticle-hydrogel composite, the distribution of nanoparticles in the gels is achieved through several means, including (a) the formation of hydrogel in a nanoparticle suspension, (b) physical introduction of nanoparticles in the prepared gels, (c) in situ formation of reactive nanoparticles, (d) employing nanoparticles as the multifunctional crosslinking agents, and (e) employing nanoparticles and conductive additives along with polymeric binders [30]. Figure 2 illustrates these approaches schematically.

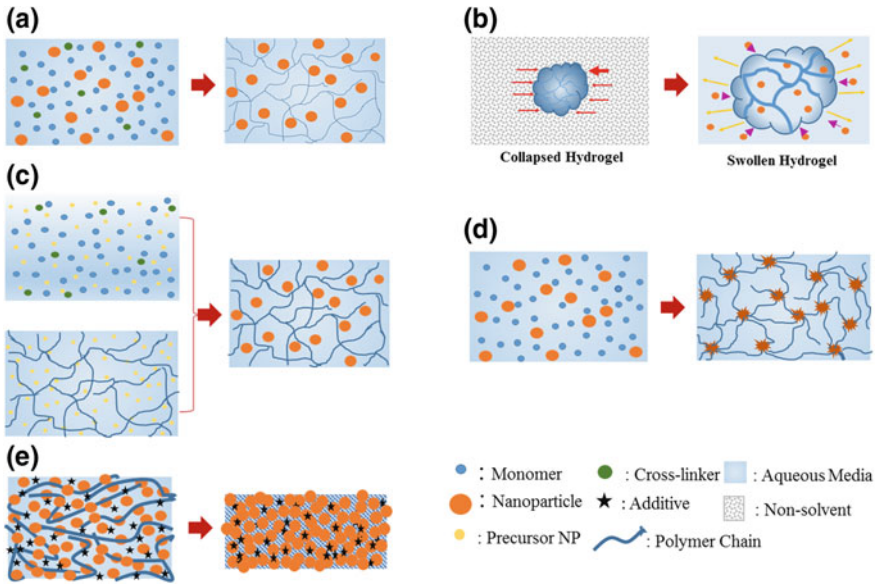

Fig. 2 Schematic representation of various methods of nanocomposite hydrogel preparation, **a** the formation of hydrogel in a nanoparticle suspension, **b** physical introduction of nanoparticles in the prepared gels, **c** in-situ formation of reactive nanoparticles, **d** employing nanoparticles as the multifunctional crosslinking agents, and **e** employing nanoparticles and conductive additives along with polymeric binders

2.2.1 Formation of a Hydrogel in a Nanoparticle Suspension

In this method, the polymerization is performed in the suspension solution of the monomers and the dispersed nanoparticles. Generally, the dispersion of nanoparticles is achieved by sonication of the suspension. In this part, the nanoparticles do not interfere with the polymerization. Ferromagnetic [38, 39] and gold nanoparticles [40] are examples of these kinds of particles. Gold nanoparticles were employed in the preparation of optically responsive hydrogel composites [41]. The weak interaction between particles and polymeric media leads to nanoparticles leaching during swelling, which is the main limitation of this method [30].

2.2.2 Physical Introduction of Nanoparticles into the Prepared Gels

Physical incorporation of nanoparticles into the gel during the polymerization, especially in non-conventional ones, is not always possible and sometimes there are obstacles to the addition of NPs during the gelation process. The electropolymerization and Au nanoparticles (Au-NP) are the best examples [30]. The Au nanoparticles cannot be used during the hydrogel preparations through electropolymerization, due to the agglomerations of Au in the electric field. To overcome this problem, the Au-NPs are doped into the hydrogel, via a "breathing in" mechanism. This mechanism consists of two steps; first, the highly aqueous swollen hydrogel is placed in an aprotic solvent (i.e. acetone) for 2 min, which is called the "breathing out" step. At the second step, the shrunk gel will be placed in an aqueous solution of citrate-stabilized Au-nanoparticles (13 nm) for 2 min (the nanoparticles have been stabilized by a chelating agent). This aqueous solution causes a swollen gel to form in the solution and the process is called "breathing in" of the suspended nanoparticles. The procedure could be repeated several times without any undesirable release of NPs during the "breathing" procedure. Since the nanoparticles have been stabilized with hydrogen bonding and physical entanglements that were induced by the chelating agent [42]. Guo et al. used the breathing mechanism for incorporation of Au-NPs into the porous anodic aluminium oxide film. For this purpose, the acrylamide gel was prepared by electropolymerization, and then, it was used as the media to absorb Au-NPs into the pores via breathing mechanism. Afterwards, the calcination is performed and the Au-NPs are trapped in the anodic aluminium oxide film [43].

2.2.3 In Situ Formation of Reactive Nanoparticles

In this approach, the nanoparticle precursors undergo a reaction to produce well-dispersed nanoparticles. It can also be called "in situ" nanoparticle formation, mostly via a reduction reaction. This method provides quite uniform distribution of metal or metal oxide NPs. In fact, the hydrogel media inhibits the aggregation of NPs during the reaction. Often, Ag-NPs are made for antibacterial purposes,

or for the addition of optical and electrical properties. Studies have shown that the size of produced Ag nanoparticles has not been varied by changing the Ag+ ion concentration. In addition, aggregation of particles has not been reported. Therefore, the Ag-NPs are created through in situ techniques [44–46].

The in situ reduction reaction could be performed during the polymerization or even after that. In antibacterial cryogels based on Ag NPs, the cryogel is swollen to the equilibrium state in $AgNO_3$ solution (for 24 h) and then the gel was added to the $NaBH_4$ solution to prepare in situ Ag NPs after proper preparation of the cryogel [47].

The mangogels were most of the time undergone the in situ preparation of ferromagnetic NPs. To exemplify, first, the metal ions were bounded to the gel then reaction with NaOH results in the in situ formation of magnetic NPs [48, 49].

2.2.4 Nanoparticles as the Multifunctional Crosslinking Agents

The employment of nanoparticles as multifunctional crosslinking groups, present at the nanoparticle surface, is one of the most interesting aspects in the nanocomposite hydrogel field. The clays with a hydrophilic nature have a great potential to be used as multifunctional crosslinkers. Various clays have been *organomodified* with different intercalants, to be used for the preparation of superabsorbent nanocomposite hydrogels, such as Bentonite, Montmorillonite (MMT), and Sepiolite [11]. In this method, the effective intercalant should be of opposite charge. For instance, MMT can be intercalated with cationic, low molecular weight materials or polymeric materials. Alkyl ammonium salts, such as hexadecyl ammonium chloride and (3-acrylamidopropyl) trimethyl ammonium chloride, or polymeric materials, such as chitosan and poly (dimethyldiallylammonium chloride), have been currently employed in this method [50]. During radical polymerization, the radical transfer to the surface of the NPs is an ordinary phenomenon, which may trigger the grafting at the surface of the particle. For this reason, the clays are called "radical killers" because they retard the radical polymerization and gelation [11]. In addition, ultrahigh mechanical properties of these nanocomposites (NC) hydrogels can be attributed to the multiple non-covalent effects between clay nano-sheets (Clay-NS) and the polyacrylamide chains [51].

Zhang et al. prepared a four-component semiconductor nanoparticle-based hydrogel, via self-initiated polymerization under sunlight. The system consists of four components: water, n,n-dimethylacrylamide (DMA), water-soluble semiconductor nanoparticles (NP), such as ZnO, TiO_2, and clay-nano-sheet (Clay-NS). NPs initiated the polymerization by sunlight. Since the crosslinking on the NP surfaces was insufficient to change the viscous behaviour to viscoelastic, clay-NSs were employed to achieve a three-dimensional structure [52].

Au NPs are also of biocompatible materials which have been modified to play the role of multifunctional (vinyl or carboxylate functionalized) crosslinkers [32, 53]. In an approach other than in situ formation of Au NPs the nanoparticles were functionalized by vinyl groups to design multifunctional Au NP crosslinkers.

The PNIPAm nanocomposite hydrogels have the thermos-switchable electrical properties [32].

The Au NPs could be functionalized by carboxylic acid using mercapto compounds and dispersed in collagen media. The employment of "zero-length" linkers is a recent method that chemically crosslinks collagen and Au nanoparticles. In fact, the coupling agents are capable of forming peptide bonds between the collagen molecules. EDC (1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide) is one example of these coupling agents. Multiple carboxyl groups are present at the surface of Au nanoparticles which enable the nanoparticles to form multiple links with the collagen developing novel properties [53].

Silica nanoparticles have been employed as multifunctional crosslinkers that adhere to different parts of the gel [54–56]. The silica NPs solution has been used to adhere the PDMA-based hydrogel surfaces. In that study, a droplet of silica solution binds the swollen polymer network. In this case, the diameter of the employed nanoparticle must be comparable with the gel network mesh size (crosslink density). The network chains can be adsorbed on the nanoparticles surfaces binding the particles to gel pieces. Particles act as *connectors* between gel surfaces. The adsorbed chains also form bridges between particles. Particle adsorption is considered to be irreversible as the binding to the gel networks occurs through numerous attachments. Monomers have the ability to detach from a particle surface, and other repeating units (from the same or a different network strand) could be replaced. Such exchange processes allow large deformations and energy dissipation under stress [54].

2.2.5 Nanoparticles and Conductive Additives Along with Polymeric Binders

NC hydrogels of graphite and silica have been used in the production of rechargeable lithium-ion batteries. More recently, electrodes of Si nanoparticle (SiNP) slurries have received attention. In these systems, the binders are used to fix the active material to the anode. The more interactions (either hydrogen bond or ionic) between binder and SiNPs, the more efficient the batteries are. Different binders, such as PVDF, PAA, CMC, alginate and phytic acid, are present during the polymerization and formation of conductive NC hydrogels [57–60].

NC hydrogels have been used in the production of rechargeable lithium-ion batteries with different nanoparticles like graphite and silica [60]. More recently, electrodes made from Si nanoparticle (SiNP) slurries instead of graphite (traditional anode), have received attention. In these systems, the binders are used to hold the active material together in the anode. The point is that the binder concentration in the slurry is much less than the nanoparticle concentration and other additive concentrations (15 wt% binder vs. 43% Si NP and 42% C as conductive martial [58]). The binder could be a previously prepared polymer [59] or synthesized in situ during anode preparation [57]. The more interactions (either hydrogen bond or ionic) between the binder and SiNPs, the more efficiency of the batteries are owing

to less volume change (for high capacity batteries). The polymeric binders could act as dual-functional materials to improve binding and conductivity of the electrodes. The life cycle of the electrode can be extended by enhancing mechanical and electrical properties (integrity). Different binders, such as PVDF, PAA, CMC, alginate and phytic acid, are present during the polymerization and formation of conductive NC hydrogels [57–60].

2.3 How Nanoparticles Improve Mechanical Strength of Hydrogels?

Mechanisms of energy dissipations in tough hydrogels include reversible crosslinking or fracture of polymer chains, the transformation of domains in polymer chains or crosslinkers, as well as fracture and pullout of fibers or fillers. Mechanisms of maintaining elasticity in tough hydrogels can be attributed to the interpenetration of long-chain networks, hybrid physical and chemical crosslinkers, high-functionality of crosslinkers, and the presence of networks with long monodisperse polymer chains [24]. Many tough hydrogels have been produced based on these mechanisms, such as hydrogels of poly (vinyl alcohol) with crystalline domains, double-network systems, hydrogels with hybrid chemical and physical crosslinkers, hydrogels with high-functional crosslinkers, systems with transformable domains, topological hydrogels with sliding crosslinkers, and tetra-arm polymer hydrogels [25]. It is believed that employing a combination of these techniques would be a promising strategy to design next-generation tough hydrogels. For instance, a tough hydrogel may integrate fiber reinforcement at the macro-/meso-scale, high-functionality crosslinkers at the micro-scale, and hybrid crosslinkers at the nanoscale [24].

Examples of high-functional crosslinkers which are used for production of tough hydrogels include crystalline domains in polymer networks [i.e. poly(vinyl alcohol)], exfoliated nano-clays that can crosslink various polymers (i.e. polyacrylamide [61], poly(N-isopropylacrylamide [62], and poly(ethylene glycol) [63]), polyacrylamide crosslinked by chitosan nanofibers [64], and graphene oxide [65].

It is believed that nanoparticles act as multiple crosslinkers. The suggested mechanisms explaining the toughness these hydrogels exhibit will be explained in the following. Based on Flory's network theory, the number of polymer chains that can be crosslinked by a crosslinker is defined as the functionality of the crosslinker. Typically, common physical and chemical crosslinkers have functionalities less than 10; in addition, generally, a single polymer chain connects two adjacent common crosslinkers. When polymer chains are ruptured under deformation, the connections between crosslinkers are eliminated, and consequently, fracture of the network is commenced. In order to achieve high elasticity in hydrogels, large crosslinkers with very high functionality (e.g. over 100) must be incorporated into the polymer networks. In these networks, multiple polymer chains may connect two

adjacent crosslinkers; and these chains usually do not have uniform lengths. In other words, parallel to the polymerization, *grafting* happens on the surface of the nanoparticles and multiple crosslinking occurs. Therefore, as the polymer networks are deformed, relatively short chains may be ruptured or detached from the high-functionality crosslinkers, but the long chains can still maintain the elasticity of the hydrogels [24].

Depending on the employed nanoparticles, the physical adsorption and desorption of building blocks of polymer chains may increase the non-covalent and reversible interactions (which act like crosslinks). Poly(acrylamide)s and silicates show a great potential for these interactions. The shear thinning characteristics (induced by reversible interactions) of this type of hydrogel composite can expand the hydrogel composite application, especially in the biomedical field [54, 55, 66, 67].

2.4 Characterization Methods of Nanocomposites Hydrogels

Various techniques have been employed to characterize nanocomposite hydrogels structural, mechanical, thermal, electrical, and optical properties. The physico-chemical structure of these hydrogels is often studied by X-ray diffraction (XRD), transmission electron microscopy (TEM), small angle neutron scattering (SANS), and Fourier-transform infrared spectroscopy (FTIR) [11].

Based on the XRD data, the lattice related data (crystal planes, shape, and constants) can be obtained [61, 68–70]. XRD has also been used to study the extent of intercalation and exfoliation. The interlayer spacing (d) is commonly determined from the XRD patterns as the arbitrary intensity versus 2θ, based on Bragg's law [71]. To study the diffracting angles less than 0.05°, small-angle X-ray scattering (SAXS) and SANS have been employed, mainly because of their sensitivity and ability to make long-range measurements. SANS can be adopted on various types of specimens and may be assisted to probe the polymer-clay interaction, interfacial polymer conformations, phase transition, and gelation mechanism [71–73].

While the XRD/WAXS does not reveal useful information for $2\theta \cong 2$, TEM provides visual evidence of the nanoparticle distribution. TEM can also provide useful information on crystals development, morphology, and size [48]. The interactions between the clay platelets, the intercalating agent, and the polymer can be studied by FTIR techniques [74].

The thermal behaviour of the nanocomposite hydrogels can be studied by Differential Scanning Calorimetry (DCS) and Thermogravimetric analysis (TGA). Often, the mechanical properties of the nanocomposite hydrogels are investigated by dynamic mechanical analysis (DMA), oscillatory rheometry, and compression and tensile tests [11].

2.5 Types of Nanocomposite Hydrogels and Their Applications

2.5.1 Inorganic Ceramics and Non-metal Nanoparticles

In the last decades, inorganic ceramics mostly used as counterparts have attracted attention in hydrogel field on account of their versatility, great mechanical strength, biocompatibility and reasonable price. A range of bioactive nanoparticles has been reported to be used in various biomedical applications. These bioactive nanoparticles include hydroxyapatite (nHA), synthetic silicate nanoparticles (i.e. Laponite), bioactive glasses (SiO_2, Na_2O, CaO, MgO, P_2O_5), silica, calcium phosphate, glass ceramic, and b-wollastonite [51].

Table 1 presents typical clay-based nanocomposite hydrogel preparations and their application. These clay-based NPs are used most in inorganic ceramics in the nanocomposite hydrogel field. They act as multifunctional crosslinkers giving great potential for functionalization and grafting. Various polymeric networks like PAA, PAAm, PEG, and chitosan have been incorporated. Based on Table 1 data, the majority of hydrogels were synthesized by aqueous solution polymerization via free radical copolymerization, which has been induced by redox initiators. Meanwhile, the inverse suspension polymerization has rarely been used to produce granular hydrogels.

The employment of the synthetic silicate nanoparticles (nanoclays) has great influence on the physical and mechanical properties of the hydrogels, which can be attributed to their anisotropic, plate-like nature, and their high aspect-ratio [56, 66]. Studies showed that the addition of silicates will improve the elongation of the polymeric hydrogels, mainly due to the formation of physically crosslinked networks [56]. The physical adsorption and desorption of building blocks of polymer chains can enhance the non-covalent and reversible interactions, which act as crosslinks. The unique bioactive properties of the synthetic silicates make it capable of being employed as an injectable tissue repair matrices, bioactive fillers, or therapeutic agents [51]. The nanocaly incorporation even renders greater mechanical properties, stretchability, and self-healing properties of the hydrogel [27].

The composite hydrogels, as drug release vehicles, may increase the biocompatibility by “hiding” the nanoparticles within the hydrogel, and also by preventing nanoparticle movement from their targeted site in vivo. This morphology of hydrogel phase (e.g. porosity) can also control the kinetics release profile and balance the burst release [4].

A class of SAPs (i.e. superporous hydrogels and SPHs) has been developed by Chen et al. [75] to be used in pharmaceutical applications. A variety of techniques have been employed to synthesis porous hydrogels, including foaming, microemulsion polymerization, porogen incorporations, freeze-drying, and phase-separation [76–78]. Typical SEM images of thermally dried particles of porous and non-porous superabsorbent hydrogels at different magnifications are displayed in Fig. 3.

Table 1 Various methods of clay preparation before nanocomposition and its incorporation in hydrogel networks

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
Kaolin	–	P(AAm-co-AMPS)	Thermal-induced (persulfate) aqueous solution polymerization	Method d	Super absorbency	[132]
	Suspended in SDS	PAA	Ultrasound induced (persulfate) solution polymerization	Method d	Removal of brilliant green dye from water	[83]
	–	Collagen-co-PAA-PSA	Thermal-induced (persulfate) solution graft copolymerization	Method d	Enhancement of gel strength and super absorbency	[133]
	–	Urea formaldehyde and polyphosphate potassium in core: P(AA-co-AAm) in shell	Inverse suspension polymerization	Method d	Controlled release and super absorbency by core-shell structure	[134]
	& MMT, sedimentation with water, filtered and then dried at 80 °C	P(AAm-co-AMPSNa)	Redox initiation (persulfate) and aqueous solution polymerization	Method d	Removal of Cu(II), Cd(II), and Pb(II) ions	[68]
	–	PAA	Redox initiation (persulfate) and aqueous solution polymerization	Method d	Porous, highly swelling rate and capacity	[77]
	& MMT, Mica modified and intercalated by quaternary alkylammonium-exchanged (3-acrylamidopropyl) trimethylammonium chloride)	PAA	Inverse suspension polymerization	Method d	Reactive clays, super absorbency	[135]

(continued)

Table 1 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
Mica	Modified and intercalated by quaternary alkylammonium-exchanged	PAA	Inverse suspension polymerization	Method d	Reactive clays, Superabsorbency	[136]
Attapulgite	– Organification with hexadecyltrimethyl ammonium bromide (HDTMABr) – Acidified	PAAm	Thermal-induced (persulfate) aqueous solution polymerization	Method d	Salt-resistant Super absorbency	[137]
	–	Chitosan PAA-itaconic acid (IA)	Redox initiation (Vc/Peroxide) aqueous solution polymerization	Method d	Adsorption of malachite green	[81]
	–	N-Succinylchitosan-PAAm	Inverse suspension polymerization (persulfate)	Method d	Thermal stability and superabsorbency	[138]
	–	PAA	Thermal-induced (persulfate) aqueous solution polymerization	Method d	Superabsorbency	[139]
	–	Chitosan-PAA	Aqueous solution polymerization (persulfate)	Method d	Adsorption of Hg(II) ions from aqueous solution	[91]
	–	Chitosan PAA	Redox initiation (Vc/Peroxide) aqueous solution polymerization	Method d	Adsorption of La(III) and Ce(III)	[92]
	–	PAA hydroxypropyl cellulose	Redox initiaton (Fenton reagent) graft polymerization	Method d	Adsorption–desorption of the rare earth elements, La (III) and Ce(III)	[94]

(continued)

Table 1 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
MMT	Dispersed in water under ultrasonication for 1 h	PAAm	Redox initiation (persulfate) and aqueous solution polymerization	Method d	Stretchability, toughness, and self-healing	[61]
		PAA	Redox initiation (persulfate) and aqueous solution polymerization	Method d	Negative impact of nanocomposite on residual monomer	[80]
	Homogenized with sodium cations	Chitosan-g-PAAm	Thermal-induced (persulfate) aqueous solution polymerization	Method d	Antibacterial and superabsorbency	[140]
	Intercalated by chitosan	PAMPS	Thermal-induced (persulfate) aqueous solution polymerization	Method d	Nontoxicity, high gel strength, superabsorbency	[141]
	Suspension modified with a sodium carbonate powder	PAA	Redox initiation (persulfate) and aqueous solution polymerization	Method d	Superabsorbency	[142]
	Ultrasonicated in water	N-isopropyl acrylamide (NIPAm) and acrylic acid (AA) onto CMC was	Thermal-induced (persulfate) graft copolymerization	Method d	Removal of Cu(II) and Pb (II) ions thermoresponsive	[62]
		Polysaccharide pullulan (PULL) with polyvinyl alcohol (PVA)	– No polymerization – Electrospinning	Method d	Supecansorbency	[143]

(continued)

Table 1 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
Zeolite	& Nano Ag Ultrasound for 1 h in acetone	PAA PAAm	Redox initiation (persulfate) and aqueous solution polymerization	Method d and magnetron sputtering method	Antibacterial Removal of chemical oxygen demand (COD) wastewater	[126]
	–	CMC PAA	Thermal-induced (persulfate) graft polymerization	Method d	Controlled delivery of zinc micronutrient	[144]
	Prepared in 2,2,2-Trifluoroethanol	homo-poly (butylene succinate)	Electrospun fibers	Method d	Antimicrobial drug-delivery	[145]
Bentonite	Intercalated by the hydrochloride solution of AAm	PAA crosslinker: sugar	Thermal-induced (persulfate) solution polymerization	Method d	Superabsorbency	[146]
	–	PMAA-grafted-cellulose	Thermal-induced (persulfate) graft polymerization	Method d	Removal and recovery of thorium(IV)	[93]
Halloysite	–	Chitosan PAA	Thermal-induced (persulfate) graft polymerization	Method d	Adsorbent to remove ammonium from synthetic wastewater	[87]
Rectorite	–	Chitosan PAA	Thermal-induced (persulfate) graft polymerization	Method d	Adsorbent to remove ammonium from synthetic wastewater	
Illite Smectite	Dispersed in the aqueous solution of CTAB	sodium alginate-g-P (SA-co-styrene)	Micellar solution polymerization (with SDS)	Method d	Adsorbing methylene blue	[88]

(continued)

Table 1 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
Sepiolite	Dispersed in water and sonicated	kappa-carrageenan-g-PAAm	Thermal-induced (persulfate) solution polymerization	Method d	Adsorption of cationic dye	[84]
Tourmaline	–	PVA PAA	Thermal-induced (persulfate) solution polymerization	Method d	Adsorption capacity for Pb^{2+} and Cu^{2+}	[89]
Hydrotalcite	Synthesized by urea method and intercalated by sodium methyl allyl sulfonate (SMAS)	PAA PAAm	Inverse suspension polymerization	Method d	Salt-resistance	[147]
Hydroxyapatite	Vortexing and sonication to	PEG diacrylate	Cross-linked via photopolymerization. (IRGACURE initiator)	Method d	Highly extensible, tough, and elastomeric nanocomposite	[63]
	Prepared by precipitation of disodium hydrogen phosphate and calcium chloride	Cellulose-g- polyacrylamide	Suspension polymerization (persulfate)	Method c	Removal of Cu (II)	[90]
Laponite	–	PDMA PNIPAm	Redox initiation (persulfate) and aqueous solution polymerization	Method d	Self-healable	[27]
		Telechelic dendritic macromolecule (binder) PSA	– No polymerization – Solution mixing	Method d	Self-healing and moldable for biomedical application	[148]
	Mixed with Semiconductor NP (TiO_2, ZnO, CdTe),	PDMA	Self-initiated polymerization under sunlight	Method d	Semiconductor NP-based Hydrogels	[52]

(continued)

Table 1 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
	Exfoliated	Sulfobetain polymers (poly dimethyl (acrylamidopropyl) ammonium propane & butane sulfonate)	Redox initiation (persulfate) and aqueous solution polymerization	Method d	Swelling and deswelling	[149]
	–	PEG alginate	Ionically crosslinked by Ca ions	Method d	Fabrication by 3D printing (clay provide viscosity and shear thinning ability)	[150]
	Gel/solution exfoliation method	PEO	–	Method d	Cell cultivation – Biotechnological applications such as injectable matrices, biomedical coatings, drug delivery, and regenerative medicine	[67]

These nanocomposite hydrogels prepared by in-situ formation of reactive nanoparticles (method c) and by nanoparticles with the ability of multifunctional crosslinking methods (method d)

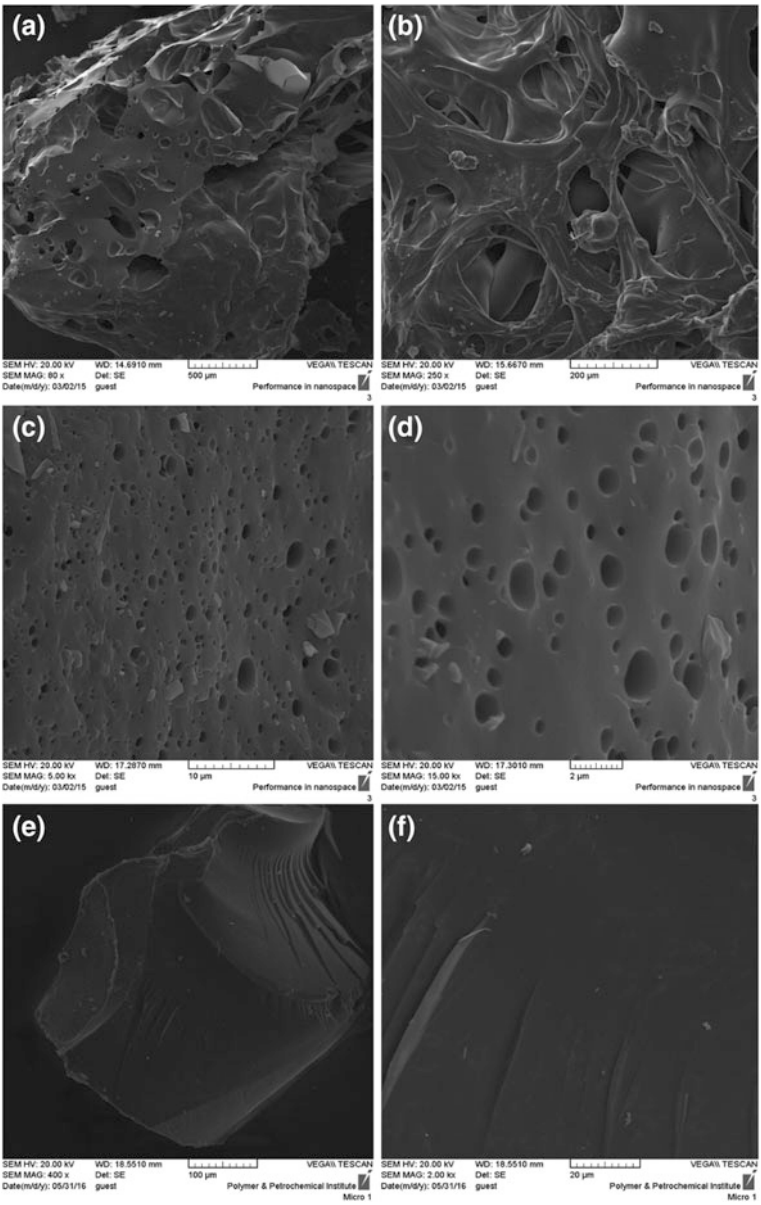

Fig. 3 Typical SEM images of porous superabsorbent hydrogel particles in **a** 500 μm magnification, **b** 200 μm magnification, **c** 10 μm magnification, **d** 2 μm magnification, and non-porous superabsorbent hydrogel particle in **e** 100 μm magnification, **f** 10 μm magnification

The SPHs were originally intended to be used in gastric retention applications. The prompt swelling of the SPHs can be attributed to the increased capillary permeability of the interconnected pore structure. The weakness in mechanical properties was mainly overcome by the development of the second-generation SPH composite (SPHCs) and the third-generation SPH hybrids [1]. Demirtas et al. [79] have synthesized and characterized polyacrylamide-based SPHCs-containing hydroxyapatite. The compressive modulus of this SPHC was 6.59 N/mm^2, where the non-composite SPH has a compressive modulus of $\sim$0.63 N/mm^2.

Effects of composition and nanocomposition of superabsorbent hydrogels on their properties have also been investigated. In accordance with the other polymer composites, the presence of nanoparticles can significantly enhance the mechanical and thermal properties [11]. Besides, the optical and electrical properties of the superabsorbent hydrogels have been improved when nanoparticles have been employed [1]. However, the absorbency properties, i.e. free swelling capacity, swelling rate, reswellability, and saline sensitivity, have been pervasively influenced by the type and the content of the employed clay. Since the clays act as multifunctional crosslinkers, their hydrogels can be brittle. Moreover, in these hydrogels, employing a higher content of the clay may result in a reduction in the absorbency [11]. Composite hydrogels generally possess a slower swelling rate but exhibit a higher saline absorbency, due to the clay nature or organomodification. Moreover, the employment of the nanocomposite would have other negative impacts, such as an increase in the residual monomer content [80].

Some common inorganic components which have been used in nanocomposite hydrogels include attapulgite [81], montmorillonite [68, 82], kaolin [83], sepiolite [84], vermiculite [85], rectorite [86], halloysite[87], illite/smectite [88], tourmaline [89], and hydroxyapatite [90]. The nanocomposite superabsorbent hydrogels were also applied in water treatment and purifications processes.

These nanocomposite materials have been used for the adsorption of heavy metal ions; i.e. Pb^{2+}, Cu^{2+} [62, 68], and Hg^{2+} [91], as well as for the elimination of radioactive and rare earth elements; i.e. thorium (IV) and lanthanide (III) [92–95]. Compared to other low-cost adsorbents, fast adsorption kinetics and higher adsorption capacities are provided by the super-hydrophilic network and chelating groups of the hydrogels [49]. Other advantages of using adsorptive hydrogels include easy separation and effective desorption for the recovery and enrichment of pollutants [96]. The incorporation of the proper amount of inorganic components, not only boosts the adsorption rate but also improves the adsorption capacity [62, 68].

Efficient removal of dyes forms effluents is of great importance in textile the industry. Nanocomposite hydrogels are a good candidate to be tailored for this purpose. They have been tailored to be employed for separation of anionic (Silica sol) [97] and cationic dyes (Titania) [98]. Successful removal of dyes, such as malachite green (Attapulgite) [94], methylene blue (MMT) [82], methylene orange (MMT) [82], and Safranine-T (Titania) [98], has been reported using composite hydrogels. Figure 4 displays the swelling, and the methylene blue absorption of superabsorbent polymer films, from different perspectives.

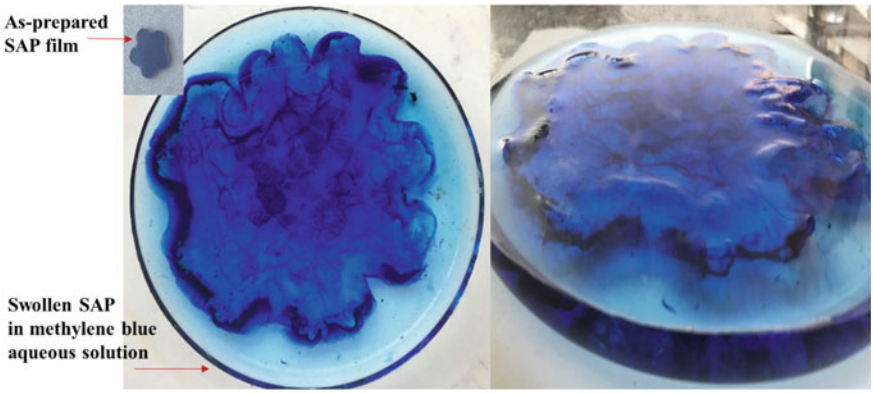

Fig. 4 Typical illustration of dye absorbency of superabsorbent hydrogels: absorption of methylene blue solution by superabsorbent polymer at different perspective

Tracking the migration of the hydrogel, which has been used as a cartilage repairing material, is a challenging task because the sensitive monitoring must be non-invasive [99]. The employment of hydrogels with desirable fluorescence properties would solve this problem. In this regard, different concepts have been employed, including polymerization of fluorescent monomers, functionalization of polymers with organic fluorophores, using fluorescent carbon dots (CDs), and semiconductor nanocrystallites [quantum dots (QDs)] [35, 99–101]. Polysaccharides are suitable candidates to be used in the synthesis of fluorescent polymeric materials. Alginate, chitosan, hyaluronic acid, dextran, and cellulose are polysaccharides commonly utilized for this purpose [99]. It has been shown that the fluorescent monomers and functionalized polymers appear to lose their luminescent properties. Therefore, the CDs are often preferred as they present high fluorescence, chemical stability, biocompatibility, and low toxicity. Recently, a novel CDs/PAM composite hydrogel with both excellent mechanical and fluorescence properties has been prepared [102].

Detection of enzymes by nanotools is of great importance; stable sensing that is very sensitive could be provided by self-assembled NPs in hydrogel media. Ruiz-Palomero et al. have reported laccase enzyme detection by immersing graphene quantum dots (GQDs) into nanocellulosic hydrogels. Noncovalent interactions between the sensor (GQDs/NC) and the analyte (laccase) have led to the stable and sensitive detection of the analyte [103].

The tracking problem can be addressed with semiconductor nanocrystals, with size-dependent emission property, can be produced in a simple synthetic process. For example, the size-dependent emission property of the CdSe nanocrystals results in blue to red emissions, with very pure colour. Chang et al. used CdSe/ZnS nanoparticles [quantum dots (QDs)] embedded in the cellulose matrices. The cellulose–QDs hydrogels displayed strong photoluminescence emission besides good compression strength [35].

2.5.2 Silicon-Based Nanoparticles

The presence and necessity of silicon in the human body are of the best reasons to use these inorganic nanoparticles for hydrogel preparation [51]. Addition of nHA and silica to the poly(ethylene glycol) (PEG) media enhanced the elasticity, mechanical strength, biological stability, and cell adhesion [63, 66]. In this case, ionic interactions could be the reason for elasticity enhancement in the gels [51]. Synthesized and modified silica nanoparticles were also used to prepare highly flexible Poly(acrylic acid)-based nanocomposite hydrogels. The silica nanoparticles were functionalized by a vinyl group, which may act as filler and multifunctional crosslinker. Entanglement trapped in the glassy polymer layers on the nanosilica leads to this flexibility [104]. The employment of sol-gel transition for preparation of silica has also been reported; this silica was further used for the preparation of a keratin-silica hydrogel, with the potential to be used for wound dressing [105].

The mesoporous silica nanoparticles (MSN), as drug vectors, have been incorporated into 3D scaffolds. The functionalized MSN has been synthesized and evaluated by different techniques: BET model for measuring the surface area, dynamic light scattering for measuring particle size, and TEM for evaluating the particle shapes. The matrix-forming self-assembling peptide, different MSNs, and precursor cells were combined to prepare injectable cell- and MSN-containing scaffolds. For this purpose, the self-assembly and coordination interactions between cells, matrices, and nanoparticles are required. Surface functionalization of MSN as well as its size, have a great impact on its nanocarrier internalization characteristics. The COOH-functionalized MSN exhibits less sensitivity to the hydrogel matrix, and in comparison with the monolayer cell culture, its internalization has been strongly enhanced in the hydrogel matrix [34].

Table 2 represents the typical silicon-based NCH preparation methods and their application. These NCHs have introduced novel properties to the hydrogel networks including toughness stretchability and self-healing which is owed to their multifunctional crosslinking role. These NPs could inherently enhance the mechanical properties of soft hydrogels. Various concepts have been explored for preparation of stretchable tough hydrogels, i.e. nanocomposition [56], micellar copolymerization [106], and hydrophobic association [107]. An example of a highly stretchable tough hydrogel under tension has been displayed in Fig. 5. The hydrogel film can be extended to desirable elongations (the displayed elongation ratio is more than 15 mm/mm).

2.5.3 Carbon-Based Nanoparticles

Carbon nanotubes (CNTs) and graphene, as the most used carbon-based nanoparticles, have attracted much attention to be used in various biomedical applications, such as actuators, conductive tapes, biosensors, tissue engineering scaffolds, etc. Table 3 summarizes typical carbon-based NCH preparation methods and their applications. In contrast to clays, the CNTs exhibit hydrophobic nature; therefore,

Table 2 Various preparation methods of silcon-based NP before nanocomposition and its incorporation into the hydrogel networks

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
Silica sol	–	PAAm Poly(diallyl dimethyl ammonium chloride) (DADMAC)	Thermal-induced (persulfate) aqueous solution polymerization	Method a	Removal of methyl orange from aqueous solutions	[97]
Silica CNT CNC	1-Sol-gel 2-SiO_2/Na_2O	PDMA	Thermal-induced (persulfate) aqueous solution polymerization	Method d	Adhesives for gels and biological tissues	[54]
Silica	Vinyl hybrid silica prepared by sol-gel reaction	PAAm	Thermal-induced (persulfate) aqueous solution polymerization	Method d	Highly stretchable and super tough nanocomposite	[151]
Silica	Vinyl silica prepared by methacryloxypropyl trimethoxy silane	PAA	Thermal-induced (persulfate) aqueous solution polymerization	Method d	Highly stretchable and super tough nanocomposite	[104]
Silica	Prepared by TEOS sol-gel reaction	Keratin	Siloxane network	Method d	Wound dressing	[105]
Mesoporous Silica	– Sol-gel reaction in alkaline solution (methanol and water) in the presence of CTAB – NH_2 and COOH functionalized NPs	Peptide	–	Method d	Drug vectors into injectable 3D scaffold	[34]

(continued)

Table 2 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
Sodium Silicates	–	Colloidal silica	Siloxane network	Method d	Cell encapsulation	[152]
Silica	–	PDMA	Redox initiation (persulfate) and aqueous solution polymerization	Method d	Resilient and stretchable hydrogel	[55]
Nanocrystalline silicon	Ultrasonication in presence of monomer under dry nitrogen and then degassing by freeze-pump-thaw cycles	– Ethylene glycol dimethylacrylate – 2-hydroxyethyl acrylate	Laser-induced thermal crosslinking Polymerization	Method d	Semiconductor by green process	[153]

These nanocomposite hydrogels prepared by the formation of NCH in the NPs solution (method a) and by nanoparticles with the ability of multifunctional crosslinking methods (method d)

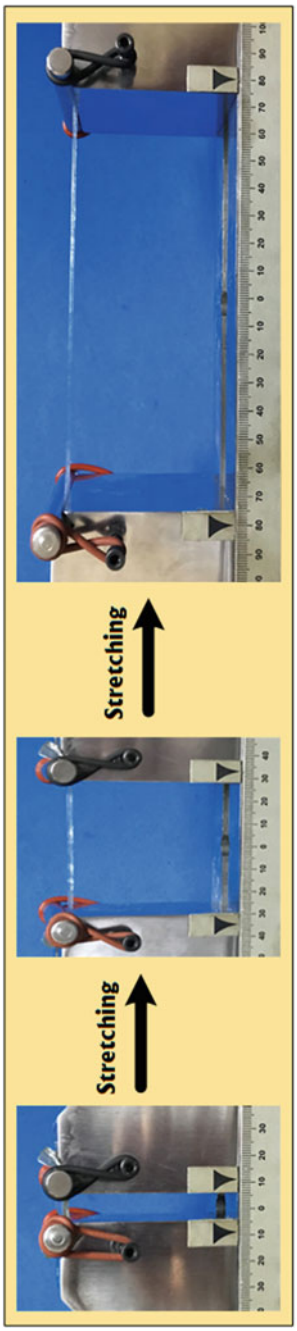

Fig. 5 Typical highly stretchable tough hydrogels under tension; the as-prepared hydrogel film (left) has been elongated to elongation ratio of ~15 mm/mm

Table 3 Typical carbon-based NCH preparation methods and their applications

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
GO	– Synthesized using Hummers' method – Sonicated	PAA	Dual ionic crosslinking Solution polymerization	Method d	Self-healable, super tough	[109]
GO	Synthesized using Hummers' method Sonicated	PNIPAm	Chemically and ophysically crosslinked Redox initiation (persulfate) and aqueous solution polymerization	Method d	Near-infrared light-responsive ultrahigh tensibility	[111]
Graphene nanosheets	Reduced GO to chemically converted grapheme and sonicated	Methacrylated chitosan	UV-crosslinkable conducting	Method d	3D structured biocompatible scaffold by 3D printing	[154]
Graphene	Simultaneous reduction of GO	PEGDA	UV-induced photopolymerization	Method d	Electrically conductive hydogel	[110]
GO	Synthesized by oxidizing graphite and ultasonication	PAAm	Redox initiation (persulfate) and aqueous solution polymerization	Method d	Tough and highly stretchable	[65]
Graphene quantum dots	Synthesis of sulfur and nitrogen codoped graphene quantum dot	Oxidize Nanocellulose (NC)	Aqueous solution in ultrasonic bath then heated with a heat gun	Method d	Eco-friendly and cost-efficient Nanotools detecting the laccase enzyme	[103]
GO	–	Poly (acryloyl-6-aminocaproic acid)	$-Ca^{2+}$ induces the formation of the 3D cross-linked Thermal-induced (persulfate) aqueous solution polymerization	Method d	Superior mechanical properties and self-healing Drug delivery	[155]

(continued)

Table 3 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
CNT	Coating by gelatin methacrylate for better dispersion	Gelatin methacrylate	Hybrid hydrogel Photo-induced polymerization (Irgacure)	Method d, e	Cell encapsulation	[108]
CNT	CNT dispersed in PEG compounds, various surfactant and then sonicated	4-arm PEGAA PEG dithiol (linear crosslinker)	PEG remains in triethanolamine (TEA) in phosphate buffered saline for a week and then the same molar ratio of PEGAA and PEGdithiol reacted	Method a	Neural tissue engineering, sensor technology as electrode coatings, and drug delivery	[156]
CNT	Pristine CNT No surfactant	PMAA	In situ radical polymerization (aqueous dispersion)	Method a	Pulsatile drug delivery	[157]
CNT TiO_2	First TiO_2 dispersed and sonicated in deionized water then polymer solution and CNT solution were added	Poly (3,4-ethylenedioxythiophene (PEDOT) poly (4-styrenesulfonate) (PSS)	Radical polymerization	Method a	Flexible lithium ion battery electrodes	[158]

The NCH has been prepared by formation of hydrogel in NPs suspension (method a), in situ formation of NPs (method c), acting as multifunctional crosslinking (method d) and the polymeric network binding NPs (method e)

dispersion of CNTs in hydrogels is a potential challenge. In order to induce hydrophilicity in these systems, different approaches have been employed: modification of CNT surfaces using various polar groups, i.e. amines (NH_2), hydroxyls (OH), and carboxyls (COOH), use of single-stranded DNA (ssDNA), proteins, and surfactants, as well as by grafting hydrophilic polymer chains to the CNT surfaces. The high electrical conductivity of CNT-reinforced hydrogels makes these components ideal candidates to be engineered for various electorally conductive tissues, including cardiac tissues, nerves or muscles [51]. In hybrid nanocomposites, the slightest amount of COOH-functionalized CNTs may significantly increase the tensile strength of methacrylated gelatin hydrogels in the interconnected porous structures. The addition of CNT does not interfere in the porosity and cell-growth ability of the hydrogel. The highly aligned structure with tight intercellular junctions, along with the electrical conductivity of the CNTs results in the formation of this conductive network [108].

Graphene sheets can also provide high mechanical strength (by acting as crosslinking agents), and excellent conductivity of heat and electricity in hydrogels. In order to ensure the miscibility of the hydrophilic polymer and graphene sheets, the sheets are often treated by strong oxidizers to form graphene oxide (GO). Thus, GO can be crosslinked to the media, both physically and covalently. The GO can be employed to produce stimuli-responsive hydrogels [51]. Generally, GO is introduced into the nanocomposite hydrogels by physical mixing, in solutions, or by in situ polymerization of water-soluble monomers. The latter strategy is believed to be more efficient in terms of obtaining tough and stretchable nanocomposite hydrogels [109].

Electrically conductive hydrogels of polyethylene diacrylate, containing GO, has also been prepared by photopolymerization. In these conductive gels, the GO crosslinker has introduced electrical properties to the network [110]. The ability of GO to form crosslinks leads to the design of self-healable and tough poly (acrylic acid)-based nanocomposite hydrogels using GO and Fe^{3+} ions. Amazing dual cross-linking effects through dynamic ionic interactions has been developed: Fe^{3+} ionically crosslinked to carboxylic acid groups of the hydrogel backbone and then linking GO nanosheets to the backbone through Fe^{3+} coordination. The proposed mechanism explains the tough and self-healable behaviour of the gels based on the energy dissipation through dynamic *breakage* and *recombination* of ionic interactions. Furthermore, the GO nanosheets, coordinated on to the backbones, act as stress-transfer centres, which transfer the stress to the polymer matrix, and meanwhile, they maintain the configuration of the hydrogels [109]. These nanocomposite hydrogels can facilitate the development of asoft materials to be used in various biomedical applications.

In another research, a combination of GO nanosheets and thermoresponsive poly(N-isopropylacrylamide) (PNIPAM) polymeric networks, resulted in light-responsive nanocomposite hydrogels with ultrahigh tensile strength. These novel properties which are essential for designing smart actuators, remote light-controlled devices, and artificial muscle, can be attributed to the GO nanosheets, which are physically crosslinked to the amide groups of the PNIPAM chains via hydrogen

bonds in the presence of the chemical crosslinker of N, N-methylene bis acrylamide (MBA) [111].

2.5.4 Metal and Metal Oxide Nanoparticles

Various types of nanocomposite hydrogels have been fabricated, using different metallic and metal-oxide nanoparticles, including gold, silver, copper, iron oxide (Fe_3O_4–Fe_2O_3), ZnO, titania (TiO_2), alumina, etc. [51, 112]. In fact, the physical interactions between polymer and nanoparticles are not sufficient to provide enough mechanical strength. However, functionalization of nanoparticles will improve the mechanical strength by providing multiple crosslinking nodes in the network [51]. According to their physical, electrical, magnetic, and antimicrobial properties, various applications for imaging agents, conductive scaffolds, drug delivery systems, switchable electronics, actuators, and water treatments have the uses been developed for these hydrogels [112]. Mechanical properties also can be manipulated via magnetic field induction [26].

Thermo-responsive magnogel based on PNIPAm has been synthesized for drug delivery application; anti-cancer therapeutic drugs can be released by a magnetic field and temperature variation. In other to stabilize the Fe_2O_3 NPs, various modifications have been employed including oleic-acid, polyhedral oligomeric silsesquioxane (POSS) and nitro-dopamine PEG-dicarboxylic acid functionalization. This functionalization results in the better responsive performance of the nanocomposite hydrogel [113]. Table 4 represents the metal oxid-based NCH preparation methods especially for magnogels (ferrogels) and their applications.

Recently, ferrogels (magnetic hydrogels), which contain immobilized nanomagnetic particles (e.g. γ-Fe_2O_3, Fe_3O_4, Co Fe_2O_4), have attracted considerable attention. The magnetic hydrogels can quickly respond to an external magnetic field (MF), which acts as a distance-force (noncontact-or-remote force) device/system. This characteristic facilitates the incorporation of these hydrogels in various biomedical applications [38], i.e. in tissue engineering and cell/drug delivery. During the cell-growth process, limitation of available cells in the porous hydrogel is a great challenge which can be overcome by implementation of magnetic hydrogels. In fact, the required biological agents can be bound to the magnetic nanoparticles (MNPs) by applying external MF. In addition, the magnetic scaffolds can be stimulated by physical cues via interaction between MNPs and an alternating magnetic field (AMF) [37].

In order to microfabricate and 3D print hydrogels, two main strategies have been employed using microengineered hydrogels for tissue engineering including: "top-down" (hydrogel formed and cell cultivated in the fill media; for larger hydrogels) and "bottom-up" (every part of the microgels contains cells and then they are assembled into the desired shape; for microhydrogels) [114]. Magnetic microgels can be assembled in a way to form complex tissue structures in a controlled manner via MF. Several assembling techniques have been explored, including those based on microfluidics [114], nanotextured surfaces

Table 4 Typical most-used metal oxide NPs, their NCH preparation methods and their applications

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
ZnO	Calcination (at 850 °C) of entrapped "zinc acetate di-hydrate" in PAA gel	PAA	Thermal-induced (persulfate) aqueous solution polymerization	Method e	Biotechnology	[70]
ZnO	$ZnNO_3$ hydrolyzed and then turn to ZnO crystals by heating	CMC	Crosslinked by maleic, succinic, and citric acid used as crosslinker	Method c	Antibacterial	[122]
ZnO	Synthesized by zinc acetate dihydrate and sodium hydroxide	Chitosan	NC hydrogels were lyphophilzed	Method b	Wound dressing	[118]
ZnO	Synthesized by zinc acetate dihydrate and sodium hydroxide	β-chitin	Freeze-dried	Method a	Wound healing	[121]
ZnO	Synthesized using zinc acetylacetonate monohydrate, oleylamine and oleic acid at 240 °C under argon flow	PNIPAm	– Linear polymer by radical polymerization – UV-induced crosslinking reaction	Method d	Hydrogel as antibacterial coating	[31]
CdSe/ZnS	COOH-functionalized Core-shell QD by octyl-amine modified PAA	Cellulose	Crosslinked by sodium hydroxid and urea ligand formation	Method d	Fluorescent semiconductors and optoelectronics	[35]
Fe3O4 magnetic particles	Sonicated in PVA/DMSO solution	PVA	Freezing-thawing cycles	Method a	Magnetic properties for Controlled Release of Drug	[38]

(continued)

Table 4 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
magnetite (Fe_3O_4) and maghemite (Fe_2O_3)	Synthesized in hydrogel network by NaOH	PAMPS	Photo-induced radical polymerization	Method c	Magnetic response hydrogels for water treatment	[49]
Ferrimagnet	Ferrofluid mixed with hydrophobic phase	Hydrophobic phase: styrene and divinyle benzene Hydrophilic phase: AAm and MBA	Anisotropic microfluidic device. – The hydrophobic monomer core with magnetic material is encapsulated by a hydrophilic monomer droplet suspended in fluorocarbon oil	Method a	Rotational control by applying an external field in biomedical application	[39]
magnetite (Fe_3O_4) and maghemite (Fe_2O_3)	In situ mineralization and coprecipitation of $FeCl_2$ and $FeCl_3$	Gelatin	Solution and physical crosslinking	Method c	Actuators	[48]
Fe_3O_4 magnetic	$FeCl_3{\cdot}6H_2O$ and sodium oleate Iron-oleate complex then it was treated by oleic acid up to 318 °C to form hydrophobic Fe_3O_4. Their surface were treated by PEG and polyhedral oligomeric silsesquioxane	PNIPAm poly-ethylene glycol (PEG)	Redux initiation aqueous solution polymerization	Method d (functionalized NP)	Theranostic application e.g. long distance control of drug delivery by MF	[113]

(continued)

Table 4 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
γ-Fe_2O_3	–	Chitosan modified by catechol	Chemically and physically crosslinked by pH variation	Method d (physical crosslinking: complex)	pH and magnetic responsive Drug delivery	[159]
Fe_3O_4	Coprecipitated in basic media alginate-coated in a suspension	Alginate and PAAm	Redox initiation and aqueous solution polymerization then ionically crosslinked by Fe $(NO_3)_3$	Method a	Soft robotics, clinical operations, tough, and stretchable magnogel	[160]

The NCH has been prepared by formation of hydrogel in NPs suspension (method a), in situ formation of NPs (method c), acting as multifunctional crosslinking (method d) and the polymeric network binding NPs (method e)

(micromolding) [114], acoustic and magnetic fields (photolithography) [115], and surface tension (emulsification) [39].

The magnetic gels have shown the ability of pulsatile release of drugs, through low-frequency oscillatory MFs. Recently, an intelligent Fe_3O_4 MNP-PVA hydrogel has been designed to control the drug release by "on" and "off" modes [37, 116]. When the MF was intensified, the on-off magnetization can change the volume of the ferrogels, and subsequently, affect the swelling ratio. Upon applying an MF, the nanoparticles tend to get agglomerated together [37]. The reduced porosity and volume result in "close" configuration, and subsequently, the rate of drug delivery will be minimum. On the "off" mode, the volume and swelling ratio are increased, and the drug would be delivered at it's highest rate. Furthermore, the magnetic-sensitive hydrogel has shown outstanding flexibility and elasticity [38]. The magnetic-thermosensitive hydrogels have also been used for controlling the drug release rate. The AMF can adjust the hydrogels temperature. By increasing the temperature (above lower critical solution temperature (LCST)), the network will collapse and the drug diffusion would be "off"; and then, by reducing the temperature, the drug diffusion status would be "on" and the drug can be released [37]. This ability of magnetic gels to raise and control the temperature remotely has been used in cancer therapy. The concentration of Iron Oxide and the amplitude of MF are influential factors for controlling the generated heat. The local hyperthermia feature of the magnetic hydrogels makes them a promising injectable hydrogel system, especially for cancer therapy. The functionalized magnetic NPs provide better performance during swelling and deswelling phenomenon (considering no release of NPs, and subsequently less toxicity for biological application) [26].

Mechanical properties also can be manipulated via magnetic field induction [26]. Thermo-responsive magnogels based on PNIPAm have been synthesized for drug delivery application; the anti-cancer therapeutic drugs can be released by the magnetic field and temperature variation. In other to stabilize the Fe_2O_3 NPs, various modifications have been employed including oleic-acid, polyhedral oligomeric silsesquioxane (POSS) and nitro-dopamine PEG-dicarboxylic acid functionalization. This functionalization results in better responsive performance of nanocomposite hydrogel [113].

The poly(2-acrylamido-2-methyl-1-propane sulfonic acid) P(AMPS) magnetic composites have been prepared and employed for removal of toxic metals. The iron oxide can confer ferromagnetic property into the gel. These gels can be employed for absorbing toxic ions, i.e. Pb^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Cr^{3+} [49].

Colonization of microorganism on the surface of the medical devices, such as implants, may result in severe infections. Therefore, the antibacterial media with the lowest cytotoxicity would be of great importance. Various metal and metal oxides nanoparticles such as silver, gold, copper, TiO_2, and ZnO have been applied in the hydrogels to improve their antimicrobial properties [117].

Zinc oxide is the metal oxide which has been used in hygienic applications such as cosmetics. Recently, the ZnO NPs have also been used as antibacterial agents against both gram-positive [118] and gram-negative bacteria [119] and showed no cytotoxicity at concentrations of up to 10 wt% NP. Various antibacterial

mechanisms have been proposed to explain their antibacterial role, such as the formation of reactive oxygen species (ROS), and the release of Zn^{2+} ions [119, 120]. The ZnO NPs with uniform crystal structures have been successfully incorporated into poly(*N*-isopropylacrylamide) (PNIPAAm) hydrogel layers. In order to better disperse the NPs, the surfactants mediums of oleylamine and oleic acid have been employed. The antibacterial properties of these hydrogels can be altered by changing the thickness of the NP film [31]. Recently, β-chitin hydrogel/nZnO composite bandage has been fabricated and used for wound dressing applications. It has shown antibacterial effects against *E. coli* and *S. aureus*; however, the cytotoxicity of the hydrogels has been increased at elevated concentrations of ZnO NPs [121]. Furthermore, a flexible and microporous chitosan-ZnO nanocomposite hydrogel has been developed and tested for wound dressing purposes. In vivo studies revealed that this nanocomposite hydrogel has great potential to be used as a bandage for burn wounds, chronic wounds, and diabetic foot ulcers [118]. In another approach, the carboxymethyl cellulose (CMC)-based nanocomposite hydrogels were prepared by oligomeric acrylic acids, such as maleic, succinic or citric acid. The ZnO nanoparticles were synthesized in the presence of CMC to avoid agglomeration, which is known to be the main problem in zinc oxide nanocomposite hydrogel production. In fact, the polysaccharide structure, which has numerous hydrogen bonds, can effectively act as a template for nanoparticle growth. This nanocomposite hydrogel has shown a promising swelling ratio, and also great antibacterial activity against both gram positive and gram negative bacteria [122].

Metals are also used in the hydrogel network to add more functionality such as biocidal and electrical activity to the soft material. Table 5 summarizes preparation methods of the most-used metals in NCHs and their applications. Silver is the most studied antiseptic agent and has a long history in activity against gram-positive and gram-negative bacteria, fungi, protozoa, and certain viruses. Since the silver ions have shown concentration-dependent toxicity, care must be taken in the incorporation of silver in medical devices [29]. However, silver does not have the hazards associated with the accumulation of other heavy metals [29]. Factors, affecting the biocidal activity of silver nanoparticles (Ag NP) include particle size, the shape of the particle, and the dispersion status. The smaller particle size offers larger surface-to-volume ratio, which consequently enhances the antibacterial activity. In addition, the Ag NPs with triangular architecture has shown a better antibacterial effect against *E. coli* compared to the rod or spherical-shaped Ag NPs. Furthermore, for biocidal activity, the binding of Ag NPs to polymer networks is more important for effectiveness than the size of nanoparticles. The utilization of polymer supports for Ag NPs results in an increase in the stability of the particles, preserve them against aggregation, and also, increases their biocompatibility [29]. The antimicrobial activity of silver can be attributed to the strong bonding between the silver ion and the biological molecules containing sulfur, oxygen, or nitrogen. It is believed that the complex, which is formed between proteins of bacteria and the silver ion, can interfere with the metabolism and eventually, it disturbs the power functions of the bacteria. It can also prevent the cellular reproduction by interaction

Table 5 Typical most-used metals and their NCH preparation methods and applications

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
Ag	In situ reduction ($AgNO_3$, Acetic acid, $NaBH_4$ as the Ag NP-forming agent)	Chitosan/ sodium tripolyphosphate	No polymerization Ionically crosslinked by polyanions	Method c	Drug delivery Antibacterial	[69]
Ag	Reduction of Ag ions in swollen cryogel	Methacrylated carboxymethyl chitosan PEGDA	Photopolymerization on ice, and lyophilizing(cryogel)	Method c	Antibacterial tissue eng.	[47]
Ag	Reduction of Ag ions in swollen hydrogel	PVA Sodium alginate PAAm	Thermal-induced (persulfate) aqueous polymerization (IPN)	Method c	Antibacterial	[44]
Ag	Reduction of Ag ions in swollen hydrogel	PNIPAM PSA	Redox initiation (persulfate) Aqueous polymerization	Method c	Antibacterial	[45]
Ag	Maleimide-coated silver nanoparticles	Furfuryl-gelatin	Diels–Alder Cycloaddition-based cross-linking	Method d	Drug delivery systems, improved mechanical properties	[124]
Ag	Reduction of Ag ions in swollen hydrogel	poly (vinyl pyrrolidone) (PVP) PAAm	IPN redox initiation and aqueous polymerization	Method c	Antibacterial	[46]
Ag	Reduction of Ag ion	PAA	In situ polymerization and reduction of Ag ion	Method c	Conductive hydrogels	[127]
Ag	(PVP)-coated silver nanoparticles	PAAm	Redox initiation (persulfate) and aqueous polymerization	Method e	optical biosensor	[128]
Ag	Reduction by one-pot green chemistry technique using starch and glucose	PVA	Freeze-thaw	Method a	Antimicrobial dressing scaffold	[123]

(continued)

Table 5 (continued)

NP	NP preparation	Polymeric matrix	Polymerization method	NCH preparation	Application and feature	References
Ag	Reduction of Ag ions in cross-linked hydrogel	Dialdehyde hemicelluloses Chitosan	–	Method a	Antibacterial	[161]
Ag	Reduction of Ag ions in hydrogel	Chitosan (CTS) and acrylic acid (AA)	Redox initiation (fentone) and solution polymerization	Method c	Catalytic reduction of organic dyes	[129]
Ag	Using biodegradable gelatin as a stabilizing agent	Gelatin PNIPAm	Redox initiation (persulfate) and aqueous polymerization	Method c	Antibacterial thermosensitive	[125]
Au Pt	Citrate-reduced gold prepared by Frens method PVP-protected Pt NPs prepared	PAAm	No polymerization	Method b Breathing in	Dispersed metal nanoparticles in porous anodic aluminum oxide	[43]
Au	Solution	PAAm	Electropolymerization in the presence of $ZnCl_2$	Method b Breathing in	Biosensors and solvent-switchable electrical properties	[42]
Au	Tiopronin (N-(2-Mercaptopropionyl) glycine) protected gold nanoparticles	Collagen	Nanoparticles crosslinked to collagen via EDC (1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide) coupling agent	Method d	Photothermal therapies, imaging, and cell targeting	[53]
Au	Reduced (by $NaBH_4$) and then functionalized (by allyl mercaptan)	PNIPAm	Thermal-induced solution polymerization (AIBN and THF)	Method d	Tunable thermo-switchable electrical properties	[32, 33]
Cu	Synthesized by reduction reaction (starch capping) and modified a silica coating by inverse emulsion	Starch	Using urea	Method c	Antibacterial	[36]

The NCH has been prepared by formation of hydrogel in NPs suspension (method a), physical incorporation of NPs into the hydrogel networks (method b), in situ formation of NPs (method c), acting as multifunctional crosslinking (method d), and the polymeric network binding NPs (method e)

with DNA [29]. The immobilization of Ag NPs has also been reported in synthetic hydrogels, such as poly(acrylic acid) and poly(methacrylate) [30]. Recently, the introduction of Ag NPs into different bio-based and biocompatible systems, such as (PVA) [123], gelatin/chondroitin sulfate [124], PVA/sodium alginate/poly(acrylamide) [44], and gelatin/N-isopropylacrylamide [125], has gained more attention.

Various studies deal with a physical dispersion of Ag NPs via in situ synthesis, in which the Ag NPs were often dispersed into the zeolite–poly (acrylamide-co-acrylic acid) hydrogels, using radical graft copolymerization and magnetron sputtering methods [126]. These antibacterial hydrogels were used for water treatment applications. Generally, the silver nanocomposite hydrogels, which have been prepared via radical graft copolymerization, display better biocidal activity. This feature is in accordance with their better dispersion which has also been confirmed by XRD result [126]. In another approach, the silver nanoparticles were synthesized in situ in the swollen hydrogel media. The superabsorbent hydrogels were based on poly(vinyl alcohol) (PVA), sodium alginate (Na–Alg), and poly (acrylamide). The Ag ion loading is proportional to the antimicrobial activity, and can be affected by the concentration of a silver ion, crosslinking density of hydrogel network, as well as the Na-Alg/PVA ratio [44]. Chitosan nanocomposite hydrogel beads have also been prepared by synthesizing Ag NPs in situ. The chitosan in these systems has been ionically crosslinked to the sodium tripolyphosphate. The amine and hydroxyl groups confer on to the chitosan the potential to interact with various metal cations, i.e. Ag^{+}, Zn^{2+}; therefore, the Ag NPs are expected to be distributed uniformly in the hydrogel beads, which is also consistent with the XRD results. Moreover, the effect of Ag NPs on the drug loading has been evaluated. It has been shown that an increase in the Ag NPs content would result in a decrease in the drug loading. It is attributed to the variation of the less porous structure of the chitosan induced by interactions between Ag ions and chitosan [69]. As it has been previously stated, the Ag NPs are incorporated into the polymer matrix physically; as a result, the continuous release of NPs to the surrounding environment is plausible. To overcome this deficiency, the Ag NPs have been covalently bonded to the furan-modified gelatin. The benzotriazole maleimide has been employed to cap the Ag NPs during in situ formation, and then, the click chemistry, Diels–Alder (DA) cycloadditions, were employed to crosslink the furan-modified gelatin to provide a mild reaction condition [124]. Multiple crosslinking effects on Ag NPs has increased the elastic modulus almost three folds. In addition to the antimicrobial applications, the Ag NPs embedded in the hybrid hydrogels, have also been employed as optoelectronic [127, 128] and catalytic materials [129]. For example, in the glucose-responsive Ag NP hydrogels, the absorbance strength of the localized surface plasmon resonance (LSPR) is decreased by an increase in the concentration of glucose. This property has been employed for the production of optical enzyme biosensors [128].

Gold is another metal element which has been used in biomedical application [30, 51, 53]. The Au NP hydrogels have been used as stimuli-responsive and switchable conductive materials. The distance variation of Au NPs during external stimulation (e.g. temperature and pH) is the main reason for the changes in its conductivity. The Au NPs have also been used for antibacterial applications, remote-controlled microfluidic valves, and surface plasmon resonance (SPR)-based sensors. However, the high-cost Au has limited incorporation of Au NPs in large-scale applications [30]. In general, the Au NPs cannot enhance the mechanical properties of the hydrogel. However, Au NPs in thiol-modified biomacromonomers can improve the gel strength. In order to hydrogel form and reform during and after printing, this nanocomposite hydrogel has been designed to represent *dynamic* crosslinking by functionalization of the Au NPs to act as multiple crosslinking agents [130].

It is believed that Au NPs are biocompatible and capable of being easily functionalized by biomolecules. The size and shape of these biocompatible NPs can be engineered; the combination of these unique features make Au NPs excellent candidates use in various applications like new contrast agents for imaging and novel photothermal therapies, biomedical applications, and drug delivery [53].

3 Summary and Outlooks

Hydrogels have tremendous potential to be tuned to obtain the desired physicochemical properties in contact with an aqueous media. The need for engineered hydrogels with specific properties results in outstanding developments in the conventional hydrogels which often offer poorer properties. The softness of the hydrogels provides necessary and sufficient resemblance to the biological and natural systems, while this softness would defiantly affect the mechanical properties which in turn restrict the application of the gels. Inspired by nature, nano-modification can promote the properties and performance extensively. The nano-scale incorporation of minerals, as a hard component, not only confer better mechanical properties but also introduce other functionalities, such as stretchability and stimuli-responsiveness into the hydrogels. The facile techniques of nanomodification can be simply employed to shift from conventional hydrogels into smart ones.

The stimuli-responsive hydrogels trigger the idea of smart hydrogels as multifunctional materials. The nanocomposite properties can be manipulated by altering the pH and the temperature of the surrounding media. In addition, the mesh size of the nanocomposite hydrogels network can be regulated by electrical and magnetic fields. This on-off behaviour enabled the gel to change its shape, to move, and also to releases certain drugs. Quantum dot nanoparticles offer photoluminescent

properties to the nanocomposite hydrogels. The supramolecular-like behaviour and reversible crosslinking, introduced by the hydrogen bonding or ionic interactions, have resulted in self-healable hydrogels.

The engineered hydrogels have received much attention and are used in various applications, including actuators, biosensors, controllable drug delivery, artificial muscles, etc. The clinical applications of hydrogels can limit the type of hydrogels used. Various pristine and modified bio-based macromolecules have been introduced into the networks to design engineered hydrogels, which are tough, stretchable, resilient, or self-healable. Recently, click-chemistry has assisted in producing biobased hydrogels [109, 110] with various functionalities, including photopatternable, antibacterial, antifungal, and anticancer. This chemistry provides an efficient, selective, and mild situation to prepare gels with improved properties; the Au nanocomposite hydrogels with superior mechanical and electrical properties, are of examples of the employment of the click-chemistry (Diels-Alder reaction). The click-chemistry, "thiol-ene" rection has been employed to prepare 3D structured cell encapsules, using acylated-modified, sulfobetaine-derived starch, and dithiol functionalized PEG [131]. The mechanical and swelling properties, as well as gelation time, can be easily tuned in physiological condition.

Another aspect of the formation of hydrogels is the engagement of relatively simple radical polymerization. This advantage has extended hydrogel application extensively, owing to the ability to construct complicated structures precisely. Also, 3D printing is a newfound way in hydrogel fields to produce well-defined volumetric objects. The important factors in 3D printing include viscosity, gelation mechanism, and speed. The incorporation of nanoclays is an efficient way to modify the viscosity and shear-thinning effect of the hydrogel.

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