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Soft and flexible hydrogel templates of different sizes and various functionalities for metal nanoparticle preparation and their use in catalysis

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ABSTRACT

Hydrogels are important functional materials with a myriad of potential applications. As the chemically stable and interlocked polymeric network retains vast amounts of water without dissolving, the use of hydrogel matrices for preparation of metal nanoparticles in situ is feasible, and readily applicable in the catalysis of various aquatic and non-aquatic reactions. The functional groups in the hydrogel network can act as both chelating and capping agents for metal nanoparticle preparation from metal ions and for their stabilization; thus, the metal particles are protected from the atmosphere hindering the oxidation/deactivation and aggregation, allowing an increase in their stability and longevity. The functional groups binding ability in hydrogel matrices allow metal ions with different oxidation state such as Fe, Co, Ni, Cu, Ru, Au and so on, to be loaded into the hydrogel matrices. Then, these metal ions can be reduced/precipitated to their metallic particle forms inside hydrogels of different dimensions using green chemicals (those with no hazardous impact on the environment) or non-toxic chemical reducing agents such as $NaBH_4$, H_2, citrate, ethylene glycol, etc., depending upon the nature of the metal ions. The hydrogel-supported metal nanoparticles can be successfully used for the reduction of nitro compounds, hydrolysis of various hydrides and degradation of toxic species such as dyes, chlorohydrocarbons, pesticides, insecticides and so on. In this review, a flexible and highly adaptable platform for the design of soft and versatile interfaces with an outlook toward their use in material science, engineering and catalysis for in situ metal nanoparticle preparation within hydrogels for the catalysis purpose is addressed. In addition, even *ex situ* prepared metal nanoparticles can be readily incorporated within hydrogel matrices for various purposes are considered. The techniques outlined here afford robust hydrogel–metal composite systems with excellent control over size, composition and topography of the interfaces. Further directions from soft and flexible reactor of polymeric network at various dimensions, providing a continuously and environmentally workable milieu for designing and developing advanced technology are also addressed.

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Contents

1. Introduction

Natural characteristics, such as soft, flexible, elastic and wet nature, make hydrogels an indispensable engineering material for many advanced material design [1–4]. In addition to the abundant functional groups that exist within hydrogel matrices are useful for specific tasks. Because of their biocompatibility; the versatility, ease of synthesis and the ability to prepare at various dimensions have made hydrogels a frontrunner in many fields [5–9]. Hydrogels with bulk, micro and nano dimensions are useful and have ubiquitous applications ranging from diagnostic tools to sanitary applications as well as drug delivery and environmental applications [10–14]. Hydrogels are hydrophilic polymeric chains that are connected via covalent bonding generating a three-dimensional network either in macro or micro/nano dimensions, additionally physical interactions such as hydrogen bonding and electrostatic interactions, as well as hydrophobic interactions are present [15,16]. In addition to covalent bonds between polymeric chains, there can also be further physical bonding upon absorption of metal ions. For example, the hydrogel network is knitted with metal ions via the functional groups on the polymer chains in 3D, as in the case of Ca-alginate hydrogels that are crosslinked via Ca(II) or other metal ions [17–23]. Alginate hydrogels are formed by physical crosslinking of alginate with various metal ions in addition to Ca(II), and are used as biomaterials for many different purposes with various formulations: from effective agents (drugs, proteins, yeast, insecticides, enzymes, etc.) to template materials for cell growth [24–35].

Hydrogel networks play a pivotal role in tissue engineering due to the resemblance of the three-dimensional network structure to the extra cellular matrix (ECM) environment, combined with additional functionalities which can be exploited [36–46]. The bulk hydrogels are mostly macroporous (>50 nm) and even superporous with the pore sizes of up to several micron sizes, and the porosity can be tuned by the degree of hydrophilicity of the functional groups, and the amount of crosslinker used during synthesis. As the size of hydrogel decreases from bulk to the micro and nanometer size, the porosity is also reduced to mesoporous (between 50 and 2 nm) and microporous levels (2 nm and below) [47–51]. The tune-ability of the pore structure also provides extraordinary advantages for the absorption and desorption of various species [52–56]. Interestingly, hydrogels can be chemically modified to introduce new functional groups for specific targets and can also be imprinted for specific recognition of species [57–66].

The confined environments of micelles, reverse micelles, polymeric stabilizing agents such as blocks and amphiphilic polymers, capsules, liposomes and dendrimers have been widely investigated for preparation of metal and non metal particles [67–82]. Metal nanoparticles, semiconductors, inorganic oxides, and quantum dot synthesis have also been well studied, especially in the confined space of surfactants, inorganic templates and polymeric stabilizing agents [83–90]. It is known that the nanostructure of the metal particles is greatly affected by the preparation technique [68,91–101]. The size, shape and geometry of the nanoparticles are strongly dependant on the employed method; therefore, it is of great importance to have a template that is modifiable in terms of functional groups, has adjustable impermeability with regard to the porosity and is readily adjustable with respect to size and shape. All these characteristics do exist in polymeric hydrogels that can be readily prepared in various sizes with different functional groups [30–32,47,53,74]. Moreover, additional functionality such as magnetic field responsive behavior can be induced on the hydrogel network to provide advanced functionality [102–106].

Hydrogels or polyelectrolytes with binding capability to various metal ions can be used for the in situ preparation of metal nanoparticles and/or clusters of these metal ions [107–122]. The absorbed metal ion, that is held in position by the functional groups on the hydrophilic structures, multilayered poly electrolytes [123–129], dendrimers [130–132], block copolymers [133–136], spherical structures and shells [137–139], microgels [95,140–145],