Colloids and Surfaces A: Physicochem. Eng. Aspects 439 (2013) 43–68

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Polymer-immobilized nanoparticles

Samia Mahouche-Chergui[a], Mohamed Guerrouache[a],
Benjamin Carbonnier[a,*], Mohamed M. Chehimi[b,**]

[a] Institut de Chimie et des Matériaux Paris Est – Equipe Systèmes Polymères Complexes, UMR 7182 CNRS–Université Paris Est Créteil, 2-8 rue Henri Dunant, 94320 Thiais, France
[b] Univ Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR CNRS 7086, 15 rue J-A de Baïf, 75013 Paris, France

HIGHLIGHTS

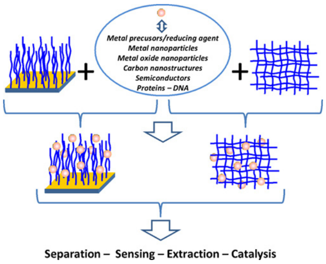
- Polymer-immobilized nanoparticle hybrids are unique systems for a broad range of applications.
- Multistep and one pot strategies are available to design polymer–nanoparticle hybrids.
- Applications include separation, sensing, extraction and catalysis.
- Unprecedented performances are achieved via the synergy of polymers and nanoparticles.

ARTICLE INFO

Article history:
Received 11 February 2013
Received in revised form 9 April 2013
Accepted 10 April 2013
Available online 18 April 2013

Keywords:
Polymeric supports
Immobilized nanoparticles
Separation
Sensing
Biomolecules
Catalysis

GRAPHICAL ABSTRACT



ABSTRACT

We review methods to prepare polymer-immobilized nanoparticles through a plethora of strategies in view of developing systems for separation, sensing, extraction and catalysis. The emphasis is on methods to provide (i) polymer brushes and grafts; (ii) monoliths and porous polymer systems; (iii) natural polymers and (iv) conjugated polymers as platforms for anchoring nanoparticles. The latter range from soft biomacromolecular species (proteins, DNA) to metallic, C60, semiconductor and oxide nanoparticles; they can be attached through electrostatic interactions or covalent bonding. It is very clear that physicochemical properties of polymers (e.g. sensing and separation) are enhanced by anchored nanoparticles, while polymers provide excellent platforms for dispersing nanoparticles for e.g. high catalytic performances. We thus anticipate that the synergetic role of polymeric supports and anchored particles will increasingly be exploited in view of designing unique hybrid systems with unprecedented properties.

---

* Corresponding author. Tel.: +33 149781114.
** Corresponding author.
E-mail addresses: carbonnier@icmpe.cnrs.fr (B. Carbonnier), chehimi@univ-paris-diderot.fr (M.M. Chehimi).

Abbreviations: AIBN, azobisisobutyronitrile; anti-BSA, anti-bovine serum albumin antibody; anti-MG, anti-myoglobin antibody; ATRP, Atom transfer radical polymerization; BSA, bovine serum albumin; CDI, 1,1′-carbonyldiimidazole; CNT, carbon nanotube; EDC, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide; GMA, glycidyl methacrylate; GNPs, gold nanoparticles; HSA, human serum albumin; LSZ, lysozyme; MWCNT, multiwalled carbon nanotube; NPs, nanoparticles; NHS, N-hydroxysuccinimide; PAA, poly(acrylic acid); PCOOH, carboxylic acid functionalized polymer from oxidized PGMA; PDEAEMA, poly(dimethylaminoethyl methacrylate); PEDOT, poly(3,4-ethylenedioxythiophene); PGMA, poly(glycidyl methacrylate); PHEMA, poly(2-hydroxyethyl methacrylate); PHBHV, poly(3-hydroxybutyrate-co-3-hydroxyvalerate); PI, polyimide; P(NAS-co-EGDMA), poly(N-acryloxysuccinimide-co-ethylene glycol dimethacrylate); PNIPAM, poly(N-isopropyl acrylamide); PMPTAC, poly((2-methylpropenoyloxyethyl) trimethylammonium chloride; PPGL, poly(polyglycidol); PPyAg, polypyrrole/Ag nanoparticle nanocomposites; PPyCl, chloride-doped polypyrrole; PPyCOOH, poly(pyrrole-co-carboxylated pyrrole); PPyDS, dodecyl sulfate-doped polypyrrole; PPyNSE, N-succinimidyl ester-functionalized polypyrrole; PPyNT, polypyrrole nanotube; PPyOS, octadecyl sulfate-doped polypyrrole; PPySO_4, sulfate-doped polypyrrole; PPyTS, tosylate-doped polypyrrole; POEGMA, poly(oligo(ethylene glycol) methacrylate); PS, polystyrene; P(S-co-MAA), poly(styrene-co-methacrylic acid); P2VP, poly(2-vinyl pyridine); P4VP, poly(4-vinyl pyridine); PNVP, poly(N-vinyl pyrrolidone); RAFT, Reversible addition–fragmentation chain-transfer polymerization; SERS, surface-enhanced Raman scattering; SPR, surface plasmon resonance; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction.

0927-7757/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.04.013

1. Introduction

Immobilization of microspheres and nanoparticles (NPs) is the subject of numerous studies pertaining to the design of polymer nanocomposites [1–5], supported catalysts [6–10], bioactive colloidal crystals [11], inverse opals for novel optical materials [12], latex templated-hollow inorganic capsules [13,14], immunodiagnostic assays [15]; "Pickering" emulsion polymerization for making latex particles [16] and film-forming composites [17] or Janus particles [18]; chemo- [19–22] and biosensors [23–25], tunable plasmonic nanostructures [26], hybrid porous monoliths for separation science and technology [27–29], biocidal polymer/metal nanoparticle composite coatings [30], and so on. Particularly, in the recent years, the literature has witnessed an impressive progress of investigations on polymer coatings, grafts and particles as supports for anchoring nanoparticles. This is actually due to several factors: polymer chains are flexible and may contain a variety of functional groups that are able to efficiently immobilize nanoparticles and their precursors by dispersive or van der Waals, electrostatic, hydrogen or covalent bonds.

The chemical composition of the support is also important as virtually the number of polymeric platforms is unlimited, ranging from natural to synthetic ones. Homopolymers, copolymers and block polymers can be synthesized from several monomers and monomer mixtures of different natures. In addition, polymer chain length and numerous combinations of monomers constituting the polymeric supports could be tuned in order to optimize the final polymeric material architecture and its performances.

Another reason for the rush in designing polymeric platforms for anchoring nanoparticles is the ease of preparation via well established chemical [31–33], electrochemical [34] and radiation-induced routes [28,35–37]. As far as natural polymers are concerned (e.g. cellulose or chitosan), they bear OH and/or amino groups that are prone to further organic reactions or to serve as reducing agents for metallic salts.

Particles can be attached by in situ synthesis from complexed metallic salts or by adsorption of pre-fabricated nanoparticles or biomacromolecules. In addition, one can design polymer coatings with controlled hydrophilic/hydrophobic characteristics, positive or negative charge, response to external pH or thermal stimuli, and finally with high resistivity or conductivity. It is therefore clear that combining polymer coatings; of different nature, shape, chemistry and physical properties; together with nanoparticles (metal, oxides, semi-conductors, biomacromolecules) permits to the colloid and surface scientist to design infinity of systems for a plethora of applications.

We shall consider in this manuscript hard, inorganic nanoparticles (metals, semi-conductors, oxides, quantum dots, etc.) as well as soft, organic nanoparticles such as proteins and DNA fragments (Fig. 1).

Depending on their nature, NPs impart magnetic, electrical, optical, catalytic, biorecognition and biocidal properties to the hybrid polymer-based systems. The choice of NPs is thus dictated by the target application. For example, metallic particles enhance electron conduction [41,42] or alter optical properties [43,44] of sensing layers and devices. In catalysis, polymer-immobilized metallic and bimetallic NPs were shown to be highly effective in the reduction of oxygen [10,45], methanol oxidation [46,47], or Suzuki C–C coupling reaction [7,8,48] to name but a few reactions. Biorecognition is another aspect, and latex-immobilized antibodies or antigens permit to design immunodiagnostic assays [15,49]. Biocidal property can be provided by silver nanoparticles immobilized onto polymer coatings. This topic is described at length in the literature and summarized here by Chang Ming Li and co-workers in this special issue [50]. The authors stress the increasing antibacterial effect for smaller size of silver NPs.

Although an important number of nanoparticles can be immobilized to the surface, the mechanism of anchoring them to the said polymer surfaces remains an important issue. Nevertheless, for each type of nanoparticles, strategies have been developed, tested and proved efficient for anchoring the nanostructures. Towards this end, two general ways are envisaged: immobilization of metal ions followed by reduction into NP; use of pre-fabricated (metallic, oxide, semi-conducting) NPs or proteins for immobilization on reactive surfaces. Still, the success of immobilization of NPs or metal ion precursors depends on the functional groups provided by the polymeric support and which could undergo van der Waals, electrostatic, hydrogen or covalent bonds. Hydrophobic interactions constitute another route and proved efficient for anchoring proteins [51]. They concern the interactions of the support and the biomacromolecule when both are immersed in water; the surface-biomacromolecule interaction being strong enough to overcome the surface-water and biomacromolecule–water interactions.

The strategies outlined above concern multistep approaches for polymer-immobilized NP hybrid systems. It is to note that one can also design polymer-immobilized NP by one single step route. In this way, both the polymer and the NPs are synthesized simultaneously via photochemical [35,37,52,53], electrochemical [54] or chemical polymerization routes [55].

In this review we tackle the design of polymer-immobilized NPs systems by considering the following sections:

- General methods of making polymer materials as platforms for anchoring NPs.
- Case studies and applications of selected polymer-immobilized NP systems taken from the authors published material and from the literature. This important applied section will consider the immobilization of particles (metals, oxides, semi-conductors, CNTs, proteins, DNA) on
  (i) vinylic polymer brushes and grafts,
  (ii) polymer monoliths and porous polymer supports,
  (iii) natural polymers, and
  (iv) conductive polymers.

We will then finish by concluding remarks and future prospects.

Note however, that we will not cover separately the preparation of nanoparticles, the reader is referred to the excellent review by Luque and co-workers [56] on physical and chemical routes for making nanoparticles. Polymer-assisted synthesis of nanoparticles has been reviewed by Rozenberg and Tenne [4].

2. Methods of making synthetic polymer supports

In this section we briefly outline the various approaches for making polymer supports which we consider in this review: thin vinylic and conjugated polymer films, and polymer monoliths.

2.1. (Ultra)thin polymer films

We summarize the most investigated methods for making ultrathin polymer films. The general routes are the so-called "grafting from" and "grafting onto". For "grafting from" methods, the emphasis is on surface-initiated free radical polymerization, controlled radical polymerization methods (CRP) such as atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain-transfer polymerization (RAFT) [32]. Photopolymerization is another route, and has been widely employed recently to make grafted polymer films [36,37]. The method is versatile; the propagating species could be radicals (most applied approach), cations and anions [37]. Iniferter (*ini*tiator–trans*fer*–*ter*minator) is a controlled radical photopolymerization based on reversible chain