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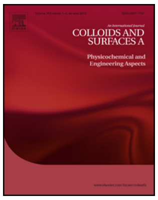

Elaboration of hybrid silica particles using a diazonium salt chemistry approach

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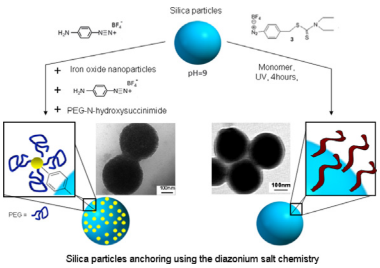
HIGHLIGHTS

- Covalent surface modification of silica particles.
- Nanoparticles.
- pH sensitive polymer.
- Diazonium salt chemistry.
- Colloid and surface science and technology.

GRAPHICAL ABSTRACT



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ABSTRACT

We demonstrate that the reaction of diazonium salts with silica particles in basic media can provide reactive surface functionalities which are able: (i) to initiate the growth of polymers and (ii) to immobilize iron oxide nanoparticles at the surface of silica particles. Using this strategy, we synthesized hybrid >silica core@poly(acrylic acid) shell particles and magnetic hybrid materials composed of silica cores surrounded by a dense covalent attachment of magnetic iron oxide nanoparticles and polyethyleneglycol chains. Advantages of this functionalization approach rely not only on the simplicity, rapidity and efficiency of the procedure but also on the formation of strong silica aryl surface bonds, highly suitable for a wide variety of potential applications in colloid and surface science and technology.

1. Introduction

Core–shell particles are attracting a great deal of interest because of the diverse applicability of these colloidal particles, which can be used for the elaboration of photonic crystals [1], in multi-enzyme biocatalysis [2] or in drug delivery [3]. They have become a source of advanced materials as they exhibit unique improved physical and chemical properties over their single-component counterparts [4]. Many methods to engineer such materials with controlled precision have already been given in the literature [5]. Silica is viewed as an important inorganic component in hybrid core–shell particles because of its surface stability, biocompatibility and its versatility with respect to surface modification [6]. Different polymerization methods have been employed to produce colloidal particles that consist of silica cores modified with a polymeric shell. For example, Armes et al. in 2001 used an aqueous ATRP approach to synthesize various and well

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defined polymers from silica particle surface [7]. In this work, a bromosilane was used to modify the surface of silica particle. Kohri et al. used a surface-initiated enzymatic vinyl polymerization to synthesize organic–inorganic hybrid core–shell particles to provide a silica core and a polyacrylamide shell covalently attached to the core surface [8]. A silane coupling agent was used to modify the silica particles with the polymerization initiator. Using a combination of self-assembly of preformed nanoparticles onto larger spheres and colloid reduction chemistry, Halas et al. reported a general strategy for the formation of solid-core/metal-nanoshell particles [9]. Small gold nanoparticles were covalently bound via amine group linkages on 3-aminopropyltriethoxysilane-modified silica particles. The same group studied the deposition of preformed gold nanoparticles onto silica particles functionalized with various groups [10]. The type of functional compound present on the silica nanoparticles was found to have an influence on the coverage of gold nanoparticles and clusters on the silica particles: amino and thiol functional groups permit to bind the gold nanoparticles, whilst only minimal attachment to methyl and diphenylphosphine moieties was observed. Such organosilane ligands have been widely used to impart a broad range of functionality on the surface of silica particles [11]. However, the method suffers from many drawbacks. Self-condensation of the silane coupling agent poses problems in tuning the surface density of the functionalities and often results in irreproducible surface coverage [12]. In a recent study by Bruce and coworkers, the effect of various reaction conditions was studied to assess the density of surface amine groups capping silica-coated magnetite nanoparticles [12]. The authors clearly pointed out the difficulties of this procedure, wherein the surface density depends critically on various reaction conditions.

Therefore, developing efficient and reproducible functionalization strategies for obtaining strong and stable linkages between the silica particle surface and the organic/inorganic coating still remains challenging. Diazonium salts chemistry has been successfully applied to the modification of carbon-based [13], and metallic [14] planar or nanoparticle surfaces, affording strong carbon or metal carbon linkages [15]. Thanks to this method, a covalent bond is established between the metallic surface and the organic layer during the grafting step. This has been demonstrated on metals by XPS [16], by ToF-SIMS [17]. For the oxide surfaces, several examples of grafting have already been published for example for TiO_2 [18] or CuO [19]. In the latter case, a Cu—O—C bond has been identified by XPS, indicating the existence of a covalent bond with the oxide surface.

Concerning oxide particles, our group succeeded very recently in grafting aryl groups derived from diazonium salts on the surface of iron oxide NPs by taking advantage of the transformation of the diazonium species to diazoates in basic media [20]. This original and reproducible strategy afforded a monolayer of functional aryl groups grafted to the NPs. This grafting approach has been expanded to grow from the surface of oxide nanoparticles different types of polymer [21], for fluorescence labeling [22] and more recently for the dense covalent attachment of magnetic iron oxide nanoparticles onto silica particles [23]. This approach is considered as bringing some new methodology for the surface modification of nanomaterials.

In the present study, we explore the potential of aryl diazonium coupling agents to be used for the preparation of hybrid silica–polymer materials. The diazonium salt was used to introduce reactive functions that are able to initiate the polymerization from the surface of silica particles. To demonstrate the versatility of this grafting method, the diazonium salt was also used as a covalent linker between the surface of silica particles and iron oxide NPs modified by polyethyleneglycol chains. Corresponding reaction pathway to fabricate the hybrid silica particles is depicted in Fig. 1.

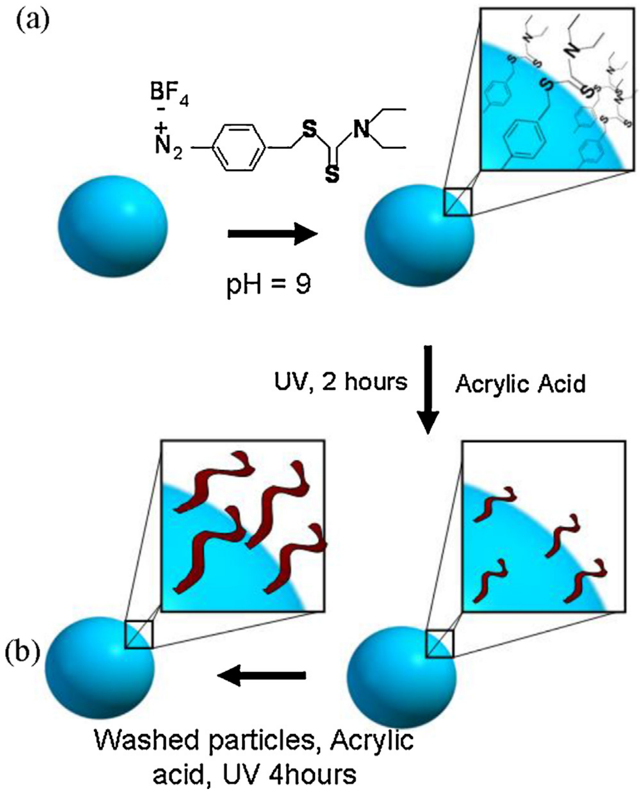

Fig. 1. Scheme of the reaction pathway used for the growth of polymers from the surface of silica particles by using the diazonium salt chemistry to introduce polymerization initiators.

2. Experimental

2.1. Materials

We used ammonium hydroxide solution, 25% (Sigma–Aldrich), absolute ethanol (Honeywell), deionized water, tetraethoxysilane (TEOS, GPR Rectapure, VWR Prolabo) for the silica particles synthesis. Phenylenediamine (Sigma), tetrafluoroboric acid (ACROS), terbutylnitrite (Aldrich) thionyl chloride, 2-(4-aminophenyl)ethanol (Aldrich), diethyldithiocarbamate (Aldrich), 4-nitrobenzyl chloride (Aldrich), Raney Nickel (Aldrich) were used for the synthesis of 4-aminophenyldiazonium tetrafluoroborate and 4-(((diethylcarbamothioyl)thio)methyl) benzenediazonium tetrafluoroborate. $FeCl_3{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$, NaOH (Aldrich) were used for the synthesis of iron oxide (magnetite) nanoparticles. All the solvents and acrylic acid were obtained from Acros and used as received. Commercial NHS–PEG (Sunbright MA-050TS) was purchased from NOF America Corporation

2.2. Characterization

Infrared spectroscopy was performed upon dried samples with a FT-IR Spectrometer Tensor 27 from Bruker equipped with a golden gate for analysis in the range between 400 cm^{-1} and 4000 cm^{-1}. Transmission electron microscopy (TEM-CM100, Philips) operating at 80 keV was used to determine the size and morphology of the synthesized particles. Samples for TEM were prepared by drying one droplet of 0.5 vol% of particles onto a carbon-coated (300 mesh) grid. The thermal and decomposition characteristics of the materials were determined by thermal gravimetric analyses, conducted on a Netzsch STA 409C, in the temperature range of 10–800 °C with a heating rate of 10 °C/min under a flow of air at 80 mL/min. The electrophoretic mobility of the particles was determined at 23 °C