



# Gold-decorated polymeric monoliths: *In-situ* vs *ex-situ* immobilization strategies and flow through catalytic applications towards nitrophenols reduction



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## ABSTRACT

Monolithic polymers with micrometer-sized channel-like pores and primary amine as chelating surface functionality were prepared via a two-step synthetic route. UV-induced free radical polymerization of N-acryloxysuccinimide (NAS) and ethylene dimethacrylate (EDMA) yielded to nucleophilic sensitive monolith. Subsequent surface grafting of ethylene diamine through displacement of the N-hydroxysuccinimide (NHS) leaving groups provided pores with dual hydrophilic and chelating surface properties. Amino-containing monolith was used as versatile platform for supporting gold nanoparticles (GNPs) through complexation of either preformed Au<sup>0</sup> nanoparticles or Au<sup>3+</sup> precursor salt followed by *in situ* reduction. All synthesis and surface functionalization steps were performed within micro-columns and were confirmed to occur to a large extent using a combination of experimental methods such as *in-situ* micro-Raman spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis and pressure permeability tests providing information on morphology, porosity, flow-through properties and surface distribution of gold nanoparticles. Continuous flow catalytic activity of the nanostructured monolithic columns towards hydride-mediated reduction of nitrophenol isomers, namely 2-nitrophenol, 3-nitrophenol and 4-nitrophenol, and 4-nitroaniline was postulated on the basis of UV–vis spectroscopy characterization suggesting presence of the corresponding amino-derivatives. This study conclusively shows that the *in-situ* strategy for the surface immobilization of gold nanoparticles enables high reaction yield while maintaining unaffected the monolithic column permeability.

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## 1. Introduction

The drive towards miniaturization and high throughput processes in the fields of chemistry, biology and nanotechnology has led to the development of numerous methods and strategies to design microreactors with outstanding performances [1,2]. Porous polymers can be engineered through a variety of innovative synthesis strategies affording functional materials with well-controlled porosity and surface functionality [3]. Polymer-based porous monoliths are among the most promising materials for

microscale flow-through applications [4–9]. Indeed, through simple free radical polymerization of commercially available monomers, monoliths with a nearly end-less range of surface functionalities can be prepared in different formats such as films, capillary columns, microchips and discs [10–13]. The judicious choice of the chemical nature and amount of porogen(s), polymerization duration and content of crosslinker in the polymerization mixture provides control over the size of the channel-like pores. Surface chemistry and porosity govern surface (re)activity and permeability characteristics, respectively, that are materials' key performances for applications under flow-through operating conditions. The attractiveness of these porous materials is further enhanced by their high chemical stability over a broad range of pH together with the combination of mechanical strength and fast

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mass transport [14]. Due to these intrinsic properties, monoliths were initially developed by the group of Svec as stationary phases for chromatographic and electrochromatographic applications [15]. To date, the technology of monolithic stationary phases has been extended to nearly an unlimited range of solutes, from hydrophobic, hydrophilic, ionic and chiral low molecular weight molecules [16–21] to peptides and proteins [22]. Comprehensive and well-documented study on chemical engineering and separation potentiality of polymer monoliths can be found in Ref. [23–25].

The immobilization of metal nanoparticles on monolith surfaces has been recently proposed as an efficient strategy to expand the range of their surface-dominated properties while enhancing significantly surface area [26–29]. Silver nanoparticles were aggregated on the surface of glycidyl-methacrylate based monoliths through dynamic loading of the corresponding colloidal solution to design surface enhanced Raman spectroscopy microfluidic devices for trace-detection of proteins [30]. In this case, although the presence of nucleophile-sensitive glycidyl-groups, the monolith was used as-obtained after polymerization step without any specific surface treatment. Gold nanoparticles have received a lot of attention as they can easily be synthesized and functionalized through the well-known Turkevich [31]/Frens [32] method and thiol-mediated surface chemistry, respectively. Since the first report by Connolly et al. [33] in 2010 on the preparation of methacrylate-based monolith modified by GNPs, many authors discussed the use of related nanomaterials for detection, separation, concentration and catalysis purposes [34–39]. The group of Berkeley used thiol-modified monolithic supports prepared from generic epoxy-reactive monolith through reaction with cysteamine. Such an approach was further extended to the development of solid phase microextraction supports [40]. Besides the use of thiol-containing monoliths, monoliths with surface-grafted primary amines as GNPs-chelating groups were also considered [33,41]. UV-driven thiol-yne click reaction was implemented for the grafting of primary amines on the monolith surface affording subsequent control over the spatial deposition of gold nanoparticles along the monolithic column.

Recently, supported metal/metal oxide-based nanoparticles, particularly the ones made of Au, Ag, Pt or Pd referred to as noble metals, have been widely investigated as organometallic nanocatalysts. Indeed, immobilization of nanometals on solid supports affords efficient solutions to prevent nanoparticles aggregation and to control metal loading. Successfully achieved reactions entail carbon–carbon coupling [42,43], hydrogenation [44], hydrodechlorination [45], hydration [46], electrochemical processes [47] [48], pollutant degradation [49], to quote but a few. Among them, chemoselective conversion of nitro-arenes into the corresponding aromatic amines is of utmost importance for the treatment of water resources. Indeed, nitrophenols, nitrobenzenes, nitroanilines have been listed by numerous environmental protection governmental agencies as major pollutants that are likely to induce organs damage, skin irritation and central nervous disorders through prolonged or repeated exposure, even at low concentration. Moreover, the resulting anilines are of high interest for various industrial chemical processes. Methods for the reduction of NO<sub>2</sub> into NH<sub>2</sub> may involve the use of either metal boron hydride or hydrogen and both processes can be catalyzed by noble metal nanoparticles [50,51]. They are two conventional strategies for the synthesis of hydrogenation catalysts based on noble metal nanoparticles-loaded solid supports relying on either in situ reduction, i.e. in the presence of the support, of precursor metal salts by various reducing species or the adsorption of preformed nanoparticles [52,53]. A plethora of solid supports including zirconia-based yolk-shell nanoreactors [54], magnetic core–shell nanomaterials [55–57], silica beads, nanospheres and nanofibers

[58,59,45], zinc oxide-containing ceramic paper [60], methacrylate and conducting polymers [61,62] has been used in this context. It has been shown in many reports that surface modification of the supports with amino groups allowed stable and robust anchorage of the metal favoring the catalytic activity of the composite catalysts [55,58,63].

Polymeric hollow fiber and carbon nanotube membranes have been proposed as alternative metal nanoparticles-containing supports with monolithic-like morphology for the catalytic reduction of nitroarenes [64–66]. The use of monolithic-like supports enabled continuous operation conditions without the need for tedious and costly additional recovery step of the catalytic supports while maintaining high activity and selectivity.

In this work, we propose the use of macroporous polymeric monoliths with pore surface-grafted protonated primary amines as efficient chelating groups for the immobilization of gold nanoparticles. To date most authors reported on the use of monoliths with native primary amino as chelating groups for gold nanoparticles, hence the motivation for this work [33,41]. Both *in-situ* and *ex-situ* approaches are considered relying on reduction of metal salt precursor and adsorption of preformed colloidal gold onto the monolith surface, respectively. *In-situ* approach provides homogeneous dispersion of gold nanoparticle along the monolithic column which is a key parameter to provide micro-reactors with efficient catalytic properties. The as obtained nanostructured monoliths were applied to the reduction of mono-nitro compounds in the presence of NaBH<sub>4</sub> as reducing agent.

## 2. Experimental

### 2.1. Instrumentation and materials

Fused silica capillaries (75 μm I.D., 375 μm O.D.) were obtained from Cluzeau (Bordeaux, France). A Spectrolinker XL-1500 UV crosslinker (Spectronics, Westbury, NY, USA) equipped with six lamps (6 × 15 W, 365 nm) was used to photoinitiate the polymerization process. An HPLC pump (Shimadzu LC-10ATVP, Champs sur Marne, France) was used to flush monolithic columns for the chemical functionalization and rinsing steps. Morphology and surface chemical structure of the polymeric monoliths were evaluated using scanning electron microscopy (SEM) with the help of a LEO Gemini 1530 SEM apparatus (Leo Elektronenmikroskopie, Oberkochen, Germany) Raman microscopy using LabRAM HR apparatus (Horiba Jobin Yvon), respectively. Observations were performed for polymer samples as obtained after polymerization and surface chemical modification. Capillaries were cut at different places and small pieces were deposited on a SEM support with a silver-containing solution. The samples were dried under reduced pressure and coated with a thin layer of platinum (2 nm) with the help of a sputter coater Cressington 208 HR (Elektronen Optik Service, Dortmund, Germany). UV–vis absorption spectra were carried out on Agilent Cary 60 UV/VIS Spectrometer.

### 2.2. Chemicals

*N*-Acryloxysuccinimide (NAS), ethylene dimethacrylate (EDMA), 2,2'-azobisisobutyronitrile (AIBN), 3-(trimethoxysilyl)propyl methacrylate, sodium hydroxide (NaOH), hydrochloric acid (HCl), were purchased from Fluka (Isle-d'Abeau, France), isopropanol (Carlo Erba) and ethylene diamine (EDA) (Alfa Aesar). HPLC grade acetonitrile (ACN), toluene (dry) gold (III) chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O), gold nanoparticles (20 nm diameter; stabilized suspension in citrate buffer; 6.54 × 10<sup>11</sup> nanoparticles/ml), 2-nitrophenol, 3-nitrophenol, 4-nitrophenol and 4-nitroaniline were purchased from Sigma Aldrich (Isle-d'Abeau, France). All the

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