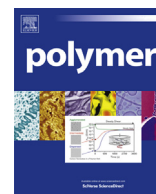




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Gold nanoparticles immobilized on porous monoliths obtained from disulfide-based dimethacrylate: Application to supported catalysis

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ABSTRACT

In this work, we report on the design and synthesis of an original methacrylic monolith bearing selectively cleavable disulfide bridges. One such monolith was prepared by thermally-induced free-radical copolymerization using a disulfide-based labile dimethacrylate, *i.e.* bis(2-methacryloyl)oxyethyl disulfide, and ethylene glycol dimethacrylate as comonomers, as well as toluene as a porogenic solvent. Upon dithiothreitol-mediated reduction of the disulfide moieties within the as-obtained disulfide-bearing monolith, thiol functions were formed at the pore surface of the resulting monolith, which was confirmed by means of *in-situ* Raman spectroscopy, while the pore size distribution was analyzed by mercury intrusion porosimetry. Immersion of the thiol-functionalized porous material in a chloroauric acid solution allowed for successful chelation of Au³⁺ ions. Subsequent hydride-mediated reduction of the latter in the presence of NaBH₄ gave rise to the generation of gold nanoparticles (AuNPs) that were immobilized at the monolithic pore surface. The efficiency of this hybrid material based on AuNPs@porous monolith as a heterogeneous supported catalyst was further demonstrated through the reduction of a relatively toxic dye commonly used in textile and dye industries, *i.e.* Eosin Y. Notably, no loss of catalytic activity was observed by using this hybrid supported catalyst after 6 consecutive runs.

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1. Introduction

In this era of great efforts towards the development of more and more eco-friendly processes, heterogeneous supported catalysis appears as an appealing field of research due to actual ever-growing environmental concerns/requirements [1,2]. Among this field, nanometal-based catalysis has gained a tremendous interest, as supported nanometals present unique properties compared to their bulk material counterparts that make them advantageous in different applications. In the broad area of catalysis, gold nanoparticles are probably the most commonly used nanometals [3–11]. During the last decade, not only gold [12–14] but also palladium- [15], silver- [16], platinum- [17], and copper-based nanoparticles [18] have been applied to heterogeneous catalysis, even though they were considered a few years ago as chemically inert [19]. Different model catalytic reactions have been so far developed with such nanometal-based systems, including (di)nitroarene

[11,12,20,21], hexacyanoferrate [10] or dye reduction [4,5], and even more interesting Suzuki-Miyaura C-C cross-coupling reactions [6] or cascade reactions [22]. However, inherent properties of immobilized gold nanoparticles do not restrict them only to the catalysis area but can also have interesting applications in diverse research fields, such as chromatographic supports [23–29], antibacterial systems [30], drug delivery devices [31], sensors [32,33] and photovoltaics [34], supported biocatalysts [35] as well as Surface Enhanced Raman Spectroscopy (SERS) [36].

Thiol functions are prone to chelate gold and are generally used to anchor them in a covalent-like manner [24]. Unfortunately, thiols are also well-known to easily produce corresponding disulfide bridges under mild oxidizing conditions, such as under O₂ atmosphere, thus presenting a serious limitation to their use. However, disulfide moieties (-S-S-) can be selectively cleaved by using appropriate chemical reducing agents, such as phosphine derivatives [12,37] or dithiothreitol (DTT) [38], to cite but a few, thus being considered as protected thiols. Recently, polymeric materials bearing such disulfide bridges have largely been used in diverse applications [18,39,40], mainly because of the straightforward introduction of such chemical functions within the backbone or the

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pendant chains of the macromolecules, but also because of the subsequent readily selective cleavage of the -S-S- bond. In this regard, different studies have demonstrated that the reversible character of this chemical junction confers very interesting stimuli-responsive properties to the corresponding materials. Matyjaszewski and Gao research groups notably prepared independently atom transfer radical polymerization (ATRP) initiators from 2-hydroxyethyl disulfide (also called as bishydroxyethyl disulfide) precursor [41–43]. Such initiators were used to prepare block copolymers that could be further cleaved by selective reduction of the disulfide junction, thus allowing for the production of thiol-functionalized (co)polymers. More recently, Engler *et al.* [39] and Xu *et al.* [40] combined disulfide and carbonate chemistry to produce “smart” stimuli-responsive drug delivery devices. In a similar manner, Lu *et al.* [44] suggested a strategy for synthesizing materials for drug delivery purposes using disulfide and urethane chemistry. Finally, other interesting studies also investigated the properties of disulfide-containing polymer-based systems [45–48]. Recently, some of us also took advantage of the redox-responsive character of this chemical moiety to produce thiol-functionalized nanoporous materials through the selective triphenyl phosphine-mediated chemical reduction of a disulfide bridge positioned at the junction between both blocks of newly synthesized polystyrene-*block*-poly(D,L-lactide) copolymer precursors [12]. The subsequent immobilization of *in-situ* formed gold nanoparticles permitted the preparation of hybrid supported catalysts with high efficiency towards nitroarene reduction, even after 5 successive catalytic cycles. These few examples highlight the potential of disulfide-based chemicals to produce redox-responsive polymeric systems with unique and tunable properties.

Herein, we report on the development of original monolithic supports relying on the implementation of a cleavable disulfide-based dimethacrylate. Such porous materials can undergo selective and facile disulfide bridge reduction in the presence of DTT to afford thiol-functionalized porous monoliths. Further, the presence of thiols at the pore surface allowed for the immobilization of gold nanoparticles (AuNPs) through the so-called *in-situ* strategy involving the adsorption of Au³⁺ ions at the pore surface and the subsequent hydride-mediated reduction of the metallic cations. Such novel functional monoliths were fully characterized by means of several techniques, including mercury intrusion porosimetry, Raman spectroscopy, TGA, SEM, and EDX spectroscopy. More interestingly, advantage of the presence of immobilized AuNPs within the hybrid monoliths was taken to successfully achieve the supported catalytic reduction of Eosin Y as a model reaction. Indeed, dyes commonly used in textile and dye industry are well-known pollutants of waste water of such industrial sectors. Reduction of some of these dyes using supported or suspended gold nanoparticles may constitute a suitable pathway to transform such toxic species into more eco-friendly products. This was notably demonstrated in the case of different dyes, such as Methylene Blue [49], Safranin T [50], Congo Red [50], and Eosin Y [4,49–52].

2. Experimental

2.1. Materials

2-Hydroxyethyl disulfide (technical grade), ethylene glycol dimethacrylate (EGDMA, 98%), methacryloyl chloride (97%), Eosin Y (EY, ≈99%), D,L-dithiothreitol (DTT, ≥98%), and sodium borohydride (NaBH₄, ≥99%) were obtained from Sigma-Aldrich. Triethylamine (TEA, 99%) and hydrogen tetrachloroaurate (III) hydrate (HAuCl₄, 99.9%) were purchased from Alfa Aesar. Toluene (HPLC grade), dichloromethane (DCM, synthesis grade), tetrahydrofuran (THF, HPLC grade), *n*-hexane (Pure), and ethyl acetate (EtOAc, analysis

grade) were supplied by Carlo Erba. All reagents were used without further purification, except for 2,2'-azobisisobutyronitrile (AIBN, Acros Organics) that was recrystallized from methanol prior to use. 18.2 MΩ deionized water was filtered through a Milli-Q Plus purification pack.

2.2. Synthesis of disulfide-based dimethacrylate

2-Hydroxyethyl disulfide (3.085 g, 20 mmol, 1 equiv.), triethylamine (8.4 mL, 60 mmol, 3 equiv.) were added to 20 mL of THF in a round-bottom flask immersed in an ice/water bath. Methacryloyl chloride (5.86 mL, 60 mmol, 3 equiv.) was added dropwise to the reaction mixture via a dropping funnel. The reaction was stirred at 0 °C for 1 h, and then it was allowed to warm to room temperature overnight. The resulting heterogeneous solution was supplemented with 80 mL of dichloromethane and filtered off to remove triethylammonium salts. The organic phase was washed with 10 mL of a 0.1 M HCl solution, then with 10 mL of a 0.1 M NaOH solution, and with 10 mL of a saturated NH₄Cl solution. This organic phase was finally dried over MgSO₄, filtered, and evaporated, while immersed in an ice bath, and then dried under vacuum overnight. The product was purified over a silica gel chromatography column eluting with a 9/1 (v/v) solvent mixture of *n*-hexane/ethyl acetate. The pure disulfide-based dimethacrylate (DSDMA) was obtained in 73% yield as a yellowish viscous oil. It was stored at -18 °C with some traces of benzophenone as a free-radical inhibitor, as the dimethacrylate may be prone to easily polymerize. ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 6.12 (s, 2H, H-C=C), 5.58 (d, 2H, H-C=C), 4.40 (t, 4H, -O-CH₂-), 2.97 (t, 4H, -CH₂-CH₂-S-S-), 1.94 (s, 6H, H₃C-). ¹³C NMR (CDCl₃, 400 MHz) δ (ppm): 167.25 (s, 2C, C=O), 136.11 (s, 2C, CH₃-C=C), 126.16 (s, 2C, -C=C-H), 62.60 (s, 2C, -O-CH₂-), 37.36 (s, 2C, -CH₂-CH₂-S-S-), 18.41 (s, 2C, CH₃-).

2.3. Synthesis of macroporous disulfide-bearing monolith

The porous monolith was prepared through a free-radical copolymerization reaction of a mixture consisting of the following typical composition: DSDMA as a functional labile crosslinking monomer (0.632 g, 48 mol.%), EGDMA as a permanent crosslinker (0.464 g, 52 mol.%), toluene as a porogenic solvent (2.4 mL, 70 vol% with respect to the total comonomer amount), and AIBN as a thermal free-radical initiator (1 wt% with respect of the total amount of monomers). The mixture was sonicated for about 15 min to obtain a homogeneous solution. The mixture was transferred into a glass vial, carefully sealed, and heated during 24 h at 70 °C in order to perform the thermally-induced free-radical copolymerization. The resulting material was subjected to a Soxhlet extraction with dichloromethane as the extracting solvent for 24 h and finally dried under vacuum. Mercury intrusion porosimetry was performed to determine the pore size distribution of the porous monolith.

2.4. Selective cleavage of disulfide bridges

200 mg of the synthesized monolith were immersed in 6 mL of a 5 mM phosphate buffer solution (pH = 8) containing 128 mg of DTT during 4 days at 47 °C. *In situ* Raman spectroscopy was used to determine the efficiency of the disulfide bridge cleavage. TGA and SEM were realized before and after cleavage of the accessible disulfide bridges of the DSDMA-based monolith.

2.5. In-situ generation of gold nanoparticles within macroporous monolith

200 mg of the newly prepared thiol-functionalized monolith

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