



# Incorporation and distribution of noble metal atoms in polyacrylonitrile colloidal particles using different polymerization strategies



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## ABSTRACT

This work is focused on the incorporation of inorganic compounds into an organic framework. More precisely, noble metals are being incorporated *in-situ* in polyacrylonitrile colloidal particles (CPs) using, scalable and reproducible synthesis routes. For this purpose, oil-soluble platinum- and palladium-based precursors are used for physical entrapment based on mini-emulsion polymerization, while water soluble precursors of the same metals are used for the incorporation via chemical entrapment based on conventional emulsion polymerization. For the latter, it is shown that one can well alter the spatial distribution of the metal within the CPs by tuning the feeding strategy of the precursor. In addition, chemical entrapment requires the complexation of the metal with acrylonitrile, thus resulting in the incorporation of single atoms and dimers, as suggested by both X-ray absorption spectroscopy and indirectly by NMR-titration. The visualization of the extent of incorporation was performed by STEM-EDX on all synthesized CPs, while ICP-OES was applied for a quantitative evaluation.

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## 1. Introduction

Embedding valuable inorganic compounds, mainly metals or metal oxides, into a matrix has been intensively researched because modified and specific properties can be obtained in this way. These new functional materials are generally called doped materials or nanocomposites and exhibit a broad palette of possible combinations for various applications, such as biomass conversion [1], antibacterial purposes [2], cancer treatment [3,4], optical and electrical properties [5] and tissue engineering [6].

Conventionally, metals or metal oxides are incorporated in silica, zeolites or metal organic frameworks (MOFs) for increasing the activity in catalytic applications or gas adsorption/storage purposes. In the case of zeolite, for example ZSM-5 was doped with precious metals (Ag, Cu, Ni, Pd, Ir and Ru) to successfully enhance the activity and selectivity of methanol conversion to hydrocarbons [7] while conventional Y-zeolite was ion-exchanged with TiO<sub>2</sub> as

photocatalyst for the reduction of CO<sub>2</sub> [8]. Intensive research has been carried out on the use of zeolites as sorbent or catalyst and, even though large-scale implementations exist, the need of cheaper materials with better mechanical and chemical resistances persists [9]. As for the MOFs, high H<sub>2</sub>-storage was achieved by doping MOFs with Li<sup>+</sup> cations and replacing Me<sub>2</sub>NH<sub>2</sub><sup>+</sup> from the framework [10]. More recent studies show the incorporation of gold-coated Pd nanoparticles and doxorubicin (chemotherapy medication) inside an acid degradable ZIF-8 MOF for chemophotothermal treatment of cancer cells [3]. However, MOFs suffer from lack of thermal stability and exhibit high sensitivity towards water vapor and impurities [11]. Moreover, the use of expensive and toxic solvents for their synthesis hinders their large scale applicability [12].

Besides the supports mentioned above, carbon-based materials represent a good alternative as matrices for metal incorporation. More specifically, polymers are becoming key for developing such composite materials due to their low cost, ease of synthesis and interesting properties such as viscoelasticity or versatility in composition. [13,14] In fact, thanks to the many available monomers, the choice of possible polymers is vast, and the same applies

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for the resulting nanocomposites. Additionally, the use of polymer can simplify (in terms of costs and scalability) the ability to pattern metallic nanoparticles by an in-situ cation reduction approach [15,16]. Those polymeric matrices find also applications in bioengineering, e.g. by embedding healing agents inside core-shell polymer microbeads, which could generate a very efficient and injectable self-healing material [17]. There are also other forms of nanocomposites with polymeric matrix, for example vesicles with controllable size made from block copolymers (poly (acrylic acid)-*b*-poly (styrene)) are also used to incorporate Ag nanoparticles for catalytic purpose [18]. More importantly, in order to achieve major improvements in optic or electrical properties, the size and spatial distribution of the inorganic compound inside the polymer support have to be carefully controlled [19]. In fact, even though the incorporation of microscale (10–100 nm) inorganic entities in bulk polymers (films, membrane, etc.) is already well explored [20–23], the incorporation of metallic nanoparticles inside polymer particles (with homogeneous or heterogeneous internal dispersion) is still being investigated [24–26]. Such dispersed materials are of interest in different cases, such as tracers for enhanced detection signal (optical sensing or detection in biological systems) or catalysis by impregnating cobalt on polyacrylonitrile particles [27,28]. Compared to single-component materials such as quantum dots (QDs), dyes or metallic nanoparticles, hybrid latex particles (i.e. inorganic nanoparticles dispersed inside colloidal polymer particles) overcome many disadvantages such as cytotoxicity resulting from metal ions leaching and colloidal stability issues (less aggregation than QDs in aqueous media) [29,30].

Incorporating nano-scaled inorganic entities, usually below 10 nm, in polymer colloids has gained an increased interest since this permits very remarkable improvements of the material properties, from thermal to mechanical [31–33] to the catalytic activity [34–36]. For example, the thermal resistance of coating was increased by embedding nanosilica particles of 7 nm in 150 nm copolymer particles made from methyl methacrylate, acrylic acid and butyl acrylate via batch emulsion polymerization [33]. Closer to this work, a hierarchical conductive polymer with enhanced properties was synthesized by incorporating homogeneously distributed 10 nm TiO<sub>2</sub> nanoparticles within poly-(styrene-divinylbenzene-acrylonitrile) spheres [5]. The importance of the support was highlighted when incorporating well dispersed and stable 4–5 nm Pd nanoparticles inside mesoporous N-doped carbon made from the carbonization of melamine and glucose (with ZnCl<sub>2</sub> as porogen agent) [37]. These authors report that N-doping is improving the immobilization and dispersion of Pd nanoparticles even after using the catalyst for a hydrogenation reaction. Based on the success of embedding nanoscale inorganic materials, efforts were made to introduce single atoms within the structure. Impregnating Pd on graphitic C<sub>3</sub>N<sub>4</sub> led to mostly single metallic sites and showed increase in selectivity (nearly 100% below 363 K and 2 bar) and activity towards semi-hydrogenation reactions [38]. However, the synthesis of graphitic carbon nitride requires condensation at high temperature with release of ammonia and suffers a low yield and surface defects [39].

Nevertheless, even though those aforementioned syntheses are promising in several fields, most of them stay complex (pre-treatment of inorganic entities or many synthetic steps [22,37,40]) and expensive (use of organic solvents and other reagents [36,41]) and result in low stability and efficiency, which is far from industrial needs [42,43]. Moreover, since the price of these metal-precursors is usually much higher than that of the support itself, the incorporation and spatial distribution need to be carefully designed, understood and assessed to avoid any waste. Accordingly, the full control of the distribution of these compounds within the support is necessary.

The most popular synthetic procedure for such hybrid materials is the so-called mini-emulsion polymerization [44–46]. In this process droplets containing monomer and inorganic entities are formed and the subsequent polymerization traps physically the inorganic nanoparticles inside the polymer particles. For example, the incorporation of 20–30 nm ceria nanoparticles inside polyacrylic particles was successfully performed with an approximate 1:1 relationship (1 CeO<sub>2</sub> nanoparticle in 1 polymer particle) via seeded mini-emulsion [47]. Since the scalability of mini-emulsion is non trivial given the high shear required in the droplet formation step, different synthetic routes are desirable, especially in view of large scale industrialization.

To address all these challenges (stability, simplicity of synthesis, costs etc.), colloidal particles (CPs) of polyacrylonitrile (PAN), a nitrogen-containing polymer, dispersed in water has been prepared by emulsion and mini-emulsion polymerization with incorporation of palladium and platinum precursors during the CP formation. Moreover, besides the presence of nitrogen as immobilization agent [37], PAN was also used as precursor to produce highly microporous material via pyrolysis [48]. Creating such porosity in an immobilized noble-metal containing CPs could be of tremendous advantage for catalysis purposes. This work reports the results of several synthetic techniques achieving different spatial distributions of atomic- or nanoscale Pt and Pd inside the PAN CPs. Such different spatial distributions and the strong embedding of the inorganic entities inside the polymer matrix enable the preparation of materials with promising properties for applications in catalysis or nanoplastic tracing (via metallic fingerprint) in the environment, e.g. in waste-water treatment plant and in agricultural soil.

## 2. Materials & methods

### 2.1. Materials

Acrylonitrile (Aldrich chemistry  $\geq 99.0\%$ ), abbreviated AN, was employed as monomer. Oil soluble 2,2' Azobis (2-methylbutyronitrile), V67, and water-soluble potassium persulfate (KPS) from Merck (ACS, Reag. Ph. Eur) were employed as initiators. The initiator V67 was employed for mini-emulsion polymerization based on the recipe of Yang et al., (2015) [49]. Potassium poly (ethylene glycol) 4-nonylphenyl 3-sulfopropylether (KPE) and sodium dodecyl sulfate (SDS) were used as surfactants. Hexadecane from Sigma Aldrich (99% purity, Sigma Aldrich) was used as co-stabilizer in mini-emulsion. The oil-soluble metal-precursors used for the mini-emulsion incorporation were platinum (II) acetylacetonate (Pt(acac)<sub>2</sub>) and palladium (II) acetylacetonate (Pd(acac)<sub>2</sub>) both from Sigma Aldrich. Water-soluble precursors, K<sub>2</sub>PdCl<sub>4</sub> and K<sub>2</sub>PtCl<sub>4</sub>, purchased from ABCR (99%) and Aldrich (98%), respectively, were used for emulsion polymerization. Deionized water was the reaction medium for all types of polymerization and was stripped with N<sub>2</sub> (g) prior to the start of the polymerization. All materials were used without further purification.

### 2.2. Synthesis of different latexes with incorporated noble metals

Two polymerization procedures were employed, namely, mini-emulsion (ME) and conventional emulsion polymerization.

Mini-emulsion is an oil-in-water type of emulsion and results in a physical entrapment of the inorganic molecules in the polymeric surrounding [49]. The experimental procedure involves high-shear treatment (usually by sonication) of a two-phase system comprising an aqueous phase, containing surfactants, and an oil-phase, containing the monomer, a co-stabilizer, an oil-soluble initiator and the metal precursor. The droplets originated from the latter phase entrap the metal-precursor, and the following

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