Materials Research Bulletin 60 (2014) 498–506

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Synthesis and characterization of noble metal nanoparticles-oxidized carbonate green rust nanohybrids

Sondra Ayadi, Ludovic Legrand *

Laboratoire Analyse et Modélisation pour la Biologie et l'Environnement, LAMBE UMR8587, CNRS – CEA – Université Evry rue du Père Jarlan, 91025 EVRY Cedex, France

ARTICLE INFO

Article history:
Received 29 April 2014
Received in revised form 25 August 2014
Accepted 4 September 2014
Available online 6 September 2014

Keywords:
Supported nanoparticles
Metal-inorganic nanohybrids
Carbonate green rust
Noble-metals
Solid-state oxidation

ABSTRACT

In this study, we report new metal-inorganic nanohybrids constituted of Au, Ag or Pt nanoparticles supported on oxidized carbonate green rust particles. These nanohybrids are obtained from two successive steps in "one pot", synthesis of a carbonate green rust suspension followed by its redox reaction with noble-metal soluble precursor. In this process, carbonate green rust, a health- and environment-friendly compound, is used as both the reducing agent and the support for metal nanoparticles. The obtained nanohybrids are characterized by FTIR, XRD and SEM. They display an inorganic part that keeps the platy shape characteristic of green rust and about 1–10 metal nanoparticles of several tens of nanometers in diameter are present on both faces. By annealing at 250 °C, metal-haematite nanohybrids keeping similar morphology were obtained.

1. Introduction

Metal nanoparticles have a strong scientific and technological potential. In particular, noble metal nanoparticles (Au, Ag, Pt . . .) arouse a lot of interest for their multiple physical and chemical proprieties; no wonder they are the target of several researches in various fields including therapy [1], biology [2], analytical chemistry [3], photocatalysis [4]. There are several ways to synthesize such nanoparticles but the most common method is still by "wet chemistry". Basically, it consists in reducing a soluble metal precursor (Au^{III}, Ag^{I} or Pt^{IV}) by a soluble reducing agent in presence of a stabilizing species which keeps the formed nanoparticles from aggregation. Turkevich–Frens's method uses $AuCl_4^-$ ions and sodium citrate as both reducer and stabilizing agent and gives ~20 nm spherical nanoparticles [5,6]. With others stabilizing agents, the shape can be tuned [7,8]. In Brust's synthesis, atwo-phases aqueous–organic medium with tetraoctylammonium bromide transfer species and a strong stabilizing thiol agent are implemented and the reaction of $AuCl_4^-$ and $NaBH_4$ in these conditions allows the preparation of stable 1–5 nm Au clusters [9]. Regarding silver and platinum nanoparticles, the most common synthesis involve the reduction of Ag^{I} or Pt^{IV} soluble species by chemical reducing agents such as borohydride [10], citrate [11,12], hydrazine [13,14] or ascorbic acid [15,16]. From the polyol process displaying ethylene glycol as both reductant and solvent, various metal nanoparticules including Pt, Au and Ag could be obtained [13]. All methods cited previously may use hazardous products and cause biocompatibility or environmental problems. The "green synthesis" was therefore enhanced recently, for which environment-friendly reducing agents are used, including saccharides [17], natural extracts [18], starch [19] or even vitamins [20].

Supported metal nanoparticles can be formed following various protocols such as electrochemical reduction [21], wetness impregnation [22], alkaline (co-) precipitation [23]. The first route requires a conducting substrate, mostly graphite or carbon; the two latter ones use an inorganic solid as a support and are followed by several steps: drying, calcination and gas reduction treatment by H_2 or CO. To increase the loading in noble metal while keeping nanometric size of supported particles, an alternative route named as liquid-phase reductive deposition was recently reported [24]. It is based on the adsorption at equilibrium of noble-metal hydroxo-complex onto oxides or oxi-hydroxides solid supports and the partial conversion as a result of reduction reaction by surface OH^- ions. Despite the formation of very low size nanoparticles in any case, only Au metal could be obtained with conversion yield values from 8.5% with α-Fe_2O_3 platelets to 99% with large specific surface area ZrO_2 spheres.

Solids containing Fe^{II} ions are "green" reducing species. As the oxidation of structural Fe^{II} ions usually occurs in a very cathodic potential domain, electrons can be transferred to numerous oxidants. Indeed, the reduction of Ag^{I} and Au^{III} soluble species by iron sulfide minerals (pyrite, arsenopyrite, pyrrohotite) has

* Corresponding author. Tel.: +33 169477705.
E-mail address: ludovic.legrand@univ-evry.fr (L. Legrand).

http://dx.doi.org/10.1016/j.materresbull.2014.09.008
0025-5408/

been studied extensively [25–30]. This phenomenon is of great importance in the formation of "invisible" and native gold and silver deposits in aqueous environments. Nevertheless, the samples used for laboratory experiments until now are minerals coming from natural environments and their large dimensions are a big drawback for most of potential applications.

Therefore, we turned to other inorganic compounds called green rusts which are easy to synthesize and are more interesting in terms of shape and size. Green rusts (abbreviated GR) are layered Fe^{II}–Fe^{III} hydroxysalts belonging to the general class of layered double hydroxide (LDH); they are composed of positively charged $Fe(OH)_6$ octahedra sheets alternating with interlayers filled with charge-compensating anions and water molecules [31]. Carbonate (GRc) and sulphate (GRs) are the most-studied green rusts and the most common forms occurring in steel corrosion [32,33]. Early studies on the reduction of Ag^{I}, Au^{III} and Pt^{IV} by green rusts were reported in 2003, from Heasman et al. [34] and from O'Loughlin et al. [35]. The formation of Au, Ag and Pt metallic particles, as individual or composite nano-clusters, was evidenced by X-ray absorption spectroscopy and TEM microscopy. The fact that Ag^{I}, Au^{III} and Pt^{IV} species can be partially or entirely reduced by green rust made the authors state that such reactions might occur at the surface of these compounds in suboxic environments. Later, these green rusts modified with low metal loads (Ag, Cu, Au or Pt) were used as reducing compounds for the removal of pollutants as halogenated ethanes [36], carbon tetrachloride [37], tetrachloroethylene [38], and nitrate ions [39]. It was shown that added metal fractions provide an efficient catalytic effect for these remediation reactions. Surprisingly, the reaction mechanisms between green rust and soluble metal precursor were not discussed. Some studies have provided evidence of the formation of zero charge metal, especially by X-ray absorption spectroscopy, but details on the formed metal nanoparticles are rather scarce. As the purpose of those studies was the remediation of pollutants by exploiting the reductive capacity of green rusts rather than the synthesis of materials, the preparation of solids was done with very low quantity of soluble metal precursor, and therefore with low metal loads.

The oxidation mechanisms of green rusts have been extensively studied. This reaction can imply transformations via solution, i.e. dissolution, oxidation and precipitation of the resulting ferric solids, lepidocrocite and goethite [40,41]. Otherwise, a solid-state oxidation of green rusts involving both the conversion of Fe^{II} to Fe^{III} inside the crystal lattice and the charge-compensating loss of protons is also possible [42–44]. The resulting ferric products, named as "exGR(Fe^{III})" or as "ferric green rust" or very recently as Mössbauerite [45], keep the same apparent morphology as the initial green rusts but local disorders at nanometric scale are induced, leading to the loss or the large decrease of (0 0 l) lines in diffraction.

In a recent communication [46], we introduced the principle of a new one-pot synthesis of metal-inorganic nanohybrids for which a green rust reactive particle is used as a micro-reactor ensuring the role of both the reducing agent and the solid support for the resulting metal nanoparticles. In the present paper, we focused on carbonate green rust. The synthesis of green rust suspension and the reaction with soluble metal precursors were operated in the same solution and were monitored by potential measurements. Here, we provide a fuller description of the mechanisms and of the obtained nanohybrids, through FTIR spectrometry, X-ray diffraction, scanning electron microscopy and mass measurements. We show that Pt nanohybrids can also be obtained by this method. We present a size study of Au and Pt nanoparticles, on the basis of the reaction scheme that we previously reported, with or without considering a transfer of electrons between green rust particles during the reaction with soluble metallic species.

2. Materials and methods

2.1. Chemicals

Sodium bicarbonate $NaHCO_3$, iron chloride $FeCl_2{,}4H_20$ (>99%), iron sulfate $FeSO_4{,}10H_2O$ (>99%), potassium tetrachloroaurate $KAuCl_4$ (98%), silver nitrate $AgNO_3$ (>99%), hexachloroplatinic acid H_2PtCl_6 (>99.9%), ammonia NH_3(aq) (33%), sodium hydroxide NaOH (10 M solution) were purchased from Sigma–Aldrich. The solutions were prepared with 18 MΩ cm nanopure water.

2.2. Carbonate green rust synthesis

Suspensions of carbonate green rust were obtained from the aerial oxidation of Fe^{II} suspensions at 25 °C according to the following procedure: 50 ml of 0.4 M $NaHCO_3$ solution are introduced into a cylindrical glass cell (about 50 mm diameter) and stirred (300 rpm). The solution is purged with argon for at least 15 min and then, 10 M NaOH solution is added dropwise until pH reaches a value of 9.5. Then, 0.5 ml of 1 M $FeCl_2$ solution is introduced into the solution, the pH is re-adjusted to 9.5 and the cell is opened to air in the same time. The synthesis is monitored by recording the evolution of potential with time, using a platinum working electrode (Radiometer Tacussel) and a home-made AgCl/Ag reference electrode. The latter electrode was previously calibrated with a 0.4 M $NaHCO_3$ solution at pH 9.5 containing quinhydrone and the reference potential was found to be 0.23 V_{SHE}. Thereafter, all potentials are expressed with respect to the standard hydrogen electrode (V_{SHE}).

2.3. Reaction with noble-metals precursors

Due to the presence of ferrous ions within their lattice, the green rusts have strong reductive properties and can reduce a lot of species including metallic ions. We have done the reaction of the carbonate green rust (GRc) with Au^{III}, Pt^{IV} or Ag^{I} ions, which were prepared from gold chloride, platinum chloride and silver nitrate/ammonia solutions, respectively. Table 1 summarizes the metallic salt solutions and the volume and molar ratio values. The samples are synthesized in "one pot" from two successive steps: the first one is the synthesis of carbonate green rust suspension; the second step (the reaction of GRc with the metallic ions) is initiated by bubbling the solution with argon and adding a precise volume of the considered metallic salt solution once the potential is nearby [−0.4 V, −0.3 V]. The pH remains almost stable at 9.5 during the whole synthesis time.

2.4. Characterization

The resulting metal-inorganic nanohybrids are filtrated, rinsed with 18 MΩ nano-pure water and then left in contact with air at ambient temperature. After about 24 h of drying, the samples can be weighed and analyzed. X-ray diffraction measurements were carried out using a BRUKER D8 diffractometer with Cu Kα radiation (1.5406 Å). Scanning electron microscopy examinations were performed by a LEO 1530 (Carl ZEISS AG) microscope using in-lens or backscattered electron modes. FTIR data were recorded

Table 1
Metallic salt solutions and *R* ratio values.

Ion	Solution	Volume (mL)	Molar ratio
Au^{III}	$KAuCl_4$ (0.05 M)	0.110–4.445	$R_{Au} = \frac{3n(Au^{III})}{n(Fe^{II})}$; 0.05– 2
Pt^{IV}	H_2PtCl_6 (0.025 M)	0.166–6.666	$R_{Pt} = \frac{4n(Pt^{IV})}{n(Fe^{II})}$; 0.05–2
Ag^{I}	$Ag(NH_3)_2^{+}$(0.1 M) + NH_3 (0.6 M)	0.166–6.666	$R_{Ag} = \frac{n(Ag^{I})}{n(Fe^{II})}$; 0.05–2