Materials Science and Engineering B 205 (2016) 28–35

Contents lists available at ScienceDirect

Materials Science and Engineering B

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

Facile radiolytic synthesis of ruthenium nanoparticles on graphene oxide and carbon nanotubes

J.V. Rojas[a,*], M. Toro-Gonzalez[a], M.C. Molina-Higgins[a], C.E. Castano[b]

[a] Mechanical and Nuclear Engineering Department, Virginia Commonwealth University, 401 West Main Street, Richmond, Virginia, 23284, USA
[b] Nanomaterials Core Characterization Facility, Chemical and Life Science Engineering Department, Virginia Commonwealth University, 601 West Main Street, Richmond, Virginia, 23284, USA

ARTICLE INFO

Article history:
Received 27 September 2015
Received in revised form 4 December 2015
Accepted 15 December 2015
Available online 24 December 2015

Keywords:
Carbon nanotubes
Graphene oxide
Nanoparticles
Ruthenium
Radiation chemistry
Radiolysis
Gamma irradiation

ABSTRACT

Ruthenium nanoparticles on pristine (MWCNT) and functionalized carbon nanotubes (f-MWCNT), and graphene oxide have been prepared through a facile, single step radiolytic method at room temperature, and ambient pressure. This synthesis process relies on the interaction of high energy gamma rays from a ^{60}Co source with the water in the aqueous solutions containing the Ru precursor, leading to the generation of highly reducing species that further reduce the Ru metal ions to zero valence state. Transmission electron microscopy and X-Ray diffraction revealed that the nanoparticles were homogeneously distributed on the surface of the supports with an average size of ~2.5 nm. X-ray Photoelectron spectroscopy analysis showed that the interaction of the Ru nanoparticles with the supports occurred through oxygenated functionalities, creating metal-oxygen bonds. This method demonstrates to be a simple and clean approach to produce well dispersed nanoparticles on the aforementioned supports without the need of any hazardous chemical.

1. Introduction

The synthesis of supported metal nanoparticles is of significant importance for various applications in nanotechnology [1]. Interestingly enough, this area of research is approached from two complementary points of view. First, the need to synthesize nanoparticles with a homogeneous size and shape. Nanoparticles tend to aggregate due to their high surface area, causing deleterious effects in their physical and chemical properties, directly impacting their overall performance. Therefore, the use of organic and inorganic supports has been implemented during the nanoparticle synthesis to control the growth and hinder the formation of nanoparticle aggregates. The second point of view resides in the potential to enhance the properties of certain materials by adding metallic nanoparticles on their surface, that may result in a synergistic effect between the support and the metallic nanoparticles [2]. In this context, various types of supports such as polymers, carbon based materials, and oxides have been reported in the literature. The use of supports such as carbon nanotubes and, most recently, graphene oxide have stimulated their interest in catalysis, biosensors, and electronics, among others. These supports offer significant advantages due to their high chemical and thermal stability, high surface area, and outstanding mechanical, physical and chemical properties [2–4]. Furthermore, the surface of the carbon supports can be modified with different functionalities to trigger nanoparticle-support interactions [5,6]. The synthesis of transition metal nanoparticles on carbon nanotubes and graphene oxide has been reported with substantial interest in catalytic applications. Among those, ruthenium nanoparticles on carbon supports have been investigated for hydrogenation reactions [3,7–22]. Ruthenium is a transition metal occurring in the Group VIIIA of the periodic table with an electronic configuration of [Kr](4d)7(5s)1, displaying different oxidation states from −2 to +8 in its compounds. The most common precursor in the chemistry of Ru is the hydrated Ru(III) chloride, $RuCl_3{\cdot}xH_2O$, which is a compound that exhibits in solution a complex mixture of Ru(IV) and Ru(III) species rather than a pure source of Ru(III) [23]. Ruthenium is a very stable metal at low temperatures but usually oxidizes at high temperatures. However, in solid phase it only forms one stable oxide, RuO_2. Other oxide forms such as RuO, RuO_3 and RuO_4 are only stable at temperatures above 900 K, being volatile and toxic [24].

Various approaches have been reported in the literature with regards to the synthesis of Ru nanoparticles on carbon supports.

---

* Corresponding author. Mechanical and Nuclear Engineering Department, Virginia Commonwealth University, 401 West Main Street, Richmond, Virginia 23284-3067301, Tel.: +1 804 8284267; fax: +1 804 8277030.
E-mail addresses: jvrojas@vcu.edu (J.V. Rojas), cecastanolond@vcu.edu (C.E. Castano).

http://dx.doi.org/10.1016/j.mseb.2015.12.005
0921-5107/

Microwave synthesis of Ru on carbon nanotubes (CNTs) [8,25] and graphene [16,17] has been previously achieved at a controlled pressure, temperature, time, and atmosphere, leading to Ru nanoparticle with sizes of 2–4 nm. Another method for the production Ru nanoparticles on CNTs is through the reduction of ruthenium salt in polyol at temperatures above 100 °C, this method resulted in ~5 nm Ru nanoparticles on the CNTs [14]. Furthermore, the decoration of CNTs with Ru nanoparticles using supercritical water has been reported. In this approach, the particles are synthesized in an autoclave at ~450 °C for about 2 h giving 5 nm Ru nanoparticles on the CNTs [15]. Supercritical water has also been reported to produce Ru on graphene oxide. In this case, the reduction of Ru precursors takes place in a autoclave maintained at a temperature of ~400 °C and a pressure of 23.5 MPa for 2 h under nitrogen atmosphere, producing Ru nanoparticles of ~3 nm [11]. Carbon nanotubes have also been decorated with Ru nanoparticles through the impregnation method. In this approach, the support is initially mixed with the metal precursor and the solvent and homogeneously dispersed through ultrasonication. Then, the samples are stirred and aged for a period of time, followed by drying and reduction with hydrogen flow [9,26].

Besides the various physical and chemical methods to synthesize Ru nanoparticles on carbon supports, alternative synthesis methods that minimize the use of additional reagents, as well as the need for high temperature and pressure, or controlled environment are always sought. This would allow for potential scalability and reproducibility of the nanocomposites. Radiation chemistry has recently made significant contribution to the field of synthesis of nanomaterials and the modification of their properties for specific applications [27]. The interaction of ionizing radiation, such as gamma rays, with aqueous solutions leads to the generation of highly reducing species that can bring metal ions present in the solution down to zero valence state. Furthermore, due to the mechanisms of interaction of gamma rays with matter, the reducing species are homogeneously distributed in the solution. Consequently, the metallic atoms will also be generated homogeneously throughout the solution followed by coalescence and growth [28]. This synthesis method eliminates the need for reducing agents that may sometimes poison the nanomaterial and affect their behavior. Moreover, the synthesis is carried out in aqueous environments which is desirable for certain applications. Nonetheless, it can also be implemented with other solvents such as ammonia or alcohols [29]. Radiation synthesis has previously been used for the synthesis of a wide variety of nanomaterials, such as metallic nanoparticles, core-shell nanostructures, metal oxides, and alloys [28,30–32].

In this work, ruthenium nanoparticles have been synthesized on pristine multi-walled carbon nanotubes, carboxylic acid functionalized carbon nanotubes, and reduced graphene oxide through a radiolytic method using ^{60}Co as the gamma source. The resulting Ru-C support nanostructures were characterized with XRD, TEM, and XPS, to study the morphology of the nanoparticles and their interaction with the support. The effect of the surface modification of the nanotubes on the yield of Ru nanoparticles is evidenced and a mechanism of synthesis and interaction of the particles with the support is presented here. This work evidences the potential use of gamma irradiation as a facile and novel method for the synthesis of well distributed Ru nanoparticles on carbon supports.

2. Materials and methods

2.1. Materials

Multi-walled carbon nanotubes (MWCNTs), functionalized multi-walled carbon nanotubes (f-MWCNTs), graphene oxide (GO), ruthenium (III) chloride hydrate ($RuCl_3{\cdot}xH_2O$), and sodium dodecyl sulfate (SDS; $CH_3(CH_2)_{11}OSO_3Na$) were obtained from Sigma–Aldrich and used without any further purification. Multi-walled Carbon nanotubes were > 98% carbon basis, length within 2.5 and 20 μm and outside diameter within 6 and 13 nm. Functionalized multi-walled carbon nanotubes had an extent of labeling of carboxylic acid of > 8%, an average diameter of 9.5 nm, and average length of 1.5 μm. Deionized water (18 MΩ) obtained from an EMD Millipore Direct-Q^{TM} 3 UV water purification system was used to prepare the solutions along with high purity (99.5%) isopropyl alcohol (C_3H_8O) from ACROS Organic which was used as a radical scavenger.

2.2. Sample preparation

Samples containing the carbon-based support (MWCNTs, f-MWCNTs or GO), ruthenium precursor, and surfactant were prepared by modifying a methodology described in the literature [31,33]. As an initial step, a solution of water and isopropanol (2:1 v/v) was prepared, vortexed and stirred for ~5 min. Subsequently, a solid mixture of $RuCl_3{\cdot}xH_2O$, SDS, and either MWCNTs, f-MWCNT or GO was prepared and stored in a glass vial. Next, 20 ml of water-isopropanol solution was added to the mixtures and sonicated for ~30 min using a probe sonicator to break up the aggregates. This procedure lead to a homogeneous black suspension containing 5 mM $RuCl_3$ (0.1 mmol), 5 mM SDS (0.1 mmol), and 1 mg of MWCNTs, f-MWCNTs, or GO per milliliter of solvent.

2.3. Irradiation procedure

The aqueous solutions prepared by the procedure mentioned above were irradiated with a Cobalt-60 Gammacell 220 Excel (MDS, Nordion) that consists of a cylindrical stainless steel cage containing double sealed source pencils of Co-60. For irradiation purposes, the samples were placed into the chamber through a drawer mechanism and positioned in the outermost location in order to ensure a uniform absorbed dose distribution. The samples were irradiated at a dose rate of ~7 kGy/h (0.7 Mrad/h) until an absorbed dose of 60 kGy was achieved. Then, the suspensions were cleaned to remove any excess of surfactant and/or unreacted species. For the cleaning process, the samples were initially centrifuged followed by removal of the supernate. Next, the precipitate was redispersed in deionized water and repeated several times. Finally, the samples were dispersed in acetone for further characterization.

2.4. Materials characterization

The morphology, particle size, and particle size distribution of the resulting nanoparticles were studied by transmission electron microscopy (TEM) with a Zeiss Libra 120 Plus operating at 120 kV. For TEM imaging, a drop of the purified nanomaterial was diluted in acetone and sonicated for ~10 min. The samples were prepared by immersing a formvar-carbon coated copper grid into the diluted suspension and allowed to dry at room temperature. Particle size analysis was carried out using the Image J 4.18 v software.

The crystalline structure of the nanoparticles deposited on the carbon supports was investigated through X-ray diffraction (XRD) using a PANalytical X'Pert Pro MPD X-ray diffractometer with a copper anode (Cu Kα, λ = 1.5401 Å). The samples were prepared by depositing drops of the sample dispersion on a silicon wafer and allowing it to dry. This process was repeated until a thick layer was obtained.

X-ray photoelectron spectroscopy (XPS) was carried out using a ThermoFisher Escalab 250 X-ray photoelectron spectrometer with a monochromated aluminum X-ray source. For the analysis, few drops of the sample were deposited on a silicon wafer and allowed