



Full Length Article

Au@TiO₂ nanocomposites synthesized by X-ray radiolysis as potential radiosensitizers



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ABSTRACT

Gold nanoparticles decorated onto titania (anatase) supports were produced through X-ray radiolysis, at ambient temperature and pressure in a method that departs from traditional routes, providing an outstanding control of Au nanoparticle size and dispersion. Au@TiO₂ nanocomposites (NCs) were fabricated using different absorbed doses in the presence of NaOH, or urea, supported by 5–10 or 10–30 nm titania, to determine their effects on the Au particle size distribution and loading. Au@TiO₂ NCs fabricated at high absorbed doses (>7 kGy) had average Au NP size of 1.1 ± 0.1 nm. Large absorbed doses control Au NP size by generating an abundance of reducing species (e^-_{aq} , $H\bullet$) resulting in an increase of Au seeds. At a lower absorbed dose (0.72 kGy), the ligand affected the Au particle size distribution and a reduction in size by 20% of the Au was observed using NaOH. Au NPs were tethered to titania through oxygen as indicated by X-ray photoelectron spectroscopy analysis. The Au@TiO₂ NCs were tested for their radiosensitizing effect by monitoring decomposition of methylene blue under X-ray irradiation where the decomposition was increased by a factor of 1.8 after 15 min compared with pristine TiO₂.

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1. Introduction

Nanocomposites (NCs) of metal nanoparticles (NPs) supported on oxides are used in several medical and engineering fields in applications such as targeted radiotherapy, drug delivery, nano-electronics, optics, and catalysis [1–5]. Oxide nanoparticles acting as metal NP supports, whether TiO₂, SiO₂ or Al₂O₃, offer many advantages. One of them is a stabilization of the metal NPs achieved through the presence of the oxide support thus reducing NP aggregation which promotes a high areal density of catalytically active sites [6]. Another practical advantage is the ease of the NC recoverability [7]. Catalytic properties are well-known for several metal NPs@oxide support combinations and they are used in applications such as CO oxidation and hydrogen production [8,9]. Furthermore, specific NCs even offer radiosensitivity enhancement toward nanomedical applications [1,10]. In general, the importance of synthesizing nanocomposites of metal NPs@oxide supports is to achieve, or improve, properties of the individual components [6,7]. Several metal NPs@oxide support combinations have been synthesized to date which include Au@TiO₂, Pt@Al₂O₃, Cu@SiO₂, Ni@ZnO, and Ru@CeO₂ [11–15].

Among the different types of metal/oxide-supported NCs, Au decorated on TiO₂ (anatase) supports (Au@TiO₂) has garnered

attention due to their unique physical and chemical properties useful for biomedical, environmental, and energy applications [16]. Au@TiO₂ NCs have been studied as therapeutic agents in cancer treatment as radiosensitizers and photosensitizers [10,17,18]. For these purposes, the Au@TiO₂ NCs are delivered to the tumor and then activated either with X-rays or UV-light respectively. In aqueous environments, the interaction of highly energetic photons, such as X-rays with TiO₂ generates the emission of reactive oxygen species (ROS) capable of destroying tumor cells [18]. On the other hand, Au generates photoelectrons and Auger electrons, which ionize and destroy cancerous cells with minimal side effects to healthy tissue [19]. The combination of the ROS and the photoelectrons result in a synergism allowing for Au@TiO₂ NCs. The radiosensitization phenomenon correlates with the catalytic properties of Au@TiO₂ NCs, where the generation of electron-hole pairs (carriers) occur when the TiO₂ support absorbs a photon having a higher energy than its band gap (~3.2 eV for anatase). These carriers react with water molecules in the vicinity of the material forming ROS such as hydroxyl radicals (OH•) and superoxide radical ions (O₂•⁻), among others [20]. Deposition of noble metals on the surface of the titania is a strategy often used to modify and reduce the TiO₂ band gap. Specifically, Au decreases the band gap of TiO₂ to half of its initial value, enabling an enhancement of the photocatalytic activity [20].

Traditional methods to synthesize Au@TiO₂ NCs typically involve wet-chemical routes such as hydrothermal, impregnation and deposition-precipitation syntheses. For example, hydrother-

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mal syntheses take advantage of the solubility of metal cations in water at elevated temperature and pressure which often result in monodisperse NPs on supports [21,22]. Furthermore, some wet-chemical routes, such as those based on aqueous chemistry involve an excess of reductants as they rely on the chemical reduction of metal salt precursors in solution [21]. For the impregnation method, the support is added to a solution containing the metal precursor, then the sample is aged, dried and calcined [23]. Deposition-precipitation routes also involve a calcination process to fully reduce the Au ions on the TiO₂ supports. In this method, the metal cations are co-precipitated onto the support and can form hydroxides, carbonates and citrates depending on the type of ligand present (i.e. NaOH or urea) [11]. Subsequently, these precipitates are calcined at high temperatures (~300 °C) for several hours resulting in a dried powder [24,25]. Although wet-chemical routes have been extensively studied [21,26], there are some disadvantages associated with these methods such as slow reaction rates, which lead to secondary nuclei resulting in broad size distribution and lack of size control [27]. Deposition-precipitation methods present the drawback of formation of undesired species, such as metallic oxides, after the calcination process occurs compromising the final chemical properties of the NC [21]. The X-ray radiolytic synthesis used Other methods to synthesize Au@TiO₂ NCs are electro-chemical and sono-chemical syntheses, laser ablation and thermal decomposition routes [28–31].

Current research on nanomanufacturing techniques are directed to methods that potentially lead to a better control over NP size, distribution, and morphology of nanomaterials. Methods that do not require either higher temperature or pressure provide safer and more economical manufacturing processes for nanomaterials [32,33]. Radiolytic synthesis of metallic NPs has become an outstanding synthesis method for producing NPs with improved dispersion onto supports in non-toxic solvents, such as water and IPA, minimizing hazardous waste generation [34–36]. During a radiolytic synthesis of metal NPs, an aqueous solution containing a metallic precursor is exposed to ionizing radiation. This results in generation of hydrated electrons (e⁻_{aq}) and free radicals, such as hydrogen radicals (H•) and hydroxyl radicals (OH•). The reducing and oxidizing species generated during this process act upon the metal ions in the presence of oxidant scavengers (i.e. 2° alcohols) reducing their oxidation states. Subsequently, the reduced metal atoms coalesce and grow into NPs [37,38]. The morphology, size, size distribution, and yield of the nanoparticles strongly depend on the radiation source being used, e.g. heavy ions, protons, electrons, X-rays, or γ -rays [37]. Although radiolysis of water occurs in all cases, the linear energy transfer, LET, plays a role in the amount and spatial distribution of reducing and oxidizing species produced, which affects the nucleation and growth of the nanoparticles. [36,37]. Low LET radiation such as high energy electrons and γ -rays leads to a higher yield of reducing species per unit energy deposited along their path and generate small particles with a narrow particle size distribution (PSD) [37,39–41]. X-rays, a low LET radiation, represent an alternative to γ -rays in radiolytic syntheses [41,42], since γ -ray-based fabrication method have constraints related to safety and restrictions regarding radioactive source licensing [32,43]. X-ray devices are more accessible as they can be found in medical and research centers and the source of radiation is on/off switchable. This allows for greater exploration of X-ray radiolysis to synthesize nanomaterials. Furthermore, X-ray devices can facilitate in-situ characterization during fabrication which enables study of the metal ion reduction, nucleation and growth in real time. As a result, control in the surface chemistry, PSD and NP loading may be attainable. Techniques such as small angle X-ray scattering (SAXS) and UV–vis have been coupled with X-ray radiolytic synthesis to monitor silver NP production [43].

Indeed, Au@TiO₂ NCs have been synthesized using γ -rays, however only fixed conditions of ligand type and absorbed dose were used [44–46]. We report a clean and facile synthesis of Au@TiO₂ NCs using X-ray radiolysis performed at absorbed doses from 0.1–7.3 kGy in order compare the influence of the absorbed dose on the particle size of Au. The presence of the ligand enabled electrostatic interactions between the TiO₂ and Au-complexes in solution controlling the nucleation, growth and binding of Au NPs onto the titania surface [11]. Two titania supports were investigated which contained either a particle size distribution of (PSD) of 5–10 or 10–30 nm. Moreover, Au@TiO₂ NCs were probed for potential as radiosensitizers. For this purpose, the decomposition of methylene blue (MB) under X-ray irradiation in the presence of Au@TiO₂ NCs was determined and compared against pristine TiO₂. Herein, X-ray radiolysis is capable of fabricating Au@TiO₂ NCs in a highly controllable manner which are suitable candidates for several medical and catalytic applications.

2. Experimental procedure

2.1. Materials and reagents

Chloroauric acid (HAuCl₄•3H₂O, $\geq 99.9\%$ trace metal basis), isopropanol (C₃H₈O, $\geq 99.7\%$), urea and sodium hydroxide (NaOH) were obtained from Sigma-Aldrich. Anatase (TiO₂), as nanoparticle supports, with a PSD of 5–10 nm (99.8%) and 10–30 nm (99.0%) both were obtained from Nanostructured and Amorphous Materials Inc. Radiosensitization experiments were carried with methylene blue pure grade, the chemical was obtained from Acros organics. Deionized water (DI) (18 M Ω) was obtained from a Millipore Direct QTM 3 UV purification system and was used to prepare all aqueous solutions.

2.2. Au ion deposition with ligands

2.2.1. Au ion deposition onto TiO₂ in the presence of NaOH

First, using amber glassware, Au precursor stock solution of HAuCl₄ (2 mM) was prepared and the pH was adjusted to 8 with a NaOH solution (1 M). Subsequently, 4 mg of TiO₂ per ml of stock solution, with either a particle size of 5–10 or 10–30 nm, was added and sonicated for 5 min in order to obtain a homogeneous dispersion. After sonication, the pH was re-adjusted to a value of 8 following heating and magnetic stirring for 1 h at 80 °C. The TiO₂ support and Au ion concentrations were chosen to give a 10% nominal loading of Au NPs (by mass) onto the TiO₂ supports.

2.2.2. Au ion deposition onto TiO₂ in the presence of urea

Using amber glassware, urea was added to the Au precursor solution (2 mM) to give 0.42 M. Subsequently, TiO₂ with either a particle size of 5–10 or 10–30 nm was added at 4 mg/ml. Finally, the solution was sonicated for 5 min, followed by heating and magnetic stirring at 80 °C for 4 h. The TiO₂ support and Au ion concentrations were chosen to give a 10% nominal loading of Au NPs (by mass) onto the TiO₂ supports.

The deposition process with either NaOH or urea is important for the formation of incipient bonds between the TiO₂ and Au complexes within the solution. Furthermore, the ligands ensure that the Au NPs will nucleate and grow onto the TiO₂ during the subsequent irradiation process [11]. After the heating process was completed the solutions were centrifuged at 9000 rpm for 10 min, decanted and washed with DI water. This process was repeated three times. It is important to note that the sample preparation was performed in a dark room since the presence of light is known to decompose the gold precursors [11].

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