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Photoreductive generation of amorphous bismuth nanoparticles using polysaccharides – Bismuth–cellulose nanocomposites

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ABSTRACT

A simple and highly reproducible synthesis of amorphous bismuth nanoparticles incorporated into a polysaccharide matrix using a photoreduction process is presented. As precursor for the generation of the Bi nanoparticles, organosoluble triphenylbismuth is used. The precursor is dissolved in toluene and mixed with a hydrophobic organosoluble polysaccharide, namely trimethylsilyl cellulose (TMSC) with high DS_{Si}. The solution is subjected to UV exposure, which induces the homolytic cleavage of the bismuth–carbon bond in $BiPh_3$ resulting in the formation of Bi^0 and phenyl radicals. The aggregation of the Bi atoms can be controlled in the TMSC matrix and yields nanoparticles of around 20 nm size as proven by TEM. The phenyl radicals undergo recombination to form small organic molecules like benzene and biphenyl, which can be removed from the nanocomposite after lyophilization and exposure to high vacuum. Finally, the TMSC matrix is converted to cellulose after exposure to HCl vapors, which remove the trimethylsilyl groups from the TMSC derivative. Although TMSC is converted to cellulose, the formed TMS-OH is not leaving the nanocomposite but reacts instead with surface oxide layer of the Bi nanoparticles to form silylated Bi nanoparticles as proven by TEM/EDX.

1. Introduction

Bulk bismuth features a set of properties, which are highly demanded in many areas of materials sciences. It plays a major role in the design of new semiconductors (large Fermi wavelengths (Smith, Baraff, & Rowell, 1964), strong diamagnetism, very high magneto-resistance) (Murakami, 2006), as well as in medicine, where the rather low human toxicity of several bismuth compounds is exploited to treat different kind of illnesses (Briand & Burford, 1999). A well known example is its action against *Helicobacter pylori*, a bacterium associated with the pathogenesis of gastroduodenal ulcers (Tsang, Ho, Sun, & Chan, 2011). Further applications in medicine include the use of bismuth (and its compounds) as contrast agents owing to its large scattering contrast (Lusic & Grinstaff, 2013; Yu & Watson, 1999). On the other hand, bismuth nanoparticles (BiNPs) have been explored to a much less extent than bulk bismuth. This can be related to difficulties in producing nanoparticles with a defined size and shape. Up to date the most convenient synthesis of BiNPs includes the reduction of organometallic precursors (*e.g.* $Bi(NTMS_2)_3$) which can be stabilized using synthetic polymers (Wang, Tang, Yu, Gibbons, & Buhro, 2008). Through this approach, the size and the shape of the nanoparticles can be efficiently controlled and size dependent electronic properties can be further investigated (Yarema, Kovalenko, Hesser, Talapin, & Heiss, 2011). However, one major drawback of this strategy is the use of synthetic polymers, which limits the applicability of such systems. It would be highly desirable to employ biodegradable and biocompatible polymers such as polysaccharides for this purpose. In addition, the Bi-precursors are not readily available and must be synthesized prior to nanoparticle preparation (Lutz et al., 2012; Reith, Stiftinger, Monkowius, Knoer, & Schoefberger, 2011; Imran et al., 2013). An alternative

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is to use a photoreduction process for the generation of nanoparticles (Warren, Jackson, Cater-Cyker, DiSalvo, & Wiesner, 2007). In the course of photoreduction, photolabile Bi-element bonds are homolytically cleaved (Fischereder et al., 2013) and elemental bismuth is obtained. An excellent precursor for this purpose is triphenyl bismuth, which is cheap, readily available, non-toxic, and, most importantly, which offers photolabile Bi-carbon bonds. Moreover, $BiPh_3$ is highly soluble in several organic solvents such as toluene and exhibits thermal stability in the absence of oxygen (*ca.* 200°) (Berger et al., 2012). The interesting properties of bismuth (nanoparticles) inspired us to incorporate this element in cellulosic matrices. Problems to be addressed involve the photochemical stability of the chosen solvent/polysaccharide and to identify polysaccharide derivatives that feature a similar solubility like $BiPh_3$. In addition, the polysaccharide polarity should be tuneable in terms of hydrophilicity/hydrophobicity in order to enable a variety of applications (*e.g.* in textiles and medicine). An elegant way to achieve such a tuneable hydrophilicity/hydrophobicity is the use of polysaccharides bearing acid or alkaline labile groups. While the removal of acetate groups in organosoluble cellulose acetate requires strong bases for instance, the use of acid labile silyl ethers of polysaccharides can be easily performed with acidic vapors of HCl. In this paper, we present an approach how to tackle these problems by using trimethylsilyl cellulose with high DS_{Si} in the course of a photoreduction process of $BiPh_3$. The solubility of trimethylsilyl cellulose (TMSC) is strongly dependent on the DS_{Si} and ranges from ethanol (DS ~0.7), DMSO (~1.5) to chloroform and toluene (>2.5). Chloroform is not photochemically stable upon UV exposure (forms $Cl^{\bullet}$) therefore toluene seems to be the appropriate choice. In addition, the use of TMSC provides an elegant way to convert a hydrophobic matrix (for high DS_{Si}) into a hydrophilic one. Although other biodegradable and biocompatible polymers could be used for such a purpose as well (*i.e.* by silylation and subsequent desilylation) the use of polysaccharide derivatives provides much more potential applications due the rather high range of molar masses available, the rather good photochemical stability of many polysaccharides at $\lambda > 300$ nm and the compatibility with other biobased materials such as cellulose fibers, films and papers. This compatibility is a crucial point since it allows to coat or impregnate these materials easily. Although we do not investigate enzymatic digestability of the polysaccharide matrix in this paper, it could be relevant for a variety of applications particularly in case free bismuth nanoparticles are desired.

2. Materials and methods

2.1. Materials

Trimethylsilyl cellulose (TMSC) with a DS_{Si} value of 2.55 ($M_w = 175{,}000$, $M_n = 36{,}000$, kindly provided by the Centre of Excellence for Polysaccharide Research, University of Jena) was used for nanoparticle stabilization. Toluene (99.9%) was purchased from Sigma–Aldrich and $BiPh_3$ (95%) was obtained from ABCR, Germany.

2.2. Preparation of monodisperse bismuth nanoparticles

In a typical experiment, a toluene solution containing $BiPh_3$ (5 wt.%) and TMSC (1 wt.%) was irradiated with a HBO lamp 100W/2 under stirring in a sealed quartz glass test tube for 2 h under N_2 atmosphere. The formation of nanoparticles is accompanied with a brownish coloration of the solution. Afterwards, the particles are lyophilized and exposed to vacuum conditions for a period of 3 h at room temperature in order to remove the byproduct biphenyl.

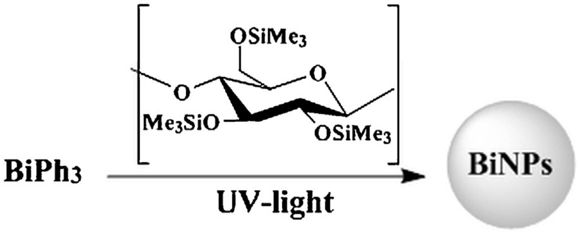

Fig. 1. Schematic overview on photoreduction of $BiPh_3$ using trimethylsilyl cellulose. For reasons of clarity, all hydroxy groups are substituted by silyl groups; the actual DS_{Si} is 2.55.

2.3. Characterization of BiNPs

The studies of size, morphology and composition of the nanoparticles were performed by means of transmission electron microscopy (TEM) and energy dispersive X-ray using a HITACHI HT7700 microscope equipped with a Bruker XFlash 6 EDS detector operated at 120 kV in high contrast mode. The samples for TEM analysis have been prepared by placing small droplets of a diluted (by ~100 × with toluene) dispersions (1 wt.%) on copper grids (300 mesh) coated with an amorphous carbon film (Ted Pella, Redding, CA) and dried at 50 °C in vacuum for 24 h prior to the measurements.

3. Results and discussion

In first trials, the generation of bismuth particles starting from toluene solutions of $BiPh_3$ without stabilizers was investigated. Even after a few minutes of UV exposure, a massive gray precipitate was observed in the solution (data not shown). This indicates a rather fast aggregation of the nanoparticles after formation of elemental bismuth, which is often observed for photoreduction processes. In general, a common strategy to control the growth of nanoparticles is to add polymers, which act as steric stabilizers preventing uncontrolled aggregation of NPs by interaction with the nanoparticle surface. However, there are several constraints on the choice of the polymeric stabilizer. It should be compatible with the solubility of the precursor (*i.e.* toluene), it should exhibit sufficient photochemical stability under the chosen conditions, it should be tunable in terms of hydrophilicity/hydrophobicity while being biodegradable/biocompatible to ensure a wide range of applications. Keeping these facts in mind, a few polymers come into the closer choice such as cellulose acetates (CA) and silylethers of cellulose. These show excellent solubility at high DS in organic solvents such as toluene and can be converted to cellulose by simple procedures (*e.g.* either by aqueous alkali treatment for CA or exposure to HCl vapor for TMSC). The use of an aqueous conversion procedure imposes the risk that the formed nanoparticles are altered by this step; therefore TMSC (Koehler, Liebert, & Heinze, 2008) was chosen as the hydrophobic polysaccharide stabilizer for Bi-NPs in order to demonstrate the proof of principle (Fig. 1)

Moreover, TMSC at high DS_{Si} is soluble in toluene and exhibits sufficient photostability under the chosen reaction conditions. The DS_{Si} of the TMSC remains stable during the irradiation, since TMSC derivatives with lower DS values would be insoluble in toluene resulting in the formation of a precipitate. However, we did not observe any precipitates during our synthesis procedures. When irradiating TMSC solutions in the absence of $BiPh_3$ under nitrogen atmosphere for 1 h, we could not detect a major decrease in the DP as proven by GPC (data not shown).

In a typical procedure, TMSC is added to solutions containing $BiPh_3$ and clear, colorless solutions with low viscosity are obtained. After exposure to polychromatic UV-light, BiNPs are formed within 2 h which can be followed by a slightly browning of the solution.