

# Solvent and stabilizer free growth of Ag and Pd nanoparticles using metallic salts/cyclotriphosphazenes mixtures



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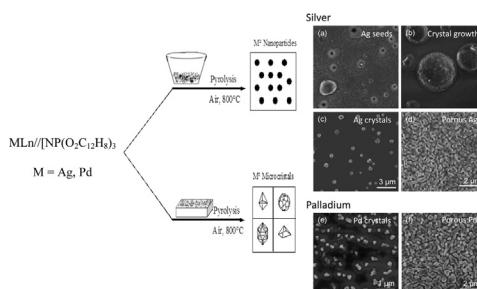
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## HIGHLIGHTS

- Pyrolysis  $MLn/N_3P_3(O_2C_{12}H_8)_3$  mixtures under air, give Pd and Ag nanoparticles.
- $AgPPh_3[CF_3SO_3]$  and  $PdCl_2$  in molar ratios 1:1 and 1:5 were used.
- Metal foams were obtained from 1:5 ratios when deposited on  $SiO_2$ .
- Using crucible supporting in 1:1 metal/trimer <2 nm Pd nanoparticles were obtained.
- The probable mechanism involves a dewetting, nucleation and ripening crystallization.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Cyclotriphosphazene is used as a sacrificial solid-state template to synthesize a range of Ag and Pd nanoparticles with diverse geometries by thermal treatment using  $MLn/N_3P_3(O_2C_{12}H_8)_3$  mixtures. The Pd and Ag nanoparticles are synthesized by solid-state pyrolysis of  $AgPPh_3[CF_3SO_3]/N_3P_3(O_2C_{12}H_8)_3$  and  $PdCl_2/N_3P_3(O_2C_{12}H_8)_3$  mixtures with molar relationships of 1:1, 1:5 and 1:10 respectively, in air and at 800 °C. The morphology of the as-prepared nanoparticles is found to depend on the molar ratio of the precursor mixture, the preparation method and of the nature of the metal. Ag and Pd, microcrystals were thermally grown on Si from the respective 1:1 precursors while that metal foams were grown from 1:5 ratios precursors on  $SiO_2$  wafers. High resolution transmission electron microscopy investigations reveal in most cases small crystals of Pd. HRSTEM measurements indicate that the formation of the Pd and Ag nanoparticles occurs through a phase demixing and dewetting mechanism. This approach has potential to be a useful and facile method to prepare metallic nanoparticles without requiring solutions or surfactants for application in electronic, catalytic and sensor materials and devices.

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## 1. Introduction

Although metallic nanoparticles have been extensively studied [1–5], both preparation and mechanism in solution phase, few

solid-state synthetic methods have appeared [6]. Most scarce is the solid-state mechanism of formation of nanoparticles. Specifically nanoparticles of Pd have been widely studied and several solution methods have been reported and their catalytic properties extensively studied [7–19]. Since the pioneering work of Turkevich [7] in the preparation, characterization and demonstration of catalytic properties of Pd nanoparticles, several preparative reports have

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appeared [8–19]. The majority of reports focus on interesting catalytic properties [8,9] but much of the early work neglected the detailed characterization of the Pd nanoparticles, which has been widespread for solution synthesized nanoparticles and nanocrystals. Recently, the growth pathways of Pd nanocrystals in solution have been examined using HRETM in-situ by trapping precursors solutions between sheets of graphene [20]. The most widely used solution based method is that reported by Miyake using  $H_2PdCl_4$  or  $M_2PdCl_4$  ( $M = Na$  or  $K$  salt as the source of metal), with poly(*N*-vinylpyrrolidone) (PVP) acting as stabilizer in an alcoholic solvent [10]. In such synthetic protocols, the type of alcohol and its water content strongly influence the resulting size of the nanoparticles.

A variant of the original Brust–Schiffrin approach using  $H_2PdCl_4$  as precursor has been also reported [11]. Additionally, a modified Turkevich [12] method has also been adapted so that rectangular Pd nanoparticles could be obtained, which uses  $K_2PdCl_4$ , ascorbic acid and CTAB as surfactant. Electrochemical methods have also become attractive options for Pd and other nanocrystal growth [13]. Using a method developed by Chaudret et al. [14] which makes use of organometallic  $[Pd(\eta-C_3H_5)_2Cl]_2$  and  $Pd_2(dba)_3$  precursors, nanoparticles of ~2 nm in size can be obtained.

In essence, there are many solution based methods for metallic nanoparticle syntheses and the optimum choice depends not only on the type, shape, size distribution and crystallinity of the resulting crystals, but on their application. Miscellaneous variants such as sonochemical [15], and microwave irradiation [16] approaches can also be used with PVP as stabilizers [17], and the use of highly controlled Au nanoparticles seeds can be used for growing Pd and Ag nanoparticles, and have allowed shape control growth of controlled bimetallic crystal systems [21–23]. More recently micrometric Pd crystals have been prepared from  $NaPdCl_4$  using PVP as a stabilizer, allowing a multitude of shapes in the resulting Pd crystals. By varying the reaction time, different morphologies such as single crystals, nanoboxes and nanocages were obtained [19]. The only reported solid state approach for preparing Pd nanoparticles known is through the thermolysis of the  $[Pd(S_{12}C_{12}H_{22})_2]_6$  cluster at 325 °C which results in Pd/PdO nanoparticles with a broad distribution of polygonal particles with sizes varying from 20 to 200 nm [24]. Pd nanoparticles deposited on graphite surfaces have also been obtained by pyrolysis of molecular containing Pd clusters in presence of  $H_2$  [25].

Silver (Ag) nanoparticles have also been widely studied and in solution many different and novel 2- and 3-dimensional shapes are possible [26] which have shown an interesting range of plasmonic properties [27–30]. For Ag, there remains a scarcity in solid-state methods for preparing nanoparticles and nanocrystals and their formation mechanism is practically unknown. To the authors' knowledge, two reports exist concerning true solid state formation of Ag nanoparticles: the pyrolysis of the salt  $Ag_2(OOC\equiv CCOO)$  can result in Ag nanoparticles with sizes in the range 20–30 nm [31] and plasma-enhanced deposition of the silver complex  $Ag(fod)(-PEt_3)$ , ( $fod = 2,2$ -dimethyl-6,6,7,7,8,8,8,-heptafluorooctane-3,5-dionato) [32] allows the formation of thin films of ~17 nm. Strategies to control shape and size are not automatically possible using these approaches.

The importance of solid state methods for metallic nanoparticle growth is the need in some instances to have methods that are 'dry' and thus compatible with certain processing requirements, such as interconnects, electrical contacts, SERS sensors for biological species and to prevent a multi-step method that required further understanding of competitive solution interactions which make drop and pin-casting of NP-containing liquids quite difficult to control [33–36]. Some technological applications such as catalysis, water purification and energy storage often require operation of devices

at high temperatures (fuel cells) and in the complete absence of liquids or water (Li-based batteries).

Metal foams also called "metallic sponge" and "macroporous metals" [37–45] have attracted the attention due to their unusual and peculiar properties such as mechanical strength and stiffness [37]. These materials can be prepared by several solution methods such as dealloying of  $M/M'$  alloys and by forming a metal-organic composite and eliminating the organic part both through dissolution and/or by calcination. However no solid-state approximations have yet been reported. The here reported method could be a useful and general solid-state route to these type of materials.

We have previously reported [46–57] a new solid state method to prepare  $M$ ,  $M_xO_y$  and  $M_xP_yO_z$  nanoparticles using organometallic derivatives of poly and cyclotriphosphazenes as molecular precursors, summarized in Fig. 1. When the respective precursor is unstable or is prepared in low yield,  $MLn/N_3P_3[O_2C_{12}H_8]_n$  mixtures can be made as useful precursors of metallic nanostructured materials [58,59]. Surprisingly, although the polymer or trimer phosphazene have a chain (in the case of Au [59]) or ring containing phosphorus atoms, the products do not contain metallic phosphates species (except when the metallic precursor compound itself contain phosphorus). Additionally, structures can be formed within porous carbon hosts directly, negating the need for second step dispersal of NPs, both as powders and directly on surfaces. In this work, we report the preparation of Ag and Pd nanoparticles from  $AgPPh_3[CF_3SO_3]/[NP(O_2C_{12}H_8)]_3$  and  $PdCl_2/[NP(O_2C_{12}H_8)]_3$  precursors. We show that the solid state method can indeed produce phase pure Ag and Pd nanoparticles with non-spherical shapes without ligand assisted growth pathways. Furthermore, since the precursors are mixtures of metallic salts and trimer, phase demixing occurs resulting in a specific dewetting and physics and chemical decomposition mechanisms that greatly influence the growth mechanism and the resulting shape and size distribution.

## 2. Experimental

### 2.1. Materials

Palladium chloride (Sigma–Aldrich) was used as purchased. The complex  $AgPPh_3[CF_3SO_3]$  was prepared using a reported procedure [60]. The cyclic trimer  $[NP(O_2C_{12}H_8)]_3$  was prepared according reported procedures [61].

### 2.2. Mixture preparation

#### 2.2.1. $PdCl_2/[NP(O_2C_{12}H_8)]_3$ mixture

The respective molar mixture of Palladium chloride (0.1 g, 0.56 mmol for the 1:1 ratio mixture) and (0.14 g, 0.789 mmol for the 1:5 ratio mixture) and the trimer  $[NP(O_2C_{12}H_8)]_3$  (0.4 g, 0.58 mmol for the 1:1 ratio mixture and 1.94 g, 2.82 mmol for the 1:5 ratio mixture) were dissolved in  $CH_2Cl_2$ , stirred for 24 h and evaporated to dryness in a vacuum at room temperature.

#### 2.2.2. $AgPPh_3[CF_3SO_3]/[NP(O_2C_{12}H_8)]_3$ mixture

$AgPPh_3[CF_3SO_3]$  (0.3795 g,  $9.583 \times 10^{-4}$  mmol) and  $[NP(O_2C_{12}H_8)]_3$  (0.5130 g,  $7.467 \times 10^{-4}$  mmol) for a molar relationship 1:1;  $AgPPh_3[CF_3SO_3]$  (0.074 g,  $1.868 \times 10^{-4}$  mmol) and  $[NP(O_2C_{12}H_8)]_3$  (0.4234 g,  $6.16 \times 10^{-4}$  mmol) for a molar relationship 1:5 and  $AgPPh_3[CF_3SO_3]$  (0.0594 g,  $1.5 \times 10^{-4}$  mmol) and  $[NP(O_2C_{12}H_8)]_3$  (0.4064 g,  $5.91 \times 10^{-4}$  mmol) for a molar relationship 1:10, were stirred in a  $CH_2Cl_2$  solution at room temperature for 24 h. After this the solvent was eliminated under reduced pressure and the solid dried in a vacuum at room temperature.

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