Journal of Solid State Chemistry 242 (2016) 182–192

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

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

Synthesis and catalytic activity of the metastable phase of gold phosphide

Deshani Fernando [a], Toni A.E. Nigro [a], I.D. Dyer [a], Shaun M. Alia [b], Bryan S. Pivovar [b], Yolanda Vasquez [a,*]

[a] Department of Chemistry, 107 Physical Sciences I, Oklahoma State University, Stillwater, OK 74078, United States
[b] Chemical and Materials Science Center, National Renewable Energy Laboratory, Golden, CO 80401, United States

ARTICLE INFO

Article history:
Received 24 January 2016
Received in revised form
6 July 2016
Accepted 8 July 2016
Available online 9 July 2016

Keywords:
Gold phosphide
Synthesis
Nanoparticles
HER
Catalysis

ABSTRACT

Recently, transition metal phosphides have found new applications as catalysts for the hydrogen evolution reaction that has generated an impetus to synthesize these materials at the nanoscale. In this work, Au_2P_3 was synthesized utilizing the high temperature decomposition of tri-*n*-octylphosphine as a source of elemental phosphorous. Gold nanorods were used as morphological templates with the aim of controlling the shape and size of the resulting gold phosphide particles. We demonstrate that the surface capping ligand of the gold nanoparticle precursors can influence the purity and extent to which the gold phosphide phase will form. Gold nanorods functionalized with 1-dodecanethiol undergo digestive ripening to produce discrete spherical particles that exhibit reduced reactivity towards phosphorous, resulting in low yields of the gold phosphide. In contrast, gold phosphide was obtained as a phase pure product when cetyltrimethylammonium bromide functionalized gold nanorods are used instead. The Au_2P_3 nanoparticles exhibited higher activity than polycrystalline gold towards the hydrogen evolution reaction.

1. Introduction

Transition metal phosphides exhibit a wide range of physical properties that make them attractive for applications in electronic [1,2] and magnetic devices [3]. Emerging applications of transition metal phosphides as catalysts in the hydrogen evolution reaction [4–10] and their activity towards hydrodesulfurization [4,11–25] have led to renewed interest in their synthesis at the nanoscale. Several methods have been developed to generate nanostructured transition metal phosphides that include: solvothermal reactions, [26] thermal decomposition reactions of single-source precursors [27–29], high temperature annealing of organometallic or solid-state precursors [30,31], reactions of organometallics [32,33] and metal nanoparticles [32,34] with phosphine or other phosphorous sources. A widely used and powerful route to produce a variety of transition metal phosphides with controlled shapes was developed by Henkes et al. [32,34], in which elemental phosphorous is formed *in situ* by the thermal decomposition of *n*-trioctylphosphine (TOP). Phosphides generated using TOP as a phosphorous source include: Ni_2P, Ni_5P_4, PtP_2, Rh_2P, Cu_3P, FeP, MnP, Au_2P_3, Zn_3P_2, Pd_5P_2, and PdP_2, among others [3,32,34–37].

Au_2P_3 is a fascinating material that exhibits unique optical and electronic properties [18,19]. For example, Weizer and Fatemi [22] carefully studied the interface of semiconductors when their surface was metallized with gold to make electrical contacts. Weizer and Fatemi reported that Au_2P_3 formed at the interface of the Au-InP system and that this phase resulted in a drop in contact resistivity by two-to-three orders of magnitude when the thickness of the Au_2P_3 was carefully controlled at the metal-semiconductor interface [22]. Additionally, many physical properties of Au_2P_3 have not been adequately studied at the nanoscale since it is a challenging material to synthesize and no methods currently exist to control the purity, shape, or size of the resulting nanoparticles. Utilizing nanoparticle templates as reactive intermediates has generated many metastable phases of intermetallic and phosphide nanoparticles [38,39]. For Au_2P_3, however, solution synthesis methods result in large amounts of gold impurities and the resulting morphology is difficult to control at the nanoscale. The aim of this work is to demonstrate that reaction parameters such as the capping agent and the morphology of the metal nanoparticle precursors can control the reactivity of the surface, determine whether the phosphide will form, and affect the overall purity of the phase.

Here, we focus on the synthesis of the metastable phase of Au_2P_3 [40] using the method popularized by Henkes et al., where preformed metal nanoparticle templates were used to retain the

---

* Corresponding author.
E-mail address: yolanda.vasquez@okstate.edu (Y. Vasquez).

http://dx.doi.org/10.1016/j.jssc.2016.07.009
0022-4596/

shape of the resulting transition metal phosphide [32,34,41]. In this work, we demonstrate that the surface capping ligand of the precursor gold nanoparticle templates determine the purity and extent to which the metastable gold phosphide phase will form. Gold nanorods, functionalized with either 1-dodecanethiol or cetyltrimethylammonium bromide (CTAB), were used to study the effect of the surface capping complex on the formation of Au_2P_3. We demonstrate that thiol-stabilized gold nanorods undergo digestive ripening to produce uniform spherical particles under the harsh reaction conditions needed to decompose TOP into elemental phosphorous. The thiol-stabilized gold particles retain a discrete spherical shape but, due to the strong Au–S bond, also exhibit reduced reactivity towards phosphorous incorporation that results in low yields of the gold phosphide. In contrast, phase pure Au_2P_3 can be obtained when CTAB functionalized gold nanorods are used as the metal precursor. Interestingly, Au_2P_3 was found to phase separate during TEM imaging experiments. Several transition metal phosphides have shown excellent activity towards the hydrogen evolution reaction (HER) [4–10]. The synthesized Au_2P_3 nanoparticles were evaluated for catalytic activity towards HER. We find that the gold phosphide particles exhibit higher activity than polycrystalline gold.

2. Experimental section

2.1. Chemicals

Tri-*n*-octylphosphine (TOP, 90%) and tri-*n*-octylphosphine oxide (TOPO, 98%) were purchased from Alfa Aesar and used as received. Hexadecyltrimethylammonium bromide (CTAB, >99%), gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, 99.999%), sodium borohydride (99.99%), L-ascorbic acid (>98%), silver nitrate (>99%), and 1-dodecanethiol (>98%) were purchased from Sigma-Aldrich. All chemicals were used without further purification. All solutions were prepared freshly with nanopure H_2O (18.2 MΩ) unless otherwise indicated. Dedicated glassware was cleaned in aqua regia prior to each reaction and rinsed with copious amounts of deionized H_2O. Manipulation of TOP was carried out in a dry, nitrogen atmosphere by employing standard Schlenk line and glove box techniques.

2.2. Synthesis of gold nanorods

Au nanorods (NRs) were synthesized by the seed mediated method as described elsewhere [42] with minor modifications. The seed solution consisted of CTAB (0.2 M, 5 mL), $HAuCl_4 \cdot 3H_2O$ (0.5 mM, 5 mL), and $NaBH_4$ (0.01 M, 600 μL). After stirring vigorously for 2 min, the solution was stored at 27 °C, and used immediately after aging (2–3 h). The growth solution consisted of CTAB (0.2 M, 5.00 mL), $HAuCl_4 \cdot 3H_2O$ (1 mM, 5.00 mL), and $AgNO_3$ (4 mM, 250 μL). Ascorbic acid (78.8 mM, 70 μL) was pipetted into the growth solution and swirled until it became colorless. Next, the seed solution (12 μL) was added to the growth solution and kept overnight at 27 °C. The nanorods were isolated *via* centrifugation (8000 rpm, 30 min) and washed twice with deionized H_2O. Au NR quality was verified by UV-Vis spectrophotometry. Once dried, Au nanorods functionalized with CTAB were dispersed in TOP by sonication and stored in a vacuum desiccator in preparation for the phosphide reaction.

2.3. Ligand exchange

Gold nanorods functionalized with CTAB were dispersed in a mixture of nanopure H_2O (1.00 mL), acetone (2.00 mL), and 1-dodecanethiol (1.00 mL) in a 5 mL-glass vial. The suspension was sonicated (5 min), vortexed (5 min) and allowed to phase separate. After 1 h, Au NRs were separated into the organic phase and isolated *via* centrifugation (8000 rpm, 30 min). The Au NRs were washed with ethanol to remove excess thiol and dispersed in TOP by sonication in preparation for the phosphide reaction.

2.4. Synthesis of Au_2P_3

The Au_2P_3 conversion reaction protocols were adopted from Henkes et. al. [32,34], with minor modifications. In a typical reaction, TOPO (2.53 g) was heated to 120 °C for 1 h under inert atmosphere while stirring with a glass stir bar. After raising the temperature to 360 °C, Au NRs (3.9 mg) dispersed in TOP (5.1 mL) were injected into the hot TOPO. The reaction time was varied from 1 to 10 h. A ratio of 1:1 or 2:1 of TOP/TOPO was used as the phosphorous/solvent source. During the course of the 10 h reaction, the color of the solution transformed from purple to green and finally to dark brown, indicating the formation of Au_2P_3. The reaction was allowed to cool to 100 °C and saturated with ethanol. The black product was recovered by centrifugation using chloroform to remove unreacted TOP and TOPO [25]. Nanoparticles were dispersed in ethanol and kept in a vacuum desiccator prior to characterization to limit oxidation of the TOP coating on the surface of the particles.

2.5. Characterization

Nanoparticles were characterized using a JEOL-JEM transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV. For TEM analysis, an ethanolic suspension of nanoparticles was cast onto a carbon coated copper grid. Powder X-ray diffraction data were collected on a Rigaku SmartLab X-ray diffractometer (Cu Kα radiation). UV-Visible spectra were taken using a DU 530 Beckman Colter UV-Visible spectrophotometer. IR spectra were recorded on a Nicolet iS50 ATR-FTIR spectrometer.

2.6. HER experiments

Electrochemical measurements were taken with an Autolab single channel potentiostat from Eco Chemie, Metrohm Autolab B. V. Rotation of the working electrode was controlled with a modulated speed rotator (Pine Instrument Company). The RHE was homemade using a glass tube containing hydrogen-saturated 0.1 M $HClO_4$ acid and a Pt wire, connected to the main electrochemical cell by a Luggin capillary. More information including illustration of the typical half-cell experimentation and RHE electrodes can also be found elsewhere [43].

Au_2P_3 nanoparticles were coated onto glassy carbon working electrodes (5 mm diameter, area 0.196 cm^2) at a loading of 50 μg/cm^2. Inks were prepared at a concentration of 9.8 mg catalyst per 10 mL of ink (76% water, 24% 2-propanol). Nafion ionomer (5 wt%, Sigma Aldrich) was added to improve the ink dispersion at 40 μL per 10 mL of ink. Inks were sonicated in ice by horn sonication for 30 s, bath sonication for 20 min, and horn sonication again for 30 s. Ten microliters of ink were pipetted onto each electrode and air dried at 40 °C for 20 min. Electrochemical break-in (50 cycles, −0.3 to 1.6 V) was required in 0.1 M $HClO_4$ acid since the electrodes were not active for HER otherwise. HER/HOR (hydrogen oxidation reaction) activities were taken anodically (scan direction did not appear to matter) during linear polarization curves at 20 mV s^{-1} and 1600 rpm. Activities were taken in a rotating disk electrode (RDE) half-cell with a reversible hydrogen electrode (RHE) reference and Au mesh counter electrode. Activities were also corrected for internal resistance (20–23 Ω, depending on the electrode).