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Nanostructured copper oxides and phosphates from a new solid-state route

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ABSTRACT

Nanostructured copper containing materials of CuO, $Cu_3(PO_4)_3$ and $Cu_2P_2O_7$ have been prepared by solid-state pyrolysis of molecular $CuCl_2{\cdot}NC_5H_4OH$ (I), $CuCl_2{\cdot}CNCH_2C_6H_4OH$ (II), oligomeric $[Cu(PPh_3)Cl]_4$ (III), $N_3P_3[OC_6H_4CH_2CN{\cdot}CuCl]_6[PF_6]$ (IV), $N_3P_3[OC_6H_5]_5[OC_5H_4N{\cdot}Cu][PF_6]$ (V), polymeric chitosan$\cdot(CuCl_2)_n$ (VI) and polystyrene-co-4-vinylpyridine PS-*b*-4-PVP$\cdot(CuCl_2)$ (VII) precursors. The products strongly depend on the precursor used. The pyrolytic products from phosphorus-containing precursors (III), (IV) and (V) are Cu phosphates or pyrophosphates, while non-phosphorous-containing precursors (VI) and (VII), result in mainly CuO. The use of chitosan as a solid-state template/stabilizer induces the formation of CuO and Cu_2O nanoparticles. Copper pyrophosphate ($Cu_2P_2O_7$) deposited on Si using (IV) as the precursor exhibits single-crystal dots of average diameter 100 nm and heights equivalent to twice the unit cell *b*-axis (1.5–1.7 nm) and an areal density of 5.1–7.7 Gigadots/in.^{2}. $Cu_2P_2O_7$ deposited from precursor (VI) exhibits unique labyrinthine high surface area deposits. The morphology of CuO deposited on Si from pyrolysis of (VI) depends on the polymer/Cu meta ratio. Magnetic measurements performed using SQUID on CuO nanoparticle networks suggest superparamagnetic behavior. The results give insights into compositional, shape and morphological control of the as-formed nanostructures through the structure of the precursors.

1. Introduction

In general, nanostructured materials can be prepared via two non-gas or vapor phase approaches: in solution or in a solid-state phase [1–3]. The most widely-known examples are in solution [4] but some solid-state [5–8] approaches have also been reported. Indeed, solution methods offer many advantages over the solid-state method, such as convenient control of the size and morphology of the nanoparticles and the ability to monitor the growth mechanism by other techniques such as optical spectroscopy for example. The solid state method, however, can more easily be incorporated into solid-state applications. For copper-containing nanostructured materials, several methods including hydrothermal techniques and sol–gel approaches, among others, have been reported [4a]. The preparation method for nanostructured CuO has been recently revised by Anadan and Yang [4a] and by Kuo and Huang for Cu_2O [4b]. Methods using ionic salts in single-batch hydrothermal or solvothermal conditions are the most common routes to obtain both Cu_2O and CuO. Direct oxidation of copper is of course a typical route to these copper oxides.

Copper oxides are p-type semiconductors having a band gap in the range 1–2 eV with excellent photovoltaic, electrochemical, and catalytic properties [4,9]. The discovery of high-T_c superconductivity in cuprates triggered interest in oxide materials as possible progenitors of exotic magnetic phenomena. Subsequent research established the important role of the two-dimensional (2D) CuO planes concerning the magnetism and superconductivity of the cuprates. The exploration of nanostructured copper-based materials as building blocks towards multifunctional materials with technological applications requires, among others, their incorporation in a solid-state phase, usually as thin films [10]. Thus the preparation methods for nanostructured materials in their solid-state phase are of great importance. Specifically for copper oxides, solid-state preparation methods have been reported [6,7,10–16]. Xu et al. [7] prepared CuO nanocrystals by a one-step solid-state reaction of $CuCl_2{\cdot}2H_2O$ and NaOH, while Kawahashi and Shiho [6] obtained hollow spheres by calcination of a polymer-coated $Cu(NO_3)_2$ salt. A different approach involves the oxidation of solid Cu under air at 400 °C to give CuO nanorods [10]. Similarly large-scale synthesis of CuO nanowires has been reported by thermal evaporation of a copper foil under oxygen flow [11] and Jiang et al. [12]

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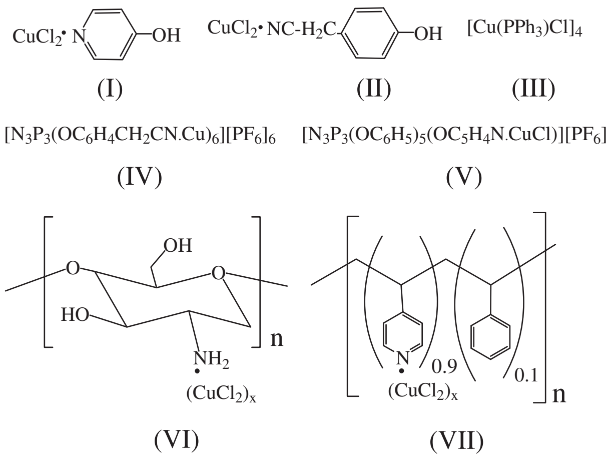

Scheme 1. Formulae of precursors (I)–(VII).

reported the preparation of CuO nanowires by heating copper substrates in air.

Recently, using the classical wet method starting from a Cu(II) salt and NaOH, the control of the morphology was achieved by a proper choice of the molar ratio of the reactants [13]. A different approach involving the spray-pyrolysis of Cu(II) salts, has been also reported [14]. Tunable forms of CuO such as doughnut-like microstructures, microplates and multilayer microspheres were obtained using a Cu(II)/ethylene glycol precursor and calcination at 400 °C [15]. CuO nanoparticles inside Al_2O_3 have been recently prepared by gelation of the respective Cu(II) and Al(III) salts [16].

Although several preparation methods for nanostructured copper oxides have been reported, there is a scarcity of knowledge surrounding the growth of copper phosphate compounds and their nanostructured forms. To the best of our knowledge, the only known report concerning nanostructured copper phosphate $Cu_3(PO_4)_2$, highlights a 3D dandelion and 2D nanowall morphology [17]. Indirect evidence of the formation of $Cu_3(PO_4)_2$ and $Cu_5(PO_4)_3OH$ in soils was also recently reported [18].

In view of the scarcity of solid-state approaches to form nanostructured copper oxides and due to their importance of copper oxides and phosphates in lithium-ion batteries for example, we have been exploring new synthetic approaches for these phases. We report here a solid-sate method to form nanostructured copper-containing materials by a new approach using molecular, oligomeric as well as macromolecular precursors. These precursors are depicted in Scheme 1 and will be denoted throughout the paper as precursors (I)–(VII). As we previously reported, the use of metallic derivatives of phosphazenes as precursors leads to the formation of phosphorus-containing nanoparticles of phosphates or pyrophosphates [19–26]. With the aim of designing an alternative method to obtain nanostructured materials of metal oxides without using phosphorus, we show that this is possible using precursors I, II, VI and VII (see Scheme 1).

Chitosan and poly(styrene-co-4-vinylpyridine), PS-*b*-4-PVP, have been chosen as a macromolecular template/stabilizer because (a) they provide oxygen coordination sites (chitosan) as well as nitrogen and pyridine (PS-*b*-4-PVP), (b) they are inexpensive and commercially available polymers, and (c) chitosan can produced in large scale. Chitosan [27,28] is a polysaccharide obtained by deacetylation of natural chitin, which is one of the important natural polymers found in the shells of crustaceans and the cell walls of many fungi. Due to its oxygen linkages to nitrogen from the NH_2 groups and OH moieties present in the polysaccharide chains, it can bind metal ions forming macromolecular metal complexes [29]. Chitosan itself can act as solution template/stabilizer for the formation of nanoparticles [29–31]. Here we show that chitosan can be successfully employed as solid-state template/stabilizer.

On the other hand, poly(styrene-co-4vinylpyridine) is an interesting copolymer due to the vinylpyridine block which binds metal ions and the styrene groups which form shells, leading to stable macromolecular complexes [32–35]. PS-*b*-4-PVP has been used in solution as a template/stabilizer of metals and other nanoparticles [36–39], but no report has appeared concerning its use as solid-state template/stabilizer of nanoparticles. We report here, for the first time, the use PS-*b*-4-PVP as a solid-state template/stabilizer for copper containing nanoparticles. For all the precursors used (I)–(VII), the pyrolysis from (IV) resulted in the highest purity CuO and superparamagnetic properties determined by SQUID were also found.

2. Experimental

2.1. Preparation of precursors

2.1.1. $CuCl_2{\cdot}NC_5H_4OH$

$CuCl_2{\cdot}2H_2O$, 0.5 g, 2.94 mmol in 25 ml acetone and 4-hydroxypyridine, 0.28 g, 2.94 mmol in dichloromethane were stirred for 1 day. The green solution was concentrated to 5 ml and diethylether was added to give a brown solid. The supernatant was extracted and the solid washed with diethylether and dried under vacuum. IR (KBr, cm^{-1}): ν(OH): 3286; py coordinate: 1617; 1587; 1448; 1376; 1319; 1293; 1204; 1059; 1031; 841; 828; 609; 528. *Anal.* Calc.: C, 26.15; H, 2.17; N, 6.10. Found: C, 25.58; H, 2.25; N, 6.99%.

2.1.2. $CuCl_2{\cdot}CNCH_2C_6H_4OH$

$CuCl_2{\cdot}2H_2O$, 0.5 g, 2.94 mmol in 25 ml acetone and 4-hydroxybenzylcyanide, 0.39 g, 2.93 mmol in dichloromethane were stirred for 1 day. The green solution was concentrated to 5 ml and diethylether was added to give a brown solid. The supernatant was extracted and the solid washed with diethylether and dried under vacuum. IR (KBr, cm^{-1}): ν(OH): 3256; py coordinate: 1617; ν(CN): 2298; 1614; 1516; 1442; 1394; 1351; 1254; 1217; 1099; 1019; 841; 947; 901; 846; 808; 770; 643; 611. *Anal.* Calc.: C, 35.89; H, 2.61; N, 5.23. Found: C, 36.06; H, 3.4; N, 5.15%.

2.1.3. $N_3P_3[OC_6H_5]_5[OC_5H_4N{\cdot}Cu][PF_6]$

Over $\{N_3P_3[OC_6H_5]_5[OC_5H_4N]\}$ 0.32 g, 0.61 mmol, 0.0785 g, 0.461 mmol of $CuCl_2{\cdot}2H_2O$ in 20 ml of methanol was added to NH_4PF_6, 0.1193 g, 0.73 mmol and the solution stirred for 24 h at room temperature. The solution was dried under reduced pressure and the solid residue extracted with dichloromethane. The solution was concentrated to a 5 ml volume and then diethylether was added. The precipitate was dried under vacuum to give 0.2 g. *Anal.* Calc.: C, 46.53; H, 3.21; N, 6.20. Found: C, 46.8; H, 3.2; N, 4.09%. ^1H NMR ($CDCl_3$, ppm) 7.13 m; 6.89 m. ^{31}P NMR ($CDCl_3$, ppm) 8.43 singlet, (N_3P_3); −144.19 heptuplet, PF_6. IR (KBr, cm^{-1}): 2968; 2938; 2880; 1591; py coordinate: 1508; 1474; 1386; 1350; 1321; 1269; 1243; ν(PN): 1178; 1164; 1109; 1070; 1035; 1009; 951; 931; 881; 838; 792; 557.

2.1.4. Chitosan·$(CuCl_2)_n$ 5:1 and 10:1

Chitosan, 1.635 g, 9.43 mmol; 2.94 g, 16.84 mmol and $CuCl_2{\cdot}2H_2O$, 0.5 g, 1.869 mmol; 0.45 g, 1.68 mmol, molar relationships of 5:1; 10:1, respectively, were stirred in CH_2Cl_2 at room temperature for 6 days. The supernatant solvent was extracted with a syringe by decantation and the green solid washed with dichloromethane and then dried under reduced pressure. IR (KBr, cm^{-1}): ν(OH), ν(NH): 3422 (broad); 3280 (shoulder); 2924; 1686 (broad); 1321; 1116; 1018; 862; IR spectra for 1:5 and 1:10 products are similar.