

# Advances in MOCVD Production of Complex Materials from Single-Source Precursors: Phase Pure Metal Phosphide Thin Films for Catalysis and Energy Applications

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## ABSTRACT

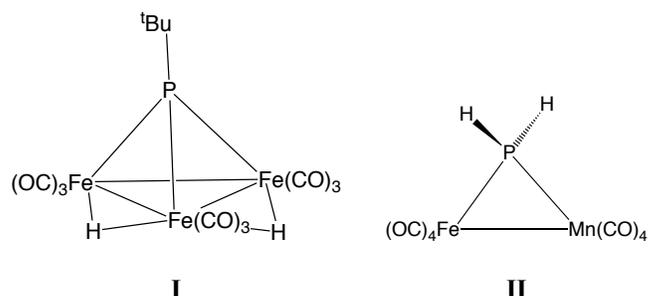
Production of phase-pure transition metal phosphides poses a significant challenge owing to the large number of possible  $M_xP_y$  stoichiometries adopted by these materials. To address these issues, single-source precursors (SSPs) have been prepared that target specific  $x:y$  ratios. The SSPs are based on metal carbonyl clusters that contain phosphorus. Phase pure materials that have been prepared from this method include  $Fe_3P$ ,  $Fe_2P$ ,  $FeP$  and  $FeMnP$ . Doped materials are also accessible using isostructural cluster compounds. For  $FeMnP$ , the metastable hexagonal phase is obtained. The precursors are volatile and may be used for metal organic chemical vapor deposition (MOCVD) to produce thin films on a variety of substrates including silica, quartz, FTO, titanium dioxide, gold and nickel foam. The films produced in this manner show good catalytic activity for water splitting catalysis with hydrogen evolution activity increasing with increasing metal content.

**Keywords:** transition metal phosphide, catalysis, water splitting, thin films, metal organic chemical vapor deposition

## 1 INTRODUCTION

Transition metals form a wide variety of phases with the pnictogens. For iron and phosphorus alone, there are six known stoichiometries existing in nine crystal forms (Table 1) [1]. The other first row transition metal phosphides are equally diverse [1]. While preparation of transition metal phosphides may be accomplished easily by simply heating the elements to high temperatures, phase purity may be a problem using conventional “heat and beat” techniques, and we found commercial samples of  $Fe_3P$  and  $Fe_2P$  to be contaminated with the lower metal content phosphides, having only roughly ~92% of the nominal composition. Furthermore, the temperatures to achieve conversion to the various phases usually exceeds 1000 °C, making that method impractical for the preparation of nanoparticles (NPs) or thin films. In order to circumvent these difficulties, we began exploring the use of organometallic metal carbonyl pnictide compounds as single source precursors. At the time of our initial studies  $FeP$  and  $Fe_2P$  NPs were known, so we chose to target  $Fe_3P$  and used  $H_2Fe_3(CO)_9(P^tBu)$  (I) [2]. Surprisingly, the product was

found to be  $Fe_2P$ , whose formation could be attributed to the reaction of the metal phosphides with oleic acid, which is a standard component of the surfactant systems used to prepare NPs. Elimination of the oleic acid resulted in stoichiometric NPs, but their very small size (<5 nm) hampered definitive characterization. Similarly, decomposition of  $FeMn(CO)_8(\mu-PH_2)$  (II) under similar conditions resulted in  $(Fe,Mn)_2P$ , but the NPs were deficient in Mn, also attributable to preferential leaching of Mn from the system by oleic acid, even though bulk decomposition of the compound led to stoichiometric  $FeMnP$  [3].



Compound	Crystal System
$Fe_4P$	$Pmmm$
$Fe_3P$	$I\bar{4}$
$Fe_2P$	$P\bar{6}2m$
$Fe_2P$	$Imm2$
$FeP$	$Pnma$
$FeP_2$	$Pnm$
$FeP_4-\alpha$	$P2_1/c$
$FeP_4-\beta$	$C222_1$
$FeP_4-\gamma$	$C2/c$

Table 1. The known iron phosphide phases.

As a consequence, our attention turned to using these precursors for the production phase pure thin films via MOCVD, which has proven successful as will be detailed below. In the meantime, it was discovered that metal phosphide materials can be good catalysts for both the hydrogen evolution half reaction (HER) and oxygen evolution half reaction (OER) of water splitting [4], and the resultant thin films have been explored for their catalytic activity.

## 2 SINGLE SOURCE PRECURSORS

It has long been known that metal carbonyls can be decomposed cleanly into pure metal and CO. This was the foundation of the well-known Mond process for the purification of Ni [5]. While metals may catalyze disproportionation of CO to yield carbon and CO<sub>2</sub>, this process generally occurs at higher temperatures (ca. 800 °C) as employed for metal catalyzed conversion of CO into carbon nanotubes [6]. At lower temperatures, however, from our work carbide formation does not appear to be an issue and transition metal-main group element clusters such as H<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub>(P<sup>t</sup>Bu) can effectively be converted into thin films containing the metal-phosphorus ratio found in the parent compound at relatively low temperatures (ca. 350 - 450 °C [7]. The convenient aspect of these compounds is that the attached ligands leave readily: H (as H<sub>2</sub>), CO and some organic groups, such as <sup>t</sup>Bu as isobutylene). After initial success with production of Fe<sub>3</sub>P, more complex targets incorporating more than one M, and more recently more than one pnictogen, have been attempted.

### 2.1 Production of Heterometallic M<sub>x</sub>P<sub>y</sub>

Thin films of FeMnP have been prepared from the precursor FeMn(CO)<sub>8</sub>(μ-PH<sub>2</sub>) (**II**). Initial studies of decomposing this material onto glass or quartz showed significant oxidation of Mn to achieve an intimate mixture of FeP and MnO. This was ultimately traced to reaction of the substrate with the FeMnP film, and oxidation was largely eliminated for films prepared on other metal oxides that were not so susceptible to reduction, including alumina (Fig. 1), fluorine-doped tin oxide (FTO) and titanium dioxide [8,9]. The films can also be deposited on nickel foam (NF) or gold (Fig. 3) [10].

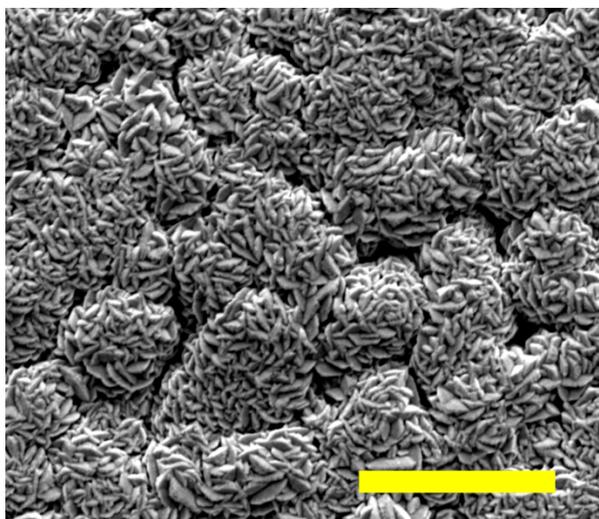


Figure 1. SEM Image of FeMnP on Al<sub>2</sub>O<sub>3</sub>.  
Scale bar = 5 μm

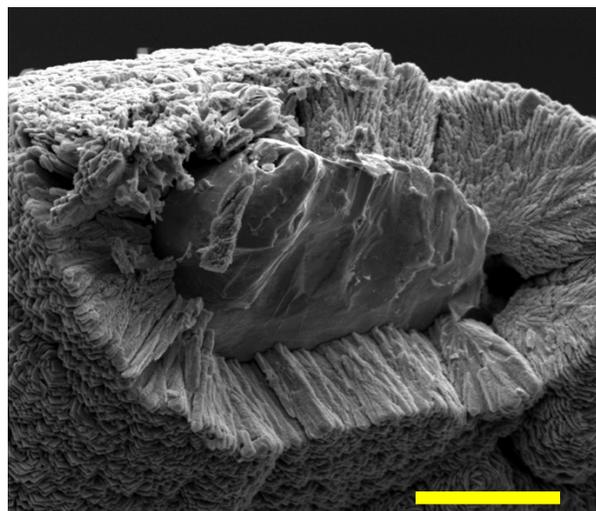


Figure 2. SEM Image of FeMnP on NF.  
Scale bar = 5 μm

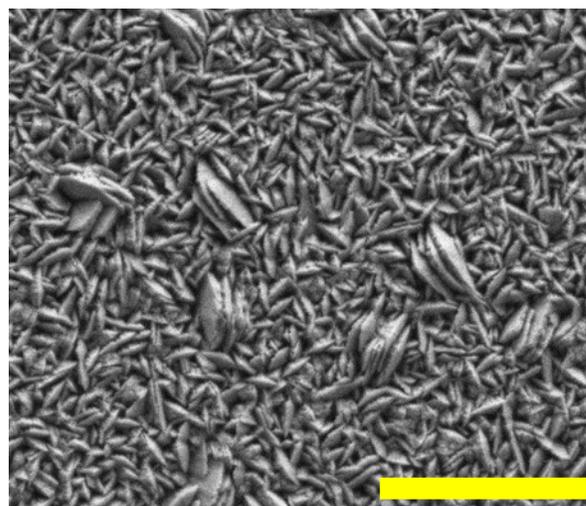


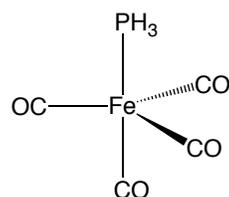
Figure 3. SEM Image of FeMnP on Au.  
Scale bar = 3 μm

An alternative strategy to the decomposition of stoichiometric SSPs is the use of isostructural clusters of different elements as co-precursors for the production of doped films. In this way, Fe<sub>3</sub>P could be doped with Co or Te by co-decomposing Co<sub>3</sub>(CO)<sub>9</sub>(P<sup>t</sup>Bu) or H<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub>Te with H<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub>(P<sup>t</sup>Bu), respectively [11].

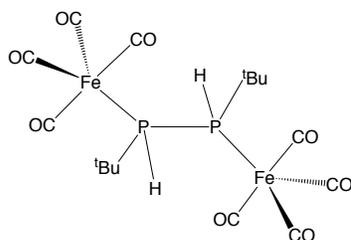
### 2.2 Production of Other SSPs of Fe and P

After success with Fe<sub>3</sub>P, we determined to explore production of phase-pure thin films of the other iron phosphides in order to evaluate the HER and OER possibilities for the various phases using phase-pure thin films. To this end, we used Fe(CO)<sub>4</sub>PH<sub>3</sub> (**III**) as a precursor to FeP. This compound was known to produce FeP NPs [12]. Decomposition under similar conditions to H<sub>2</sub>Fe<sub>3</sub>(CO)<sub>9</sub>(P<sup>t</sup>Bu), however, led to films of Fe<sub>2</sub>P, which is attributed to clean rearrangement of the

precursor to a polynuclear compound and elimination of  $\text{PH}_3$  [13]. At higher temperatures, the precursor was found to produce  $\text{FeP}$ , but this process proved to be more difficult to control and some  $\text{Fe}_2\text{P}$  was usually observed as well. This difficulty was overcome by use of either  $\text{Fe}(\text{CO})_4\text{PH}_2^t\text{Bu}$  or a polynuclear SSP. The latter was a new compound  $[\text{P}(\text{H})(^t\text{Bu})\{\text{Fe}(\text{CO})_4\}]_2$  (**IV**) prepared in our group from the reaction of  $\text{PCl}_2^t\text{Bu}$  with a mixture of  $\text{Na}[\text{HFe}(\text{CO})_4]$  and  $\text{Na}_2[\text{Fe}(\text{CO})_4]$ . Presumably  $\text{PH}_3$  is a good leaving group that gives rise to the production of  $\text{Fe}_2\text{P}$ , while the  $\text{P}^t\text{Bu}$  groups are more tightly bound to Fe and less prone to elimination. Images of  $\text{FeP}$  deposited on FTO and  $\text{Fe}_2\text{P}$  on NF are shown in Fig. 4 and Fig. 5, respectively.



**III**



**IV**

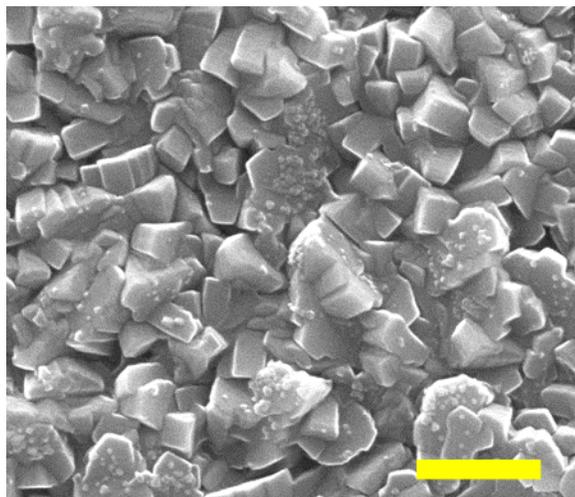


Figure 4. SEM Image of  $\text{FeP}$  on FTO.  
Scale bar = 1  $\mu\text{m}$

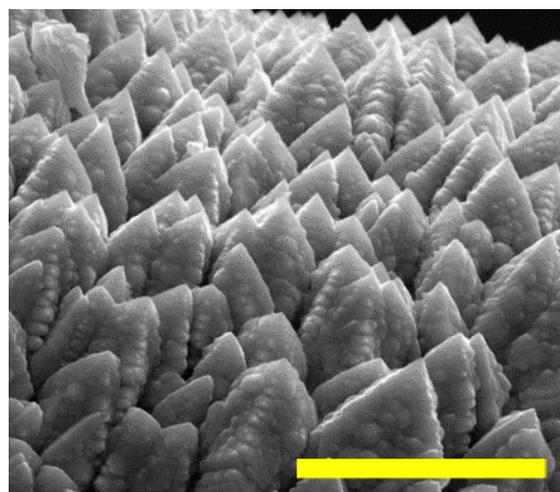


Figure 5. SEM Image of  $\text{Fe}_2\text{P}$  on Nickel Foam.  
Scale bar = 4  $\mu\text{m}$

### 3 THIN FILM PRODUCTION AND CATALYSIS

Examination of  $\text{FeMnP}$  as an electrocatalyst for water splitting on nickel foam showed that it was effective for both the HER and OER reactions [10]. The metal phosphide is retained for the HER reaction, but surface oxides formed during the OER reaction are the likely active catalysts for that half reaction. Similarly,  $\text{FeMnP}$  could be deposited on  $\text{TiO}_2$  nanorod arrays, which was the first report of deposition of phase pure thin films of a metal phosphide on a semiconductor [9]. This allowed examination of the catalyst for photo-electrocatalysis of the OER reaction for which it was found that the theoretical photocurrent density of the rutile  $\text{TiO}_2$  substrate under 1 sun of illumination was achieved. In other words, the full potential of the semiconductor was captured. The benefit of these particular systems is that the metal phosphide is conductive, leading to enhanced electrical communication between the surface metal phosphide or metal phosphide/oxide and the underlying substrate.

The series  $\text{Fe}_x\text{P}$  ( $x = 1 - 3$ ) has been evaluated for catalysis of the HER reaction. Activity was found to increase with increasing metal content. Theoretical examination of the phases suggests that the ability of hydrogen to adopt bridging binding modes to the catalytic surface may be important in promoting catalysis.

### 4 CONCLUSIONS

Chemical vapor deposition of phase-pure metal phosphide thin films can be effectively done using metal carbonyl cluster compounds that incorporate stoichiometric numbers of phosphorus atoms. The decompositions occur under mild conditions, allowing thin film production on a large number of different 2- and 3-D substrates including oxide materials (glass, quartz, FTO, titanium dioxide, alumina) and metals (nickel foam). The compounds decompose uniformly even on structured substrates such as  $\text{TiO}_2$  nanorod arrays, and the coating thickness can be varied systematically by varying the amount of precursor employed in the deposition process.

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