Preface

The discovery of carbon nanotubes and the isolation of graphene from bulk graphite were individually responsible for launching entire scientific fields of inquiry into 1D and 2D nanomaterials, respectively. Researchers are taking inspiration and insights from carbon nanotubes and graphene and applying it to new or recently rediscovered 2D materials that do possess a band gap, such as black phosphorus (BP) and red phosphorus (RP). These materials may be suitable for optoelectronic applications from the near infrared region through to the visible. Over 1000 papers were published in the last two years on this topic, compared to <100 papers in the last 200 years.

Although the element phosphorus was known for centuries, some fundamental properties of the allotropes are still not fully understood. These include, but limited to the following:

1. Red phosphorus has been found to exist as five crystalline forms all of which exhibit a reddish color. The crystal structures of type IV and V are known (Figure 1). However, the crystal structures of types II and III were not determined because of the difficulty in making larger crystals. Also, we used to think type I red phosphorus is amorphous polymer chain of P4 groups (also see Figure 1), recently studies suggested that type I red phosphorus is also crystalline, but the structure is unknown.

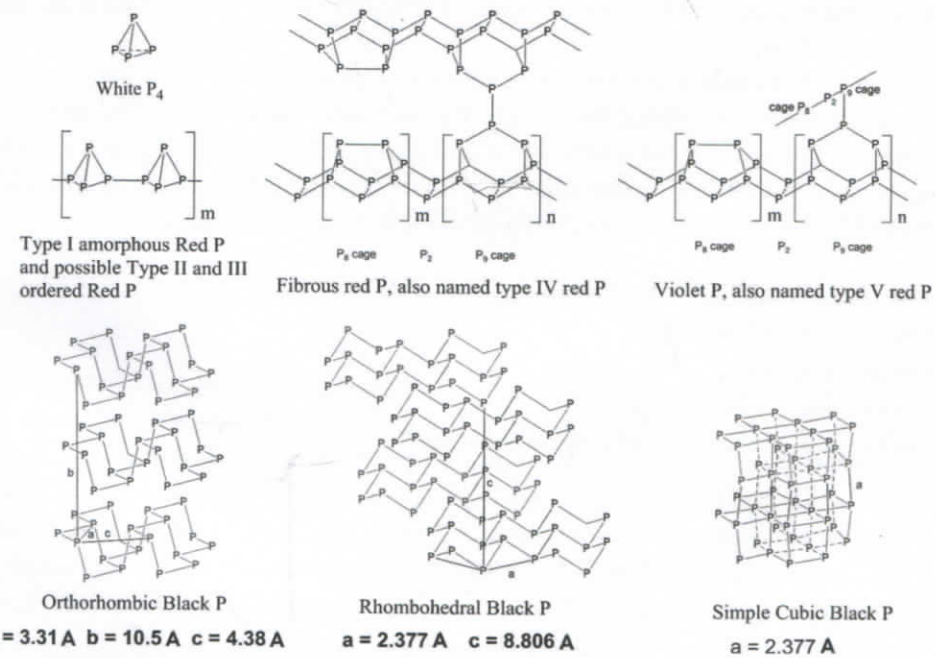

Figure 1. The structures of phosphorus allotropes.

2. It wasn't until recently that a lower pressure (<5 bar) method to obtain black phosphorus was discovered. Red phosphorus with different morphologies were reported in the last two years. The morphology and type of the phosphorus crystals are significantly affected by the catalyst, mineralizing agent, substrates, temperature, pressure, etc. Further studies are needed to understand the formation mechanisms of these phosphorus allotropes.
3. The physical and chemical properties of phosphorus are not well known. For instance, it was believed red phosphorus are not conductive and black phosphorus is more stable than red phosphorus, studies in 2016 indicted these may not be true.
4. Some small phosphorus cluster molecules (such as P20 or P60) were proposed from modeling work, however, they have not been observed from experimental work. Also, detection of small clusters is critical for understanding how white phosphorus (P4) is converted to red phosphorus upon heating.
5. The studies on the phosphide and polyphosphide, derivatives of phosphorus allotropes, grew quickly in the last two years as well, however, little is known on the chemical properties of these compounds.
6. Phosphorus nanostructures demonstrated their unique properties as catalysts for various chemical reactions.
7. Potential applications in energy, industry, health etc.

The recent interest in phosphorus nanostructures provides us a great chance to fully study the fundamental physical and chemical properties of both red and black phosphorus. The fundamental knowledge in the structure, morphology, physical and electronic characteristics of these materials is critical for further exploration into optoelectronic properties and additional semiconductor applications. This book covers the fundamental physical and chemical properties of both red and black phosphorus nanomaterials and their wide applications in energy, environmental, industrial, and clinical fields.

We try to present a comprehensive overview of phosphorus-based nanomaterials. We wish the book will help those entering the field get a quick snapshot of properties and applications of these materials. I am extremely grateful to all the authors for contributed the chapters for this book. It's my great pleasure working with staff at the ACS Books Editorial Office, especially Amanda Koenig and Harry Weisbecker, without whom this book could not have been written.

Hai-Feng (Frank) Ji, Ph. D., Professor
Department of Chemistry
Drexel University
3141 Chestnut Street, Disque 507
Philadelphia, Pennsylvania 19104, United States