

# The role of defects and solid/liquid interfacial interactions on controlling anisotropic growth of novel two-dimensional materials

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PACIFIC NORTHWEST NATIONAL LABORATORY  
*operated by*  
BATTELLE  
*for the*  
UNITED STATES DEPARTMENT OF ENERGY  
*under Contract DE-AC05-76RL01830*

Printed in the United States of America

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# **The role of defects and solid/liquid interfacial interactions on controlling anisotropic growth of novel two-dimensional materials**

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Prepared for  
the U.S. Department of Energy  
under Contract DE-AC05-76RL01830

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## Overview

Atomic-scale understanding about how interfacial properties are modified in the presence of defects and how they are correlated to the properties of nucleation and growth is critical for controlled materials growth on solid/liquid interfaces. The goal of this proposal is to establish preliminary data on the critical role of surface defects and chemical compositions of solvent on the structure, dynamics, reactivity, and free energetics at graphene/ionic liquid (IL) interfaces and their impact on two-dimensional (2D) growth of transition metal oxides on the surface. This study aims to develop generalized physical/chemical principles for directional growth at solid/liquid interfaces to achieve atomic-level control of two-dimensional materials synthesis. The proposed study of the effects of surface defects on the interfacial structure and reactivity will improve our understanding of the critical roles of heterogeneity, disorder, and solvents on 2D materials synthesis and lead to better control of directional growth of materials at solid/liquid interfaces.

## Introduction

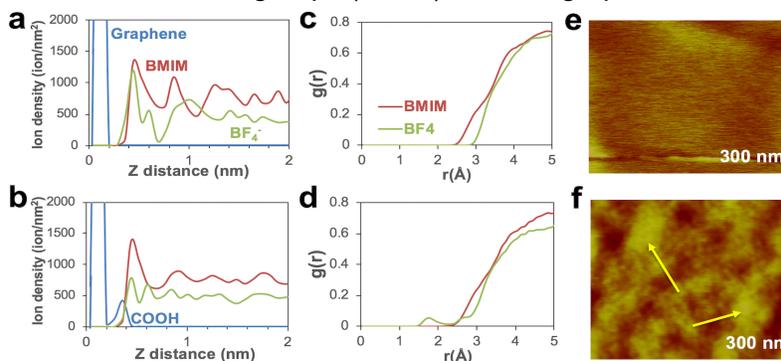
Extensive studies have shown that materials synthesis at solid/liquid interfaces to control shape, morphology, and surface architecture plays a key role in energy applications. When nucleation occurs at the solid/liquid interface, the structure, dynamics, and composition of the liquid are remarkably distinct from the bulk, particularly in the vicinity of defects.

IL-mediated synthesis of metal oxides on graphene has a great interest because of a variety of applications of graphene/IL-based composites. While studies showed that defects on the graphene surface act as nucleation sites, their exact chemical nature and how they interact with the solvent are unclear. In addition, theoretical studies showed that interaction between a defect and ILs significantly modifies graphene/IL local interfacial structures. In addition, although ILs are known to form an ordered layer structure near interfaces, the impact of the solid-like interfacial layer structure of ILs on the thermodynamics and kinetics of elementary processes such as precursor adsorption/desorption to/from the surface, their transport, and aggregation, which defines the nucleation and anisotropic growth of overlayer 2D materials, needs to be clarified. However, there is still a lack of information on the chemical nature and reactivity of precursors near the interface modified with different defects and ILs. Here we perform computational simulations of defect dynamics on structure and reactivity which are verified by concomitant experiments via advanced *in situ* topographic and structural imaging techniques to probe the solid/liquid interface at the sub-nanometer level.

## Results

We first investigated the role of surface functional groups (SFGs) at the IL/graphene interface.

We performed large scale classical molecular dynamics (CMD) simulations with 1-butyl 3-methylimidazolium (BMIM)  $\text{BF}_4$  on graphene with and without SFGs. Fig. 1 presents a density profile (a,b) and radial distribution functions  $g(r)$  (c,d), showing ion distributions projected along the surface normal and distance distribution between atoms, respectively. Compared to pristine graphene, SFGs result in distinct



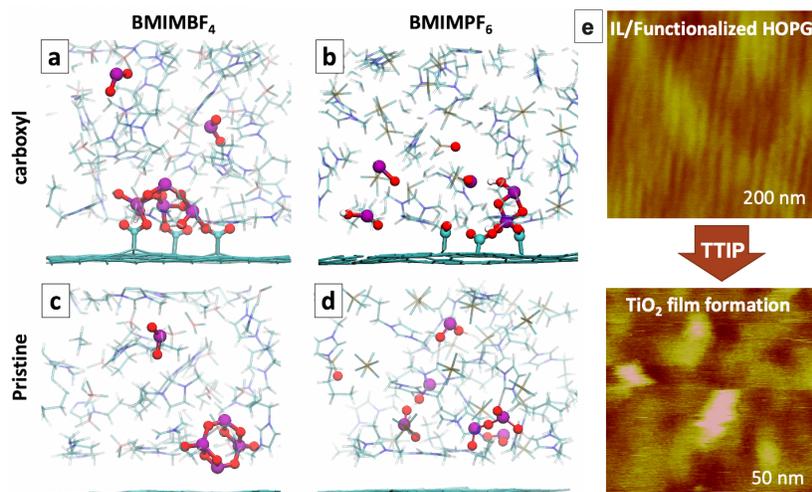
**Figure 1.** A computed density profile of BMIM/ $\text{BF}_4$  projected along the surface normal (a, b), radial distribution function  $g(r)$  (c, d) and in situ AFM images of BMIM/ $\text{BF}_4$  on clean HOPG (e) and plasma-treated HOPG (f).

interactions with the surface, lower  $\text{BF}_4^-$  density near the surface, and stronger interactions with graphene as evidenced by a peak at 1.85 Å. In situ AFM images also show a strong adsorption of IL, resulting in nanometer-sized islands (arrows in Fig. 1f) forming on a functionalized, highly oriented pyrolytic graphite (HOPG) surface (Fig. 3f). On the clean HOPG surface, however, there is nearly no IL structuring (Fig. 3e). These results substantiate the conjecture that ionic liquid ordering and dynamics are locally affected by a surface functionalization which are a critical factor to understand 2D film growth on graphene.

To investigate the effect of SFG and IL composition on  $\text{TiO}_2$  growth at the IL/graphene interfaces, we performed ab initio molecular dynamics (AIMD) simulations at 100 °C. The simulations reveal that the significant modification of IL distribution with SFGs at the interface strongly affect  $\text{TiO}_2$  nucleation not only with surface functionalization but also with IL constituents (Fig. 2). In the case of  $\text{BMIMBF}_4$  on functionalized graphene (Fig. 2a), the SFGs act as anchor to grow a  $\text{TiO}_2$  cluster resulting in a cluster formation along the lateral surface. With  $\text{BMIMPF}_6$  (Fig. 2b), on the other hand,  $\text{TiO}_2$  monomers tend to nucleate in a 3D structure formation. We also observed a fast lateral diffusion of  $\text{TiO}_2$  clusters on pristine graphene (Fig. 2c and 2d), which hinders not only  $\text{TiO}_2$  growth but ordered structural formations. Compared with the  $\text{BF}_4^-$  anion,  $\text{PF}_6^-$  strongly interacts with  $\text{TiO}_2$  monomers which also inhibits the cluster formation at the interface. In consistent with theory results, in situ AFM spectrum shows a strong  $\text{TiO}_2$  film formation with functionalized HOPG when titanium isopropoxide (TTIP) precursors are added to IL on graphene surface.

We also investigated  $\text{TiO}_2$  formation from TTIP precursor by performing AIMD simulations via a blue moon ensemble method and liquid-state NMR with a system consisting of IL and TTIP. The calculated free energy for the first isopropoxide cleavage from TTIP with  $\text{H}_2\text{O}$  reveals an exothermic process, which is more favorable in  $\text{BMIMPF}_6$  (~30 kJ/mol) than in  $\text{BMIMBF}_4$ . This indicates that solvent determines the stability of the  $\text{TiO}_2$  monomer.  $^{13}\text{C}$  NMR spectra shows an upfield shift of the O-CH peak when TTIP is added to ionic liquid. This indicates a weakened interaction between  $\text{Ti}^{4+}$  and isopropoxide in consistent with theory results.

The study enables us to investigate of the effect of functional group on graphene and composition of IL on  $\text{TiO}_2$  nucleation at the IL/graphene interface. To the best of our knowledge, these effects have not been well understood by pervious works, which will greatly enhance our understanding of 2D growth of materials at solid/liquid interfaces. The study was used as a preliminary result for FY22 Early Career Research Proposal and will lead to a publication in FY22 that will acknowledge this LDRD support.



**Figure 2.**  $\text{TiO}_2$  nucleation with  $\text{BMIMBF}_4$  (a,c) and  $\text{BMIMPF}_6$  (b,d) on functionalized (a,b) and pristine graphene surface (c,d). (f) In situ AFM images before (upper) and after adding TTIP (lower) to IL on functionalized HOPG.

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