**Two-dimensional Shape Memory Materials – a New Class of Smart Material at Nanoscale**

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**Aims of Project**

SMMs have been widely used in industry sectors like automotive, aerospace, and biomedical engineering. In 2006, Miyazaki reported the **world annual market as US$5.4 billion** (increased by a 100 fold in ten years). Miniaturization of shape memory devices/systems to micro and nano-meter scale has huge application potentials and significant market value.

Inspired by our recent discoveries of 2D shape memory graphene oxide (SMGO) and Li doped black phosphorene (P4Li2) using *ab initio* simulations, we aim to further investigate the novel shape memory mechanisms and properties of other potential 2D SMMs under different external stimuli, facilitating the development of SMM based micro/nano-devices. We will specifically focus on (1) a novel quantum mechanical shape memory effect and (2) examining a SMM design concept – adatom switch – in monolayer monochalcogenides.

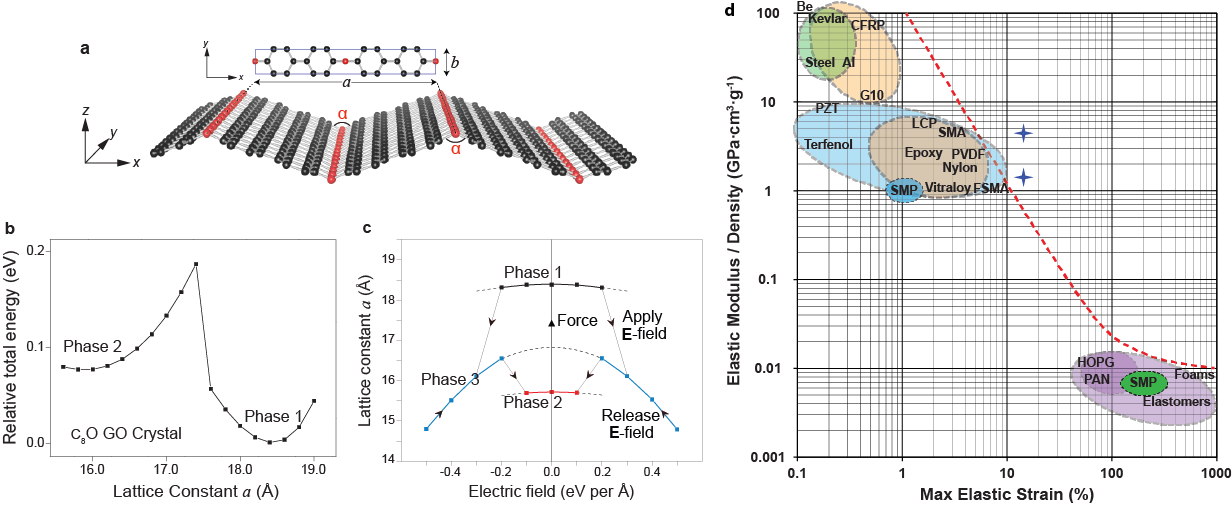
**Significance and Innovation**

It is well recognized that the miniaturization of electromechanical devices will bring a revolution to humanity in the coming decades synonymous with the effects of miniaturizing electronic devices in those previous. They promise and deliver a myriad of applications within industry, including those within the automotive, electronics, aerospace, environmental, biomedical, and defence. Devices ranging from micro/nanoscale actuators, resonators, switches, and valves have applications in tasks as diverse as information processing, molecular manipulation, and sensing.

SMMs can be programmed into different shapes and recover to their original shape under different stimuli. *Such unique “****programmable****” and “****responsive****” capabilities make them the best candidate materials in the design of intelligent and automated miniaturised devices*. Indeed, there is an appealing smart device design concept: material-as-machine, in which SMMs can be programmed for deformation/motion following a pre-determined sequence, just like machines but with greater intelligence and flexibility whereby the material can sense and react accordingly.

The last decade has seen extensive researches to demonstrate micro- or nanoscopic shape memory effect (SME) of conventional SMAs and SMPs. Unfortunately, *it has been reported that the SME of conventional SMMs completely vanishes at small size scale*, for example, when the size of a shape memory alloys is smaller than ~30 nm, and when the thickness of shape memory ceramics is below ~10 nm. Another issue associated with conventional SMMs is the thermal stimuli. It leads to a low response rate at 1 Hz and poor controllability since carefully monitoring and controlling are required to avoid overheating and damaging particularly at micro/nanoscale. Therefore, new solution is required to address the huge demand from the applications of miniaturised intelligent and automated devices.

Our recently discovered 2D SMGO (Nature Communications 7:11972, 2016) shown in Fig. 1 and black phosphorene (JACS 138:4772, 2016) are atomically thin. The shape memory mechanism is the “on or off” state of intra-molecular bond/interactions at atomic scale intrigued by electric field (E-field) or mechanical force. The inherent constraints of conventional SMMs, i.e., vanishing SME at nanoscale, low response rate, and difficulty of thermal control, are resolved. Our SMGO has recoverable strain of 14.5% and specific modulus of 4.5 GPa/(g/cm3). A survey in Fig. 1d shows that our 2D SMGO is well above the upper bound, outperforming all other conventional SMMs.



**Figure 1.** (a) Crystal structure of shape memory C8O. (b) Two stable phases with different angle a = 104o and 131o respectively. (c) Electric field and mechanical force induced reversible phase transition. (d) Superior performance of shape memory graphene oxide (represented by star symbols).

In light of the mature technologies to integrate electronic and mechanical components in MEMS/NEMS, using the 2D SMMs is feasible to design NEMS with novel functions, super-fast response speed, and accurate controllability. Given these outstanding findings, there is no doubt that further exploration of 2D SMMs is important. This project will make a significant contribution to this new research field and advance our understanding of shape memory mechanisms and properties in various 2D materials, which will provide feasible ways to realise full potential of 2D SMMs in NEMS.

**Methodology and research plan**

Our research methodology is *ab initio* density functional theory simulations. The high performance computing facilities will be provided from **Monash e-Research centre** and NCI. There are two research themes.

(1) A novel quantum mechanical shape memory effect.

Our preliminary study suggests electron injection at 0.06e/C-atom could trigger phase transition in GO C16O from the metastable phase to the stable phase. Via utilising mechanical compression, the stable phase could transform back to the metastable phase. Such a reversible phase transition is the origin of the desired SME in SMMs. The calculated recoverable strain is as high as 6.5%. We would term this phenomenon as quantum mechanical SME.

Our comprehensive study indicates the existence of multiple stable phases in monolayer GO crystals with various C/O ratio. In this task, we would like to explore quantum mechanical SME in these compounds and reveal the fundamental physical mechanisms. The obtained knowledge would allow us to design more 2D SMMs with similar effects.

(2) SME of monolayer monochalcogenides through adatoms adsorption.

Our study suggested that Li adatom adsorption could introduce two stable phases in black phosphorene. A special Li-P chemical bond stabilizes the metastable phase. Interestingly applying an external E-field perpendicular to the basal plane can turn on or off this special chemical bond, leading to the reversible phase transition and thus the SME. We denote such a special bond as *adatom switch*. Since in 2D materials all the atoms are on the surface, adatom or molecule adsorption could result in structural changes of whole crystal and generate novel multiple stable phases, which is not attainable in other materials. We propose that adatom switch could be a general strategy/approach to design 2D SMMs. In this task, we will examine this potentially general design strategy in monochalcogenide family (i.e. BP, SiS, SiSe and GeS).

There are two folds of outcomes: (1) a justified general design strategy for 2D SMMs, and (2) a set of shape memory monochalcogenide materials. Note that some of the monolayer monochalcogenides do not have intrinsic SME. Introducing adatom switch can convert these materials as SMMs.