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# Newsletter e-Science Putra

HIGHLIGHTS
- First-principles investigation of graphene, silicene and germanene
- Towards the self-healing crack
- Sparse optimal control
- Electrochemical sensing of ionizable drugs
- DNA barcoding

Welcome to the Newsletter e-Science Putra. This issue present research activities from September until December 2022 which highlights the latest research findings and activities by the faculty members.

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## First-Principles Investigation of Graphene/Silicen and Graphene/Germanene Heterobilayers

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Graphene, silicene and germanene are two-dimensional nanomaterials with various applications in novel electronic and spintronic devices. Although having multiple superior properties, they are still plagued with two major disadvantages namely zero-bandgap and needing a suitable substrate to grow. One possible solution to overcome this issue is by forming a heterobilayer where two monolayers are stacked on each other. In our work, silicene and germanene are stacked on top of graphene which works as a substrate. Stabilities and electronic properties of graphene/silicene ($Si_2C_6$) and graphene/germanene ($Ge_2C_6$) are investigated in three different stacking configurations which are top, hollow and bridge configurations (Figure 1) using density functional theory.

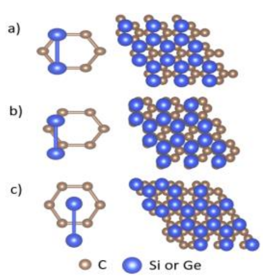


**Figure 1:** Stacking of ($\sqrt{3} \times \sqrt{3}$) R30° graphene with silicene or germanene in a) top b) bridge and c) hollow configuration.

From structural optimization, both $Si_2C_6$ and $Ge_2C_6$ are the most stable when they are in top stacking followed by hollow and bridge configuration. The stability of the structure is considered based on the largest binding energy of the stacking configuration. Due to the broken inversion symmetry from the stacking, the top configuration for $Si_2C_6$ and $Ge_2C_6$ produce a bandgap of 32 meV and 60 meV respectively (Figure 2a). $Si_2C_6$ and $Ge_2C_6$ are held together by van der Waals (vdW) forces because of the weak charge transfer from graphene to silicene or germanene monolayer (Figure 2c) and the lack of new electronic states formed from the hybridization of C, Si and Ge atomic orbitals. As perpendicular strain increases, the interlayer distance between the monolayers decreases due to a stronger vdW interaction which eventually increases the bandgap of the heterobilayers (Figure 2b).

The results have shown that the bandgap of the heterobilayers can be altered and modulated by controlling the stacking configuration and interlayer distance. This work provides useful information and options to experimentalists in the development of better materials for nanoelectronics, solar cells, optoelectronic and spintronics.

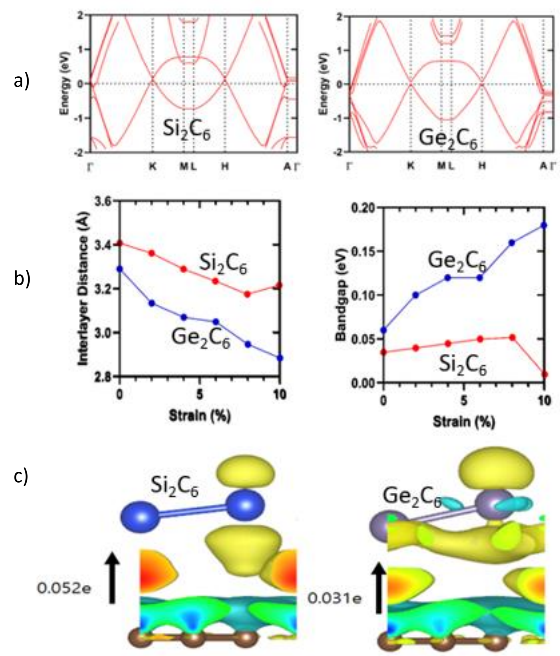


**Figure 2:** a) Band structure of top configuration heterobilayer b) interlayer distance and bandgap when strain is applied and c) charge transfer.

**References**

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# Towards The Self-Healing Crack: An Experiment With Indigeneous Bacteria

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Microbially Induced Calcite Precipitation (MICP) is a biomineralization technique that involves a biochemical process of precipitating calcium carbonate (CaCO3) crystals induced by active bacterial activity as a result of chemical reactions in the environment. Ureolysis has been reported to be more advantageous for a variety of technical applications due to its energy efficiency and ability to produce a large amount of CaCO3 in a short period of time (Figure 1). The success of the MICP process is primarily influenced by in situ conditions such as particle size and distribution, temperature, water content, and treatment conditions such as cementation solution and bacteria concentrations (Saad et al, 2023). Despite numerous advances in MICP, the obtained microorganisms are frequently associated with drawbacks such as a reduction in the population of the introduced bacteria into the soil due to competition, mechanical stress, and predation caused by the organisms' non-adaptability to the local environment. Furthermore, introduced bacteria can have a negative impact on soil microbial communities by altering the ubiquitous interactions between soil microorganisms and changing the traits expressed by these microbial communities (Dardau et al, 2021).

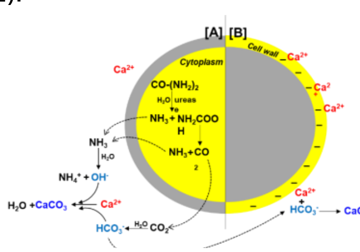


**Figure 1:** Summary of calcium carbonate ($CaCO_3$) formation via two methods; [A] Net breakdown of urea producing $NH_3$ and $CO_2$ which later were broken to form $OH^-$ and $HCO_3^-$ ions, respectively and combine with $Ca_2^+$ from the environment; [B] Negatively charged bacteria well call attract $Ca_2^+$ and form a 'nucleus' for $HCO_3^-$ attachment and form $CaCO_3$ (Dardau *et al.,* 2021).

Our research focuses on the use of indigenous bacteria species, particularly in Malaysian soil. Notably, indigenous microorganisms distributed within the soil environment can be enriched in situ (bio-stimulation) by changing local environmental conditions that promote the diversity and distribution of the existing bacterial community with required urease capabilities for various MICP applications. A recent discovery shows that Bacillus cereus and B.paramycoides can increase the calcite content of bio-stimulated MICP treatment of expansive soil with indigenous ureaseproducing bacteria by up to 205%. (Dardau 2021).

Scanning electron microscopy (SEM) microanalysis of precipitated CaCO3 crystals revealed CaCO3 crystals of various sizes (2.0m - 23.0m) with various morphologies such as agglomeratedrhomboids, cubic, flower-like, and irregular shaped crystals. XRD confirmed that the precipitated CaCO3 is mostly calcite with a few aragonites. SEM micrographs of organic and sandy clay soils treated by B.cereus and B. paramycoides revealed the formation of bio-precipitated calcium carbonate deposited on soil particles (Figure 2). As a result, the use of indigenous urease-producing bacteria as agents for MICP applications is confirmed. The findings of this study are expected to serve as a foundation for the establishment of a reference on an improved, simple, environmentally friendly, and natural bio-mediated soil improvement method based on the precipitation of calcium carbonate by in situ soilureolytic bacteria with high urease activity crystals.

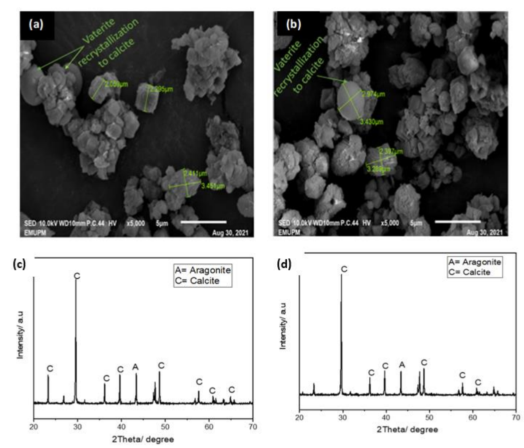


**Figure 2:** SEM micrographs of precipitated calcium carbonate crystals by (a) *Bacillus cereus* and (b)) *Bacillus paramycoides;* XRD spectra of precipitated calcium carbonate crystals by (c) *Bacillus cereus* (d) *Bacillus paramycoides*.

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# Sparse Optimal Control with Less Interference for Large-scale Interconnected Systems

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A standard optimal control problem of transferring an input into a desired output through an interconnected network is often described as a linear quadratic distributed control model as follows:

$$\dot{x} = Ax + B_1 d + B_2 u;$$

$$\dot{z} = Ex + Du,$$

where $x \in R^n, d \in R^q, u \in R^m$ and $z \in R^s$ is the state variable, disturbance, control variable, and (performance) output, respectively, $E = \begin{bmatrix} Q^{\frac{1}{2}} & 0 \end{bmatrix}^T \in R^{s\times n}$ and $E = \begin{bmatrix} 0 & R^{\frac{1}{2}} \end{bmatrix}^T \in R^{s\times m}$, with $Q = Q^T$ and $R = R^T$ is the state and performance weights, respectively. By letting the control $u = -Kx$, where $K \in R^{m\times n}$ denotes the state-feedback matrix, then the associated optimal control can be obtained by solving the following problem:

$$min_K \; tr(PB_1 B_1^T),$$

where $P \in R^{n\times n}$ is the observability Gramian satisfying the Lyapunov-Riccati (LR) equation:

$$(A - B_2 K)^T P + P(A - B_2 K) + Q + K^T RK = 0.$$

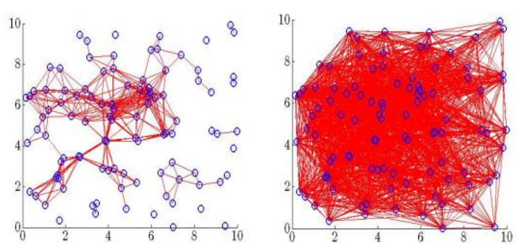

**Figure 1:** Left: Sparse-enhanced network structure; Right: Conventional structure.

This classical optimal control design often results a dense feedback matrix, implying that the optimal controllers are formed using information from all subsystems carried in $K$. However, in large networks of dynamical systems controllers that based on dense feedback matrix may impose prohibitively expensive setup cost and computation burden. Moreover, in many applications, the communication graph does not have to be fully connected since the subsystems are dynamically coupled to each other and allowed to control their own states.

Hence, it is clearly desirable to obtain a higher sparsity feedback matrix to reduce the setup cost for controllers that control the interconnected systems, especially when the size of the system is large. This kind of optimal control framework is applied to multiagent systems, optimal actuator placement, nodes selection, cellular mobile phone networks and robotics, to name a few. To generate more simple control law where the controllers can be switched off completely on parts of the time domain, the following new model is proposed and solved via the proximal alternating direction multipliers method:

$$min_K \; ||K||_0$$

$$s.t. \; tr(PB_1 B_1^T) \le tol,$$

where $P$ and $K$ satisfy the LR equation.

To illustrate the applicability of the new model formulation and solution method, a signal distribution problem of some cellular mobile network with $n^2$ unstable nodes is considered.

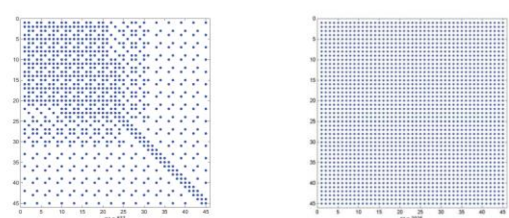

**Figure 2:** Left: Sparse feedback matrix; Right: Conventional dense feedback matrix.

From Figure 1, one can see that by letting the subsystems be dynamically coupled to each other and allowed to control their own states as long as the overall performance is within an acceptable margin, the number of local connections will be greatly reduced. Mathematically, this translates to control problems for obtaining a sufficiently sparse feedback matrix that governs the control law (see Figure 2).

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# Electrochemical Sensing of Ionizable Drugs at Liquid-Liquid Interfaces

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Ion transfer via the liquid-liquid interface has been of growing attention in several chemical and biological applications, such as the behaviour of drugs, membrane transport, and electrochemical liquid-liquid extraction. The utilization of electrochemical sensing platforms can be a solution for an on-line detection without the need of sample extraction. The method has evolved from the transfer of small molecules, such as model ions (tetraalkylammonium ion), to the detection of various bioactive substances, including amino acids, peptides, proteins, neurotransmitters, drugs, DNA, and food additives. It also offers the advantages of simplicity of instrumentation, ease of miniaturisation, and portability. Dr. Ruzniza's research group has focused on the characterization and application of ion transfer at the interface between two immiscible electrolyte solutions (ITIES) using cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

The research is based on the application of liquid-liquid electrochemistry to study the behaviour of diclofenac anions ($DCF^-$) and dibucaine cations ($DIC^+$) on such regular ITIES, and in particular on the study of the pH ranges of the aqueous phase where the target drugs are ionised. Subsequently, important modifications has been made to the ITIES to improve the analytical performance and achieve lower detection limits and better sensitivity. This miniaturisation of the interface to micrometre size leads to improved diffusion rates for molecules in the aqueous phase, resulting in higher sensitivity and lower detection limits. Some thermodynamics variables for $DCF^-$ and $DIC^+$, such as the standard Gibbs free energy of transfer, the standard transfer potential and lipophilicity were extimated. Electrochemical detection was also tested at ITIES for the direct determination of benzodiazepines drug in biomimetic (artificial serum and saliva) and biological fluids (human urine). The influence of individual components of biological fluids on microinterfaces and the concerted influence of realistic mixtures have been studied. These studies have led to new insights into the analytical chemistry of pharmaceutical substances.

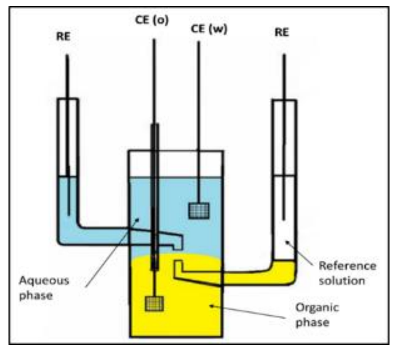


**Figure 1:** Four-electrode cell employed for macro-ITIES system.

| | | | | | | |
|---|---|---|---|---|---|---|
| Ag | AgCl | 1.0 mM $BTPPA^+Cl^-$ in 10 mM LiCl (Water) | 10 mM $BTPPA^+TPBCl^-$ (1,6-DCH) | x μM drug /$TMA^+$ in 10 mM LiCl (Water) | AgCl | Ag |

**Scheme 1:** The electrochemical cell used for micro-ITIES system.

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E.M. Almbrok, N.A. Yusof, J. Abdullah, R.M. Zawawi. Electrochemical Detection of Diclofenac and Dibucaine in Synthetic Saliva using Liquid vertical bar Liquid Micro-Interface Modified by Silicon Nitride. 2021. Int. J. Electrochemical Science. 16(11). 211254.

# DNA Barcoding Resolved Taxonomic Identity and Relationship Status for Morphologically Resemblance Butterflies of the genus

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The butterflies of the genus *Eurema* are classified under family Pieridae and typically recognised by the bright to pale lemon-yellow coloured ground wings, bordered with black apical margin on both sides of forewings (Corbet & Pendlebury, 1992). *Eurema* butterfly are notoriously difficult to identify due to their close morphological resemblance (Mal et al., 2014). This factor has limited the use of morphological characteristics for accurate species identification and have created competing arguments on the number of species, taxonomic position, and nomination of numerous subspecies. Among the species members, *Eurema hecabe* Linnaeus, 1758 is of particular interest because it was reported to exhibit several morphological variations of the black apical border pattern, and wing marking on forewing underside. These patterns were reported to differ seasonally and geographically (Corbet & Pendlebury, 1992) and by elevation (Azrizal-Wahid et al., 2015). The implementation of DNA barcoding for revealing the status and complexity of the insect genus or species have been advocated in more recent years (Hebert et al., 2003).

In this study, the phylogenetic relationships among species of the genus *Eurema* from Peninsular Malaysia were reconstructed using nucleotide sequences of mitochondrial CO1 (307 bp) and nuclear ribosomal 28S DNA (471 bp). The nucleotide compositions for *Eurema* CO1 sequences have strong AT bias similarly as observed in most insect mtDNA CO1 sequences (Tan et al., 2010). A total of twenty-eight sequences generated through PCR amplification for each gene region were concatenated and used to construct the Maximum Likelihood (ML) phylogenetic tree. The generated phylogenetic tree (Figure 1) reveals a strongly supported monophyletic group of *Eurema* conspecifics and well-resolved interspecific genetic distances, indicating the usefulness of the utilized genetic markers as DNA barcoding in local species identification. The results confirm that most of the species defined based on morphological characters here are also monophyletic by molecular data, thereby further supporting the validity of their species status and the accuracy of the morphological identification. Moreover, the phylogenetic analyses strongly support a close relationship of morphological variant species *E. hecabe* that closely related with *E. blanda* while also revealed the sister relationships of *E. andersonii* with *E. ada*.

Although the present work involves the data from partial mtDNA CO1 and 28S rRNA, the information generated is valuable in DNA barcoding study directed to the molecular identification of *Eurema* species particularly in Malaysia.

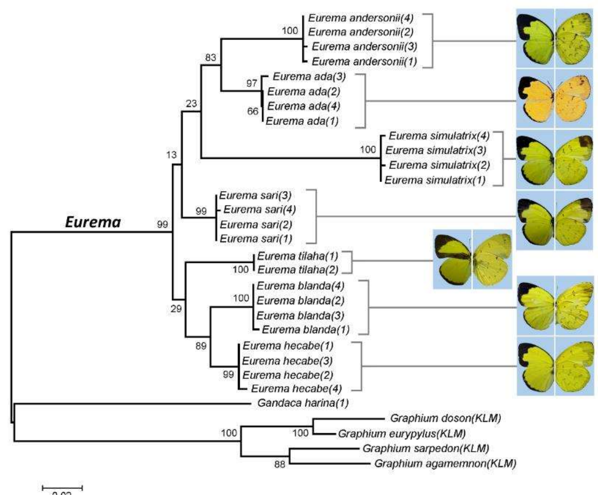


**Figure 1**. Maximum Likelihood output phylogram for CO1-28S concatenated sequence data showing seven major clades representing the seven *Eurema* species obtained from this study. Bootstrap scores are shown at the branching points. The tree was rooted with the genus *Graphium*. The butterfly figures show the comparison of morphology among the species corresponding to their respective clades. Figures of butterflies provided as upperside of the wings (left) and downside of wings (right). (Figure adopted from Azrizal-Wahid et al., 2021)

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**Science is much more than just a body of KNOWLEDGE.**
**It is a way of THINKING.**



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