On the Spectroscopic Analyses of Polytetrafluoroethylene Coated with Nano ZnO and SiO2

Maroof A. Hegazy  
National Research Institute of Astronomy and Geophysics

Rasha Ghoneim  
National Research Institute of Astronomy and Geophysics

Hend A. Ezzat  
National Research Institute of Astronomy and Geophysics

Heba Y. Zahran  
King Khaled University

Ibrahim S. Yahia  
King Khaled University - Bisha Campus: University of Bisha

Hanan Elhaes  
Ain Shams University

Medhat Ibrahim (medahmed6@yahoo.com)  
NRC., Egypt  https://orcid.org/0000-0002-9698-0837

Research Article

Keywords: PTFE, Nanocomposites, HOMO/LUMO, Thermal properties, Corrosion-inhibiting, Space application

Posted Date: January 14th, 2022

DOI: https://doi.org/10.21203/rs.3.rs-1066883/v1

License: © Medhat Ibrahim This work is licensed under a Creative Commons Attribution 4.0 International License.  Read Full License
Abstract

On polytetrafluoroethylene (PTFE) polymer nanocomposites coated with basically two metal oxides (MOs), SiO$_2$ and ZnO, as well as a mixture of the two MOs, density functional theory (DFT) computations were performed. The B3LYPL/LAN2DZ model was used to evaluate PTFE polymer nano composites suggested model structures. The physical and electrical properties of PTFE modified on surface with ZnO and SiO$_2$ coated layer by layer change Total dipole moment (TDM) and HOMO/LUMO band gap energy $\Delta E$ to be 13.0082 Debye and 0.6889 eV, respectively. Moreover, TDM and band gap energy ($\Delta E$) improved to 10.6053 Debye and 0.2727 eV, respectively, when the nanoller was increased to 8 atoms. In addition, the results of the Molecular Electrostatic Potential (MEP) and the Quantitative Structure Activity Relationship (QSAR) showed that PTFE coated with ZnO and SiO$_2$ improved electrical characteristics and thermal stability. As PTFE coated with ZnO and SiO$_2$ layer by layer, all stability characteristics, including electrical and thermal stability, were enhanced. The improved PTFE can be used as a corrosion-inhibiting layer for astronaut suits, according to the predicted results.

1. Introduction

Polymers such as polyethylene naphthalate (PEN), polyethylene terephthalate (PET), and PTFE, are known according to their corrosion resistance and electrical characteristics, as well as low coefficient of friction, high temperature resistance, and cost efficiency [1]. PTFE is a polymer matrix with a low surface energy and is chemically and thermally stable [2]. The effective manufacturing of a wide range of sensors is enabled using PTFE as a substrate for the growth of ZnO nanotubes, as well as its mechanical, physical, and chemical characteristics [3]. Nanoscale photodetectors made of ZnO nanotubes coated on PTFE substrate were demonstrated to be useful in nano-optical applications [4]. Silica is a ceramic material with several unique properties, including high hardness, corrosion resistance, and outstanding electrical insulation [5]. All these properties make SiO$_2$ and PTFE ideal materials for a wide variety of technical applications [6]. Super hydrophobic materials have become an extraordinary advantage in number of applications, including self-cleaning, anti-icing, anti-corrosion, and protective properties such as high efficiency [7]. In addition, combining SiO$_2$ with semiconductor oxide materials such ZnO [8], TiO$_2$ [9], Fe$_2$O$_3$ [10], and CuO [11] improves the self-cleaning, anti-corrosion, anti-reflective, and magnetic characteristics of nano composite materials. PTFE/SiO$_2$ composite has a superhydrophobic surface when compared to PTFE membranes [12]. PTFE/SiO$_2$ nanofibers have shown to be a reliable invention for oily vapor purification due to their excellent thermal and chemical stability [13]. Doping PTFE with SiO$_2$ reduces PTFE porosity deformation while simultaneously increasing the material's tensile strength and endurance. As the quantity of SiO$_2$ in the PTFE/SiO$_2$ composite increased, so did the mechanical characteristics [14]. The tribological efficiency of PTFE/SiO$_2$/Epoxy composites is also studied [15]. The effect of Al$_2$O$_3$ nanoplatelets on PTFE matrix was observed to increase thermal conductivity, thermal stability, and enhance mechanical properties with significant electrical properties [16]. Furthermore, the electrical characteristics of the PANI/PTFE/GO composite have improved to be employed in the fabrication of electrochemical instruments [17]. The ZnO/SiO$_2$/PTFE film over glass was made with anti-icing properties, corrosion resistance and insulation properties acting as anti-icing surface [18]. Furthermore, some derivative of PTFE such as Teflon FEP used as thermal control layer for Hubble Space Telescope (HST) [19–21]. Teflon FEP suffering from corrosion according to the space environment in the low Earth orbit (LEO) [22]. This exposes the component in space to damage and corrosion [23, 24]. Consequently, improving PTFE and its derivatives has been a valuable study for space applications [25, 26].

Knowing that physical parameters such as TDM, HOMO/LUMO band gap energy ($\Delta E$), and MEP were measured using molecular modeling. These physical parameters are regarded to be efficient predictors of electrical properties as well as the reactivity of the studied interactions [27–31]. Furthermore, QSAR provides important information on...
molecular behaviors, which evaluates the chemical, biological, and physical activity of molecules used in a numerous application [32–35].

The aim of our work is to improve PTFE with physicochemical properties using two nano MOs such as ZnO, SiO₂ separately and together to improve anti-corrosion and self-cleaning property. Molecular modelling and QSAR descriptors should be used to investigate electronic characteristics as well as thermal, physical, and chemical stability.

2. Computational Details

PTFE model molecules interacted with two nano MOs such as ZnO, SiO₂ separately and together were calculated using GAUSSIAN 09 program at Molecular Spectroscopy and Modeling unite, National Research Centre (NRC), Egypt [36]. The PTFE supposed models were optimized using DFT:B3LYP/LANL2DZ [37–39]. Electronic properties were studied including HOMO/LUMO band gap (ΔE), TDM and MESP. Furthermore, calculation was conducted for the same models using SCIGRESS 3.0 software [40] to study chemical and thermal stability. QSAR parameters were calculated for model structures using MO-G at PM6 level [41].

3. Result And Discussion

3.1 Building PTFE Model Structures:

To increase hydrophobicity, anti-corrosion and self-cleaning properties, PTFE was designed to be coated with MOs [42]. ZnO and SiO₂ were suggested as coating layers because to their anti-corrosion and self-cleaning characteristics [43, 44]. Accordingly, PTFE monomer is designed to interact with ZnO and SiO₂ separately and in mixture. The interaction of PTFE with MOs takes place via the oxygen atom of the MO [45]. Because PTFE interacts with other chemical structures via its active sides, which have four equal active sides according to the chemical formula C₂F₄, any fluor atom can interact with other chemical structures.

As indicated in figure (1-a), the PTFE monomer was made up of four units of C₂F₄ that were designed to interact with the suggested two MOs. First, the PTFE monomer was designed to interact with the two MOs that were separately coated on one side, as shown in figure (1-b) (1-c). After that, the PTFE monomer is designed to interact with a combination of ZnO and SiO₂ covered layer by layer, then as a single mixed layer of (ZnO/SiO₂) as illustrated in figures (1-d) to (1-f). Consequently, increasing the quantity of nanoparticles on the polymer surface has a significant impact on the electrical properties of the polymer matrix [46]. The PTFE monomer is next expected to be coated from both sides, as previously done with ZnO and SiO₂ individually and in combination, as shown in figure (2). As a result, the electrical characteristics represented by TDM, HOMO/LUMO band gap energy (ΔE), and MESP for PTFE supposed interactions were evaluated as follows.

3.2 HOMO/LUMO orbital distribution:

Figure 3 illustrates the HOMO/LUMO orbital distribution of PTFE and its interactions with 4 ZnO and SiO₂, and their hybrid. The HOMO/LUMO orbital dispersing of four PTFE monomers is demonstrated to be spread across the monomer chain, but when PTFE interacted with ZnO and SiO₂, the HOMO/LUMO orbitals were localized around the MO as shown in figure 3.

TDM and HOMO/LUMO band gap (ΔE) were also determined for different forms of interactions. TDM improved from 0.0000 for pure PTFE to 16.2350, 1.8486, 13.0082, 17.4318 and 11.5828 Debye for PTFE/4ZnO, PTFE/4SiO₂,
PTFE/4ZnO/4SiO₂, PTFE/4SiO₂/4ZnO and PTFE/(4ZnO@4SiO) as seen in Table 1. As well, the calculated HOMO/LUMO band gap energy show values reduced from 8.517 to 1.5347, 4.3016, 0.6889, 1.3451 and 0.9578 eV respectively. Therefore, the lowest band gap \( \Delta E \) was recorded for PTFE/4ZnO/4SiO₂ structure. It is well known that increasing the reactivity of chemical systems is always assessed by having a high TDM when the energy band gap \( \Delta E \) is minimal [47].

**Table 1** TDM (Debye) and band gap energy \( \Delta E \) (eV) for PTFE and PTFE interacted with 4ZnO, SiO₂ and a combination between the two MOs using DFT: B3LYP/LANL2DZ.

<table>
<thead>
<tr>
<th>Structure</th>
<th>TDM(Debye)</th>
<th>( \Delta E )(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>00.000</td>
<td>8.517</td>
</tr>
<tr>
<td>PTFE/4ZnO</td>
<td>16.2350</td>
<td>1.5347</td>
</tr>
<tr>
<td>PTFE/4SiO₂</td>
<td>1.8486</td>
<td>4.3016</td>
</tr>
<tr>
<td>PTFE/4ZnO/4SiO₂</td>
<td>13.0082</td>
<td>0.6889</td>
</tr>
<tr>
<td>PTFE/4SiO₂/4ZnO</td>
<td>17.4318</td>
<td>1.3451</td>
</tr>
<tr>
<td>PTFE/(4ZnO@4SiO)</td>
<td>11.5828</td>
<td>0.9578</td>
</tr>
</tbody>
</table>

Figure 4 illustrates the assumption for increasing the number of nanoparticles to 8 particles HOMO/LUMO orbital distribution. TDM and HOMO/LUMO band gaps (\( \Delta E \)) were determined. TDM improved from 0,0000 corresponding to pure PTFE to 32.9344, 0.8668, 7.8439, 10.6053 and 6.9625 Debye while the HOMO/LUMO band gap was observed to decrease from 8.517 to 0.1633, 3.2534, 0.8596, 0.2727 and 0.3684 eV for PTFE/8ZnO, PTFE/8SiO₂, PTFE/8ZnO/8SiO₂, PTFE/8SiO₂/8ZnO and PTFE/(8ZnO@8SiO₂) respectively, as indicated in Table 2. The lowest value of the HOMO/LUMO band gap was reported for PTFE/8ZnO and PTFE/8ZnO/8SiO₂ as an indication of the most possible interactions that enhanced the electrical characteristics of the PTFE. Furthermore, as the quantity of nanoparticles increased, so did the improvement of electrical characteristics. Thus, from all PTFE interactions with MO, the most enhanced PTFE structure interacted with 4 MOs was PTFE/4ZnO/4SiO₂, but with increasing nanoparticles to 8 atoms, the most enhanced structure was PTFE/8ZnO and PTFE/8ZnO/8SiO₂, which means that the electronic behavior modified with increasing number of interacted particles with PTFE polymer.

**Table 2** TDM (Debye) and band gap energy \( \Delta E \) (eV) of PTFE and PTFE interaction with 8 ZnO, SiO₂ and a combination between the two MOs using DFT: B3LYP/LANL2DZ level of theory.

<table>
<thead>
<tr>
<th>Structure</th>
<th>TDM(Debye)</th>
<th>( \Delta E )(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>00.000</td>
<td>8.517</td>
</tr>
<tr>
<td>PTFE/8ZnO</td>
<td>32.9344</td>
<td>0.1633</td>
</tr>
<tr>
<td>PTFE/8SiO₂</td>
<td>0.8668</td>
<td>3.2534</td>
</tr>
<tr>
<td>PTFE/8SiO₂/8ZnO</td>
<td>7.8439</td>
<td>0.8596</td>
</tr>
<tr>
<td>PTFE/8ZnO/8SiO₂</td>
<td>10.6053</td>
<td>0.2727</td>
</tr>
<tr>
<td>PTFE/(8ZnO@8SiO₂)</td>
<td>6.9625</td>
<td>0.3684</td>
</tr>
</tbody>
</table>

3.3 Molecular Electrostatic Potential (MESP):
MESP mapping was calculated for PTFE/4ZnO, PTFE/4SiO₂, PTFE/4ZnO/4SiO₂, PTFE/4SiO₂/4ZnO, PTFE/(4ZnO@4SiO₂), PTFE/8ZnO, PTFE/8SiO₂, PTFE/8ZnO/8SiO₂, PTFE/8SiO, PTFE/8SiO₂ and PTFE/(8ZnO@8SiO₂) utilizing DFT: B3LYP/LANL2DZ level of theory. The MESP maps were demonstrated in figure 5 to map the interaction status of nucleophilicity. The MESP map displays the measurement of the nearby charges, nucleus, and density of electrons at a particular position, that color variation of MESP map is identified as red<orange<yellow<green<blue. The color difference in the MESP diagram, red, pointed to the lowest MESP level and the highest MESP value is achieved by blue. MESP map for all considered PTFE interactions colored with intermediate colors between orange and yellow represents less electrostatic repulsion, suggesting that there is still no chance of interfering with others and representing more chemical equilibrium.

3.4 Quantitative Structure Activity Relationship (QSAR):

Table 3 defines QSAR descriptors trying to describe PTFE relationships with MOs as PTFE/4ZnO, PTFE/4SiO₂, PTFE/4ZnO/4SiO₂, PTFE/4SiO₂/4ZnO, PTFE/(4ZnO@4SiO₂), PTFE/8ZnO, PTFE/8SiO₂, PTFE/8ZnO/8SiO₂, PTFE/8SiO₂/8ZnO and PTFE/8ZnO/8SiO. Descriptors are summarized as total energy (TE), heat formation (HF), ionization potential (IP), log P, polarizability, molar refractive (MR) and molecular weight (MR).

Firstly, TE stated to describe the stability of the system, that reducing TE values make the structure toward stability [48]. TE for PTFE/4ZnO, PTFE/4SiO₂, PTFE/4ZnO/4SiO₂, PTFE/4SiO₂/4ZnO, PTFE/(4ZnO@4SiO₂), PTFE /8ZnO, PTFE/8SiO₂, PTFE /8ZnO/8SiO₂, PTFE/8SiO₂/8ZnO and PTFE/(8ZnO@8SiO) were -17005.449, -18409.137, -20012.6279, -10891.274, -931.8992, -932.3680, -11544.3399, -234.1352, 2414, -2414.11264, -25976.1659 and -25973.3683eV represent a high stable compound for PTFE/8SiO/8ZnO.

From there, HF is a significant thermal descriptor that defines the energy produced in the form of heat, as the atoms exist at potentially infinite distances are linked and form a molecule [49]. Even though HF involved, may be clarified through difference observed in the enthalpy during the formation of a single mole of a substance from its components. This occurs in its natural and full balance under the atmospheric regular characteristics of a particular temperature. Then HF were calculated PTFE/4ZnO, PTFE/4SiO₂, PTFE/4ZnO/4SiO₂, PTFE/4SiO₂/4ZnO, PTFE/(4ZnO@4SiO₂), PTFE /8ZnO, PTFE/8SiO₂, PTFE /8ZnO/8SiO₂, PTFE/8SiO₂/8ZnO and PTFE/(8ZnO@8SiO) which equal to -1570.772, -1826.101, -1963.531, -2598.762, -2457.839, -2266.677, -234.1352, 2414, -214.11264, -25976.1659 and -25973.3683eV represent a high stable compound for PTFE/8ZnO/8SiO.

After that the ionization potential (IP) were evaluated for PTFE model interactions. That the IP value reects the reactivity of a specific structure (the energy required for the material to be ionized), as the IP value decreases with increasing reactivity of certain compounds [50]. The analysis suggests that there was no important change in IP that the values recorded equal -12.980, -9.417, -9.446, -8.746, -8.953, -10.573, -9.737, -11.648, -8.420, -8.733 and -10.392. The lowest reactive and most thermally enhanced structure was PTFE/8ZnO/8SiO.

Hydrophilicity of the chemical structure was described by logarithm of the partition coefficient (log P). It calculates the solubility of the substance even in an organic solution or in aqueous solvents. As positive log P values define the hydrophobic structures while negative values indicated for hydrophilic structures [51]. Then all proposed models recorded a positive log P in which being an indicator that the structures are hydrophobic and are chemically soluble and have not affected the surrounding environment.
Consequently, polarizability is a basic property that determines how the chemical formula could be polarized in response to varying forces. Representing the responsiveness of the structural factors affect their volume and molar refractor is a descriptor which can specify the overall polarization of the mole [52]. The greater the molar refractor, the greater the reactivity of the structures which recorded to PTFE/4ZnO/4SiO with value equal to 53.616 and PTFE/8ZnO/8SiO with value equals to 79.960.

Table 3 PTFE and PTFE interaction with of ZnO, SiO$_2$ and the combination of both MOs QSAR calculations at PM6 level descriptors as Total Energy(ev), Heat of formation (HF), Ionization potential (eV), Log P, Polarizability, Molar refractive (MR), molecular weight (MW) which were calculated at PM6 semiempirical method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TE</th>
<th>HF</th>
<th>IP</th>
<th>Log P</th>
<th>Polarizability</th>
<th>MR</th>
<th>MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE</td>
<td>-17005.449</td>
<td>-1570.772</td>
<td>-12.980</td>
<td>12.374</td>
<td>28.228</td>
<td>76.442</td>
<td>802.136</td>
</tr>
<tr>
<td>PTFE/4ZnO</td>
<td>-18409.137</td>
<td>-1826.101</td>
<td>-9.417</td>
<td>10.968</td>
<td>44.629</td>
<td>1127.770</td>
<td>1127.770</td>
</tr>
<tr>
<td>PTFE/4SiO$_2$</td>
<td>-20012.627</td>
<td>-1963.531</td>
<td>-9.446</td>
<td>9.562</td>
<td>38.934</td>
<td>1042.473</td>
<td>1042.473</td>
</tr>
<tr>
<td>PTFE/4ZnO/4SiO$_2$</td>
<td>-931.8992</td>
<td>-2457.839</td>
<td>-8.953</td>
<td>8.157</td>
<td>49.835</td>
<td>1368.107</td>
<td>1368.107</td>
</tr>
<tr>
<td>PTFE/(4ZnO@4SiO$_2$)</td>
<td>-932.3680</td>
<td>-2266.677</td>
<td>-10.573</td>
<td>8.157</td>
<td>53.616</td>
<td>1368.107</td>
<td>1368.107</td>
</tr>
<tr>
<td>PTFE/8ZnO</td>
<td>-11544.3399</td>
<td>-1871.705</td>
<td>-9.737</td>
<td>9.562</td>
<td>38.636</td>
<td>1453.403</td>
<td>1453.403</td>
</tr>
<tr>
<td>PTFE/8SiO$_2$</td>
<td>-23034.5213</td>
<td>-2597.869</td>
<td>-11.648</td>
<td>6.751</td>
<td>49.139</td>
<td>1282.810</td>
<td>1282.810</td>
</tr>
<tr>
<td>PTFE/8SiO$_2$/8ZnO</td>
<td>-2414.11264</td>
<td>-2372.734</td>
<td>-8.420</td>
<td>3.940</td>
<td>77.496</td>
<td>1934.078</td>
<td>1934.078</td>
</tr>
<tr>
<td>PTFE/8ZnO/8SiO$_2$</td>
<td>-25976.1659</td>
<td>-3128.116</td>
<td>-8.733</td>
<td>3.940</td>
<td>76.588</td>
<td>1934.078</td>
<td>1934.078</td>
</tr>
<tr>
<td>PTFE/(8ZnO@8SiO$_2$)</td>
<td>-25973.3683</td>
<td>-3300.601</td>
<td>-10.392</td>
<td>3.940</td>
<td>79.960</td>
<td>1934.078</td>
<td>1934.078</td>
</tr>
</tbody>
</table>

The results throughout the expected interaction between PTFE and MOs, a coating of ZnO with SiO$_2$ on PTFE as PTFE/4ZnO/4SiO$_2$ as well as increasing MOs forming both structures such as PTFE/8ZnO and PTFE/8ZnO/8SiO$_2$ layer by layer improve electronic and thermal stability. These enhancements serve as a corrosion-inhibiting and self-cleaning layer for astronaut suits.

4. Conclusion

DFT calculations of PTFE monomer modified with 4 and 8 units of nano metal oxides ZnO and SiO$_2$ separately and hybrid were subjected to enhance chemical, physical and thermal stability. The results showed that the most improved PTFE structure is PTFE/8ZnO/8SiO layer by layer and PTFE/8ZnO, that with increasing MOs the polymer characteristics improving. MESP maps suggested that the studied structures show electronic enhancement. Furthermore, QSAR calculations indicated that coating PTFE as PTFE/8ZnO/8SiO$_2$ layer by layer improve electronic and thermal stability and hydrophobicity property. Correlating a results one can dedicated the modified PTFE with ZnO and SiO$_2$ layer by layer could be used as anti-corrosion and self-cleaning layer for astronaut suits.

Declarations
Acknowledgements

The authors extend their appreciation to the Scientific Research Deanship at King Khalid University and the Ministry of Education in KSA for funding this research work through the project number IFP-KKU-2020/10.

funding:

(King Khalid University and the Ministry of Education in KSA for funding this research work through the project number IFP-KKU-2020/10).

Conflicts of interest/Competing interest: (N/A)

Availability of data and material: (N/A)

Code availability: (N/A)

Authors’ contributions: (Dr. Maroof A. Hegazy wrote the result and discussion, Dr. Rasha Ghoneim wrote the introduction of the manuscript, Hend A. Ezzat calculated the model structures, Prof. Ibrahim S. Yahia and Heba Y. Zahran, revised the manuscript, Prof. Hanan Elhaes contribute to the result and discussion writing, and Prof. Medhat A. Ibrahim control the overall the manuscript then revised it and submitted it for publication).

References


Figures

Figure 1
Optimized PTFE and PTFE interaction with 4 ZnO, SiO$_2$ and a combination between the two MOs as

(a) PTFE (b) PTFE/4ZnO (c) PTFE/4SiO$_2$ (d) PTFE/4ZnO/4SiO$_2$ (e) PTFE/4SiO$_2$/4ZnO

(e) PTFE/(4ZnO@4SiO$_2$)

Figure 2

Optimized PTFE and PTFE interaction with 8 ZnO, SiO$_2$ and a combination between the two MOs as

(a) PTFE/8ZnO (b) PTFE/8SiO$_2$ (c) PTFE/8ZnO/8 SiO$_2$ (d) PTFE/8 SiO$_2$/8ZnO

(e) PTFE/(8ZnO@8 SiO$_2$)
Figure 3

DFT:B3LYP/LANL2DZ calculated HOMO/LUMO orbital distribution of PTFE and PTFE interaction with 4ZnO, SiO$_2$ and a combination between the two MOs as

(a) PTFE (b) PTFE/4ZnO (c) PTFE/4SiO$_2$ (d) PTFE/4ZnO/4SiO$_2$ (e) PTFE/(4ZnO@4SiO$_2$)
Figure 4

DFT:B3LYP/LANL2DZ calculated HOMO/LUMO orbital distribution of PTFE interaction with 8 ZnO, SiO$_2$ and a combination between the two MOs as

(a) PTFE/8ZnO  (b) PTFE/8SiO$_2$  (c) PTFE/8ZnO/8 SiO$_2$  (d) PTFE/8 SiO$_2$/8ZnO  (e) PTFE/(8ZnO@8 SiO$_2$)

Figure 5

DFT:B3LYP/LANL2DZ calculated MESP for PTFE and PTFE interaction with ZnO, SiO$_2$ and a combination between the two MOs as

(a) PTFE  (a) PTFE/4ZnO  (b) PTFE/4SiO$_2$  (c) PTFE/4ZnO/4SiO$_2$  (d) PTFE/4SiO$_2$/4ZnO

(e) PTFE/(4ZnO@4 SiO$_2$)  (g) PTFE/8ZnO  (h) PTFE/8SiO$_2$  (i) PTFE/8ZnO/8 SiO$_2$  (j) PTFE/8 SiO$_2$/8ZnO

(k) PTFE/(8ZnO@8 SiO$_2$)

Supplementary Files
This is a list of supplementary files associated with this preprint. Click to download.

- GAbst.jpg