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ARTICLE

Graph Theory and Matrix Approach (GTMA) Model for the Selection of the Femoral-Component of Total Knee Joint Replacement

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ABSTRACT

Total Knee Replacement (TKR) is the increasing trend now a day, in revision surgery which is associated with aseptic loosening, which is a challenging research for the TKR component. The selection of optimal material loosening can be controlled at some limits. This paper is going to consider the best material selected among a number of alternative materials for the femoral component (FC) by using Graph Theory. Here GTMA process used for optimization of material and a systematic technique introduced through sensitivity analysis to find out the more reliable result. Obtained ranking suggests the use of optimized material over the other existing material. By following GTMA CoCr-alloys (wrought-Co-Ni-Cr-Mo) and CoCr-alloys (cast-able-Co-Cr-Mo) are on the 1st and 2nd position respectively.

1. Introduction

Due to the biological and mechanical requirements, major problems for orthopedic biomaterials are their development/design and selection for particular application. Among existing applications of orthopedic biomaterials, total knee replacement (TKR) is a challenging and debating one because of simultaneous replacement and revision surgical procedure. The major severe responsible factors (for TKR revision surgery) are the aseptic loosening and tissue growth at interface of implanted region. The risk of implant loosening and wear debris can be minimized while choosing the optimized material for femoral part of the implant or femoral-component (FC) or tibial insert. Stress shielding (Young’s Modulus) mostly depend upon the material which is directly attached or interfacing the bone like femoral-component (FC) on the upper side and tibial try on the lower side. By taking under consideration this issue given design geometry of knee prosthesis, optimal and best material for the femoral part plays an important role in the aseptic loosening of prosthetic joint [1-4].

Recent days many materials are accessible which might be useful for knee joint femoral-component (FC) usage. However there are some limitations to select the material for this component, to resolve this critical problem there should be a proper tool for the selection of femoral-component (FC). To solve this critical problem there should be a proper tool for the selection of material. Usually a new material or replacement of a material with another material having better working characteristics, applied after testing and error methods or after getting experience from already done experiments. Whereas it can be han-
dled by using Multiple Criteria Decision Making (MCDM) model, misuse of material having heavy cost. MCDM is the basics of selection, grouping, prioritizing, sorting and helpful during the whole assessment of material selection process. For the selection of material not only biological, chemical, physical, electrical, mechanical and manufacturing characteristics necessary but also the knowledge of MCDM. However, the method of MCDM used widely for the material selection in engineering design and somehow in the biological engineering which is growing simultaneously.\[5-10\].

In this paper there is discussion about a method to select a femoral-component (FC) for TKR. This method having 11 scale point, totally based upon MCDM, its compressive name GTMA (Graph Theory with Matrix Approach) which is used for the betterment of durability and quality of human life by selecting an appropriate material for the femoral-component (FC) of knee joint aseptic.

2. GTMA Theoretical Explanation

2.1 Graphical Illustration of Properties

For the illustration of graph there are two main components i.e. “anchor points” and “path” associated with them. One anchor point defines a specific property of material and path associated with this point defines its relationship with other properties. Number of anchor points always depends upon the number of properties on the basis of which a material is going to be selected. If a property ‘p’ has relative importance on the other property ‘q’ then there will be an arrow head on path indicating relative importance of ‘p’ upon ‘q’.

Similarly if property ‘q’ has a relative importance on other property ‘p’ then the direction of path of relative importance will be from ‘q’ to ‘p’. To explain this graph in a better way, let’s take an example of material selection for TKR. There should be some properties depending upon which a material will be selected i.e. P1, P2, P3... P7. Here seven properties are considered so there will be seven anchor points respectively for each property. Path of relative importance will be in both directions because, if a property ‘p’ has relative importance upon ‘q’ then then there will be a relative importance of ‘q’ upon ‘p’ which is similar for the relative importance between all other properties. Graphical illustration is quick view of properties and their relative importance upon each other. If there are more anchor points or more number of properties then there will be a complex graphical illustration, therefore matrix illustration will be used to avoid this situation.

2.2 Matrix Illustration

Whenever a graph becomes more complex then matrix illustration is more helpful. Size of matrix depends upon number of anchor points. If there are N numbers of properties important for the material selection then the size of matrix will be NxN. Therefore it will be always a square matrix.

It always depends upon the numeric values of properties (R_p) and their relative importance (r_{pq}). Here R_p is the value of property ‘p’ and r_{pq} is the relative importance of ‘p’ upon ‘q’. Permanent of matrix ‘Z’ symbolically i.e. per (Z) is also known as material selection properties function. While using this permanent there is no minus sign used, so there will no any part disappear.\[11-13\]. Permanent of matrix is actually its determinant but taking all terms positive. Its mathematical expression is as follows.
For the calculation of permanent of matrix there is a program developed in computer by using C++ language to calculate suitability index.

3. Suitability Index for the Material

Material suitability index is actually a numeric measurement of a material to check in which extent this material can be selected. In the equation given above there is a material selection property function which contains measurement of properties and their correlations which is essential for the Material suitability index. Numeric value of material selection property function is known as the material suitability index. Such as material selection property function has only positive terms so that the highest value of Rp and their relative importance \( r_{pq} \) results greater value of material suitability index, to find out this index numeric values of Rp can be obtained from the data available. After obtaining these values there normalized values calculated corresponding to each property. To solve \( v_p/v_q \) here \( v_p \) is the value of property ‘p’ and \( v_q \) is the value of property q which is greater than \( v_p \). This ratio is suitable for most obligatory property. Here most obligatory property means its higher values are beneficial for selected material, whereas least obligatory properties are those which are beneficial while having low numeric values. There relative normal values can be calculated by \( v_q/v_p \), in this situation the value of \( v_q \) is less than that of \( v_p \) as well as from all other properties.

If there is no numeric values are available for some properties then there values can be adopted by fuzzy conversion scale. By using fuzzy set theory first of all find property Rp find in linguistic terms and then into fuzzy numbers. Chang & Hawng [14] discovered a numerical approximation system in which a linguistic term automatically converted into numeric value. It consists of eight conversion scale, whereas in present work eleven point scales is used as given in the table below.

![Figure 2. Eleven Point Scale for Correlation](image)

Material suitability index evaluated for the different available choices by using the equation given above and by substituting the values of Rp and relative importance \( r_{pq} \). Material having greater suitability index will be the best choice for utilization.

4. Evaluation of Femoral-component (FC) for TKR

Stage 1

At first stage to find out the properties upon which selection of femoral-component (FC) for TKR dependent as well as enlist the available choices of materials which are suitable for the femoral-component (FC) of TKR, which satisfied all the requirements of knee joint aseptic. There are some properties depending upon which we are going to select a material for femoral-component(FC) i.e. Tensile Strength(TS MPa), Density (\( \rho_g/cc \)), Elasticity Modulus (EM GPa), Elongation (%), Wear Resistance(WR), Corrosion Resistance (CR), Osseointegration.

There are some limitations for every selected property either qualitatively or quantitatively which will be suitable for the femoral-component(FC). Here are the listed material and their properties for femoral-component (FC).

Stage 2

After shortlisting find out the material relative importance relation among properties and normalize the values according to most and least obligatory properties.
Table 1. Selected materials and their Compositions for the femoral-component(FC) [9,15-20]

<table>
<thead>
<tr>
<th>Material Number</th>
<th>Material name</th>
<th>Material Composition</th>
<th>TS (Mpa)</th>
<th>EM (Gpa)</th>
<th>Density (g/cc)</th>
<th>Elongation (%)</th>
<th>WR</th>
<th>CR</th>
<th>Osseointegration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni_Ti shape-memory-alloy</td>
<td>Titanium 43.835-45.0%,Nickel 55.0-56.0%, Hydrogen≤ 6 0.0050%,Carbon ≤ 6 0.050%, Oxygen≤ 6 0.050%, iron≤ 6 0.050%, other≤ 6 0.010%</td>
<td>1240</td>
<td>48</td>
<td>6.5</td>
<td>12</td>
<td>0.955</td>
<td>0.955</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>Porous-Ni_Ti-shape-memory-alloy</td>
<td>Titanium, 16%-porosity-Nickle-49.0</td>
<td>1000</td>
<td>15</td>
<td>4.3</td>
<td>12</td>
<td>0.955</td>
<td>0.745</td>
<td>0.955</td>
</tr>
<tr>
<td>3</td>
<td>6Al-Ti-7Nb-(protasul-100 hot_forged)</td>
<td>1000-1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6Al-Ti-7Nb (IMI 367 wrought)</td>
<td>Titanium balancing, 5.50-6.50% Aluminum, 60.080% Nb, 60.050% Carbon, 60.009% Oxygen, 60.25% Nitrogen, 60.20% Oxygen, 60.50% Ta</td>
<td>900</td>
<td>105-120</td>
<td>4.52</td>
<td>10—15</td>
<td>0.665</td>
<td>0.955</td>
<td>0.745</td>
</tr>
<tr>
<td>5</td>
<td>stainless_steel_L316 (annealed)</td>
<td>Fe-balancing,17-20% Molybdenum, 0.03-0.08% Chromium, 10-14% Ni, 2-4% Carbon, 2% Mn and 0.75% Silicon</td>
<td>517</td>
<td>200</td>
<td>8</td>
<td>40</td>
<td>0.59</td>
<td>0.665</td>
<td>0.59</td>
</tr>
<tr>
<td>6</td>
<td>stainless_steel_L316 (cold-worked)</td>
<td></td>
<td>862</td>
<td>200</td>
<td>8</td>
<td>12</td>
<td>0.745</td>
<td>0.665</td>
<td>0.59</td>
</tr>
<tr>
<td>7</td>
<td>Co_Cr-alloys (wrought-Co-Ni-Cr-Mo)</td>
<td>Cobalt-balancing, 19-21% Chromium, 9-11% Nickel, 14.6-16% W, 0.13% Molybdenum, 0.05-0.15% Carbon, 0.48% Silicon &amp; maximum-2%-Mn-and-3% Fe</td>
<td>896</td>
<td>240</td>
<td>9.13</td>
<td>10-30</td>
<td>0.865</td>
<td>0.745</td>
<td>0.665</td>
</tr>
<tr>
<td>8</td>
<td>Co_Cr-alloys (cast-able-Co-Cr-Mo)</td>
<td>Cobalt-balancing, 27-30% Chromium, 2.5% Molybdenum, 0.75% Ni, 5-7% Fe, 0.36% Carbon &amp; maximum_1% Mn-and-Silicon</td>
<td>655</td>
<td>240</td>
<td>8.3</td>
<td>10-30</td>
<td>0.865</td>
<td>0.745</td>
<td>0.665</td>
</tr>
<tr>
<td>9</td>
<td>Ti_alloys (pure Titanium)</td>
<td>0.3% Fe, 0.08% Carbon,0.13% O2, 0.07% N2</td>
<td>550</td>
<td>100</td>
<td>4.5</td>
<td>54</td>
<td>0.59</td>
<td>0.955</td>
<td>0.745</td>
</tr>
<tr>
<td>10</td>
<td>Ti_alloys(6Al-Ti-4V)</td>
<td>Titanium-balancing, 5.5-6.5% Aluminum, 3.5-4.5% V,0.25% Fe &amp; 0.08% C</td>
<td>985</td>
<td>112</td>
<td>4.43</td>
<td>12</td>
<td>0.665</td>
<td>0.955</td>
<td>0.745</td>
</tr>
</tbody>
</table>
Only corrosion resistance (CR) considered as low obligatory property. Here are the normalized values.

**Stage 3**

Graphical illustration is one of most important stages. At this stage a graph is constructed by making the number of anchor points equal to the number of properties as well as their path represents their relative importance on each other and indicate their direction. As shown in the figure below.

![Graphical Illustration for femoral-component(FC)](image)

**Stage 4**

Develop a material selection matrix for femoral-component(FC) selection property function. This is a N x N square matrix having diagonal elements $R_p$ and off diagonal elements $r_{pq}$ relative importance. Matrix constructed for femoral-component(FC) is given below

**Stage 5**

Femoral-component (FC) selection properties function for the matrix and substitute the values of $R_p$ and $r_{pq}$ from step 1 and 2. Then evaluation for the suitability index starts which indicate the best material for femoral-component (FC).

**Final Stage**

In the last stage final decision will be taken by considering practical applications and experience. All possible limitations which can be faced by the user including management, availability, economic, political and environmental limitations etc. should be considered. However any type of compromise should be in the favor of higher ranked material.

**5. Result Analysis**

There are main three reasons on the basis of which any of biomaterial or any other material can be analyze, which are mechanical properties (Wear Resistance, Tensile...
### Table 3. Matrix representation of femoral-component (FC)

<table>
<thead>
<tr>
<th>Properties</th>
<th>TS (Mpa)</th>
<th>EM (Gpa)</th>
<th>Density (g/cc)</th>
<th>Elongation (%)</th>
<th>WR</th>
<th>CR</th>
<th>Osseointegration</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS (Mpa)</td>
<td>R1</td>
<td>0.458904996</td>
<td>0.711480576</td>
<td>0.157084</td>
<td>0.453022</td>
<td>0.586972</td>
<td>0.97879599</td>
</tr>
<tr>
<td>EM (Gpa)</td>
<td>R2</td>
<td>0.541095004</td>
<td>0.175992805</td>
<td>0.740687</td>
<td>0.825205</td>
<td>0.422786</td>
<td>0.55075545</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>R3</td>
<td>0.288519424</td>
<td>0.824007195</td>
<td>0.928984</td>
<td>0.73852</td>
<td>0.276162</td>
<td>0.354540174</td>
</tr>
<tr>
<td>Elongation (%)</td>
<td>R4</td>
<td>0.842915681</td>
<td>0.25931314</td>
<td>0.071016208</td>
<td>0.39153</td>
<td>0.9708</td>
<td>0.93817</td>
</tr>
<tr>
<td>WR</td>
<td>R5</td>
<td>0.546978214</td>
<td>0.174795</td>
<td>0.261479681</td>
<td>0.60847</td>
<td>0.78421</td>
<td>0.981036</td>
</tr>
<tr>
<td>CR</td>
<td>R6</td>
<td>0.413028266</td>
<td>0.5772145</td>
<td>0.723838009</td>
<td>0.0292</td>
<td>0.21579</td>
<td>0.875204</td>
</tr>
<tr>
<td>Osseointegration</td>
<td>R7</td>
<td>0.02120401</td>
<td>0.44924455</td>
<td>0.645459826</td>
<td>0.06183</td>
<td>0.018964</td>
<td>0.124796</td>
</tr>
</tbody>
</table>

### Table 4. Suitability Index for the femoral-component (FC)

<table>
<thead>
<tr>
<th>Material Number</th>
<th>Material name</th>
<th>Detailed Material Composition</th>
<th>suitability index value</th>
<th>Ranking</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni_Ti shape-memory-alloy</td>
<td>Titanium 43.835-45.0%, Nickel 55.0-56.0%, Hydrogen ≤ 6.0050%, Carbon ≤ 6.050%, Oxygen ≤ 6.050%, Iron ≤ 6.010%</td>
<td>41.7415</td>
<td>7th</td>
</tr>
<tr>
<td>2</td>
<td>Porous-Ni_Ti-shape-memory-alloy</td>
<td>Titanium, 16% porosity-Nickel-49.0</td>
<td>44.518</td>
<td>5th</td>
</tr>
<tr>
<td>3</td>
<td>6Al-Ti-7Nb (protasul-100 hot forged)</td>
<td>Titanium balancing, 5.50-6.50% Aluminum, 60.080% Nb, 60.050% Carbon, 60.25% Hydrogen, 60.20% Oxygen, 60.50% Ta</td>
<td>41.0224</td>
<td>8th</td>
</tr>
<tr>
<td>4</td>
<td>6Al-Ti-7Nb (IMI_367 wrought)</td>
<td>Titanium balancing, 5.50-6.50% Aluminum, 60.080% Nb, 60.050% Carbon, 60.25% Hydrogen, 60.20% Oxygen, 60.50% Ta</td>
<td>39.0831</td>
<td>10th</td>
</tr>
<tr>
<td>5</td>
<td>stainless_steel_L316 (annealed)</td>
<td>Fe-balancing, 17-20% Molybdenum, 0.03-0.08% Chromium, 10-14% Ni, 2-4% Carbon, 2% Mn and 0.75% Silicon</td>
<td>49.505</td>
<td>3rd</td>
</tr>
<tr>
<td>6</td>
<td>stainless_steel_L316 (cold-worked)</td>
<td>Cobalt-balancing, 19-21% Chromium, 9-11% Nickel, 14.6-16% W, 0.13% Molybdenum, 0.05-0.15% Carbon, 0.48% Silicon &amp; maximum-2%-Mn-and-3% Fe</td>
<td>48.5273</td>
<td>4th</td>
</tr>
<tr>
<td>7</td>
<td>Co_Cr-alloys (wrought-Co-Ni-Cr-Mo)</td>
<td>Cobalt-balancing, 27-30% Chromium, 2.5% Molybdenum, 0.75% Ni, 5-7% Fe, 0.36% Carbon &amp; maximum-15% Mn and Silicon</td>
<td>56.644</td>
<td>1st</td>
</tr>
<tr>
<td>8</td>
<td>Co_Cr-alloys (cast-able-Co-Cr-Mo)</td>
<td>Cobalt-balancing, 27-30% Chromium, 2.5% Molybdenum, 0.75% Ni, 5-7% Fe, 0.36% Carbon &amp; maximum-15% Mn and Silicon</td>
<td>52.2292</td>
<td>2nd</td>
</tr>
<tr>
<td>9</td>
<td>Ti_alloys (pure Titanium)</td>
<td>0.3% Fe, 0.08% Carbon, 0.13% O2, 0.07% N2</td>
<td>43.7334</td>
<td>6th</td>
</tr>
<tr>
<td>10</td>
<td>Ti_alloys(6Al-Ti-4V)</td>
<td>Titanium-balancing, 5.5-6.5% Aluminum, 3.5-4.5% V, 0.25% Fe &amp; 0.08% C</td>
<td>40.2823</td>
<td>9th</td>
</tr>
</tbody>
</table>
Strength…etc.) chemical properties (Corrosion resistance) and biocompatibility with bones as well as with tissues. According to ranking results cobalt alloys (Co-Cr-Mo) are on the high rank whereas Titanium based alloys comes on 2nd number. Although titanium alloys are used rare than Co-Cr-Mo alloys just because of their less wear resistance. [21] cobalt alloys which are based on Co-Cr-Mo system are used widely for femoral-component (FC) for TKR as well as THR (total hip replacement) due to its mechanical properties, good wear resistance, corrosion resistance and biocompatibility [22-25].

5.1 Sensitivity Analysis

This is a method which is used to validate the MADM method. Basic reason to use this analysis is to analyze the variations of properties which affect the ranking. It will increase the effectiveness of material selections outcomes. The present work deals GTMA to select a material for femoral-component (FC) of TKR. In this section will investigate flexibility, efficiency and consistency of ranked material by normalizing with new method in GTMA

Sum based linear normalization is as follows

<table>
<thead>
<tr>
<th>Material Number</th>
<th>Material name</th>
<th>GTMA</th>
<th>Modified GTMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni_Ti shape-memory-alloy</td>
<td>41.7415</td>
<td>66.4053</td>
</tr>
<tr>
<td>2</td>
<td>Porous-Ni_Ti-shape-memory-alloy</td>
<td>44.518</td>
<td>54.8321</td>
</tr>
<tr>
<td>3</td>
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For HOV Properties: \[ N_{pq} = \frac{r_{pq}}{\sum r_{pq}} \]

For LOV Properties: \[ N_{pq} = \frac{1/r_{pq}}{\sum 1/r_{pq}} \]

**Figure 4.** Correlation of Ranks between GTMA and modified GTMA

### 6. Conclusions

It is a general method which depends upon graphical illustration as well as matrix approach which helps to select a suitable material for femoral-component (FC) when a number of choices are available. In this method generally considered different properties and their correlation and then find out the suitability index and rank of the materials. It is useful for any type of quantitative and qualitative materials respectively and offers more objectives.

In further research the other parts of knee prosthesis can be optimized such as tibial try. By keeping in mind different requirements and target values for the different applications there should be different properties considered according to the problem. This paper is very help full for the researchers as well as the persons working in medical implantations.

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ARTICLE
PVA Based Polymer Electrolyte with Layered Filler Graphite for Natural Dye Sensitized Solar Cell

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ABSTRACT
Graphite nanopowder is synthesized by mechanical method using ball mill and used as filler in polymer electrolyte film based on Polyvinyl alcohol (PVA) for application in natural dye sensitized solar cell (DSSC). In the present work dye sensitized solar cell has been assembled using electrolyte system composed of PVA as host polymer, ethylene carbonate as plasticizer, LiI: I$_2$ as redox couple and graphite as filler; TiO$_2$ modified with Copper oxide (CuO) photoanode in order to provide inherent energy barrier and natural cocktail dye as sensitizer. The obtained solar cell conversion efficiency was about 3.2 % with fill factor 52% using an irradiation of 100 mW/cm$^2$ at 25º C.

Keywords:
Polyvinyl alcohol
DSSC
Graphite
Copper oxide
Cocktail dye

1. Introduction
Dye sensitized solar cells which come under the category of third generation photovoltaics, have appeared as a bewitching and promising low-cost solar cell device with potential power conversion efficiency. Sensitizers, nanocrystalline porous semiconductor based photoanode, electrolyte and counter electrode are the four major components of DSSCs [1]. The properties of metal oxide, as well as the choice of electrolyte and dye are the major components on which the performance of DSSCs depends. Therefore, the researchers working in the field of DSSCs are focusing their attention on improving one or the other component of DSSCs so that efficiency comparable to silicon based solar cell can be achieved.

The liquid electrolyte which is the most important component of DSSCs hinderers its stability as the electrolyte leaks and vaporizes with time. Thus, scientists are focusing their attention in the solidification of electrolyte such as inorganic or organic hole conductors, ionic liquids, polymer electrolyte [2-3]. For absolute performance and outstanding efficiency, polymer electrolyte should have high ionic conductivity so that transfer of oxidised and reduced species to respective electrodes can be done efficiently and also it should possess good mechanical strength and film forming properties. In this respect Poly (ethylene) oxide (PVA) has much of such exceptional properties. It has excellent ability to from complexes with the ionic salts. PVA shows good salvation property due to the presence of unpaired electrons on the ether oxygen atoms which lead to good ionic ability [4]. Thus, in the present work we have

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prepared PVA based polymer electrolyte film for DSSC. In order to make film more amorphous which will aid in fast conduction of ions we added nanoparticle of graphite as filler.

Generally, the beautiful colours of plants are due to the natural pigments such as betacyanin, anthocyanin, carotene, chlorophyll, tannins etc. These natural pigments present in various parts of the plants (fruits, flowers, stem etc) can easily be extracted and then can be used as photosensitizers in dye sensitized solar cells. These natural pigments are low in cost and environmentally safe. The synthesis of these pigments in plants is promoted by light and they appear colourful because they selectively absorb and reflect certain wavelength of visible light. As it is the known fact that white light is a roughly equal mixture of the entire spectrum of visible light with the wavelength range of 400-780 nm. When the light comes in the contact of these pigments then the conjugate bonds present in them absorb the part of the spectrum while other part is reflected or scattered. Like the transition metal compounds these pigments are also charge transfer complexes with broad absorption bands that absorb most of the colours of the incident white light.

The photoanode made up of semiconductor oxide is the heart of DSSCs. Generally, TiO$_2$ is used as semiconductor oxide for DSSCs due to its vivid properties such as easy synthesis, good stability, low toxicity and wide band gap. But TiO$_2$ can absorb only 6% of the spectral region which creates hinderers in the performance of DSSCs. In order to overcome this drawback various metal ions as well as Non-metal dopants such as nitrogen, carbon, sulphur, phosphorus etc are used for enhancing the visible light photoactivity of TiO$_2$. In this direction copper oxide has received considerable interest due to its interesting physical properties such as a superior gas sensing material, potential field emitter, powerful catalytic agent, huge application in optoelectronics and solar cells.

In the present work we fabricated DSSC with polymer electrolyte system composed of PVA as a host polymer, LiI: I$_2$ as a redox couple, EC as plasticizer, graphite as filler with cocktail dye and CuO modified TiO$_2$ photoanode. The properties like short-circuit photocurrent density (JSC), open circuit voltage (Voc), fill factor (ff) conversion efficiency and stability of the fabricated DSSC has been studied.

2. Materials and Methods

All the materials were purchased from sigma Aldrich. For the preparation of dye black grapes and spinach leaves were purchased from local markets.

2.1 Preparation of Polymer Electrolyte

The appropriate amount of PVA along with Li:I$_2$ was dissolved in distilled water for the preparation of thin film polymer electrolyte. The prepared solution was stirred for 7 hours with the help of magnetic stirrer for obtaining a homogenous solution. In the above prepared solution plasticizers EC and PC along with 1 weight percent of graphite powder with respect to PVA was added and then it was mixed thoroughly for one night. This graphite powder was synthesized by ball milling process (Retsch PM 100) the raw material was put in planetary ball milling machine for 48 hours at a rotation speed of 300 rpm. Then the final solution was cast in the polypropylene dish and by slow evaporation in ambient temperature followed by vacuum drying, a solvent free polymer electrolyte film was obtained.

2.2 Extraction and Purification of Dyes from Natural Sources

2.2.1 Beetroot (Betacyanin) Dye

Fresh beetroot pieces were washed with deionized water and crushed in mortar and soaked in ethanol for one week. Solutions were filtered out, and filtrates were concentrated in rotavapor at 40ºC and the resulting dye solution was used as sensitizers.

2.2.2 Spinach (Chlorophyll) Dye

The spinach leaves were washed thoroughly with deionized water and crushed in mortar and soaked in ethanol for one week. Solutions were filtered out, and filtrates were concentrated in rotavapor at 40ºC and the resulting dye solution was used as sensitizers.

2.2.3 Cocktail Dye

The betacyanin dye obtained from beetroot and chlorophyll dye from spinach leaves were blended at volume ratio of 1:1 to serve as natural cocktail dye sensitizer for DSSC. Chromatographic techniques were used for the purification of prepared dye.

2.3 Preparation of TiO$_2$-CuO Admixed Photoelectrode

TiO$_2$-CuO based nanoparticle was prepared as per our previous work. The cleaned ITO conductive glass plates having a sheet resistance of 18–20 Ω/cm$^2$ were used and over these plates prepared TiO$_2$-CuO nanoparticle paste was applied using doctor blade technique. The resulting film substrate was annealed in oven at 150ºC for 10 minutes.
2.4 DSSC Fabrications

For the fabrication of DSSC we immersed the prepared photoelectrode in the prepared dye inside the petridish and left undisturbed for 24 hours and it’s was covered to prevent the photo decay of the dye. Then in between the photoanode and photocathode we sandwiched the prepared polymer electrolyte.

3. Results and Discussion

Figure 1 shows the XRD pattern of 99 {80 PVA-20 LiI: I2}: 1 graphite film prepared by solution cast technique. The XRD pattern of pure PVA film shows sharp and intense peaks at 19.5° and 23.52° respectively whereas for pure graphite film it is at 25°. The peak intensity decreases randomly due to the intermolecular chain reaction resulting in enhancement of the amorphous phase. The amorphous nature of polymer is very important as this allows free ionic transportation which aids in better ionic conductivity.

The surface morphology of 99 {80 PVA - 20 LiI: I2}: 1 graphite film prepared by solution cast technique at 80X magnification are shown in Figure 2(a) and (b).

Figure 2. Optical micrograph of the polymer electrolyte film (a) pure PVA (b) 99 {80 PVA- 20 LiI: I2}: 1 graphite

Figure 3 shows that the ambient ac conductivity of the PVA based polymer electrolyte reaches 10-3 S/cm. The conductivity increases linearly up to 5 kHz. The obtained conductivity is very significant to be used as polymer electrolyte for DSSC.

Figure 4 shows the light absorption behavior of betacyanin, chlorophyll and cocktail dye coated TiO₂-CuO photoelectrodes. The pigments betacyanin, chlorophyll and mixture of both dyes show distinctive wavelength due to various sub atomic structure. The wavelength for betacyanin dye was found at 550 nm range while for chlorophyll it was found in the range of 440 nm and the mixture of both dyes a clear enhancement in the wavelength range of about 660 nm. The mixing of dyes produced wider wavelength which will increase the dyes’ ability to capture the maximum photons from sunlight and produce a continuous cycle of electrons which will results...
in improved performance of DSSCs.

Figure 4. Absorption spectra of Chlorophyll, betacyanin and co-sensitized dye coated TiO$_2$-CuO photoelectrode on ITO glass substrate

The XRD graph of prepared nanomaterial TiO$_2$-CuO is of crystalline nature devoid of amorphous phase and it is also clear from the XRD graph that no new nanocomposite material is formed (Figure 5).

Figure 5. XRD pattern of TiO$_2$-CuO nanopowder

SEM (scanning electron microscopy) image of the prepared TiO$_2$-CuO nanomaterial is shown in Figure 6(a) and (b). The small grain size (25-30 nm) absorbs large amount of dye molecules resulting in enhanced efficiency of DSSC.

Figure 6. Scanning Electron Micrograph of (a) ns-TiO$_2$ (b) ns- TiO$_2$-CuO

The cell performance of the PVA based DSSC with TiO$_2$-CuO photoelectrode sensitized with cocktail dye is shown in Figure 7. The photocurrent (Isc) was found to be 9.0 mA/cm$^2$ and photovoltage (Voc) 0.680 V. The conversion efficiency and fill factor of cocktail dye coated TiO$_2$-CuO photoanode were found to be 3.2 % and 52 % respectively.

Figure 7. Current-Voltage characteristic curve of cocktail dye coated TiO$_2$-CuO photoelectrode

4. Conclusions

In the present study, the effect of graphite filler in PVA polymer electrolyte on the performance of DSSC was verified. Ionic conductivity of the prepared polymer electrolyte was investigated by electrochemical impedance spectroscopy which was found in the range of 10-3S/cm. This is due to increase in the amorphous nature of the polymer matrix and increase in the ions mobility in the polymer system. Then the cell performance of the TiO$_2$-CuO coated DSSC is investigated. CuO is responsible for reducing the recombination rate by providing the inherent energy barrier which results in improved efficiency of the cell. Cocktail dye showed better complexation with TiO$_2$-CuO surface which aided in better charge transfer between dye molecules and TiO$_2$-CuO surface. Therefore, this dye provides more efficient incident photon to electron conversion.

Conflict of Interest

No potential conflict of interest was reported by the author.

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References


ARTICLE

Allowed Spatial Transitions and Cancellation of the Richardson-Langmuir Ban

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ABSTRACT

The ancient emission formulas of Langmuir and Richardson entered the calculations of subtle effects in semiconductor devices as basic ones. But, in the physics of semiconductor devices, these models have long played a purely decorative role, since they can describe in the most rough approximation only individual sections of the I – V characteristic. But it is precisely the fact that these formulas are basic when describing the barrier current-voltage characteristics (CVC) and prevented the consideration and use of thermoelectric effects in materials on a nano-scale. Thus, as these basic emission models actually imposed a ban on the MEASURABILITY of local thermoelectric effects, the existence of which has already been proven both phenomenologically and experimentally.

The quantum transition technique is based on classical models. But it can also be used to correct these classic formulas. The calculation of the spatial transition of electrons over the potential barrier, taking into account the polarity of the kinetic energy, gives currents that are significantly higher than the currents of Langmuir and Richardson, including in the initial section of the I – V characteristic. Moreover, ballistic currents are concentrated at energy levels close to the threshold. This effect of condensation of electrons flowing down the barrier transforms the “anomalous” Seebeck coefficients into normal MEASURABLE Local Thermal EMF, including in p-n junctions.

1. Introduction

Someone not stupid said: “Science begins where Mathematics begins.” But at the time of Newton, in fact, there was still no separation of Physics and Mathematics. And Isaac Newton, in parallel with Gottfried Leibniz, resolving Zeno’s aporia about Achilles and the tortoise, laid the foundations of a new branch of Mathematics - Differential Calculus. But Physics was built not only with the help of new sections of Mathematics. Many Physical Laws were substantiated in the simplest case with the help of algebraic equations. And the contradictions that had accumulated in uncombed Physics at the end of the last century were taken up not by a recognized scientist, but by the senior telegraph operator Heaviside, who, it would seem, in solving a particular electrodynamic problem first began to use complex numbers, and then tensors. The latest mathematics, already developed (by the same Riemann), brought by Heaviside into Physics, in fact, brought Maxwell’s electrodynamics to a modern form, implicitly gave Schrödinger an operator approach, prompted Einstein to build the Theory of Relativity within

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the framework of Geometry extended by Riemann.

Thus, by introducing independently advanced Mathematics into primitive Physics, Heaviside actually raised entire sections of modern Theoretical Physics to a pedestal. And this, in principle, would be nice if the entire Physics described by dense formulas began to be brought up to the mathematical level of these sections. But the editors artificially torn these sections away from all of Physics. And, referring only these (Theoretical) sections to Fundamental Physics, they did more harm than they helped. And, thus, they hurt themselves, as they broke away from reality. That is why, in fact, both the Quantum Theory and the Theory of Relativity went to the wrong steppe. And to restore the connection of THEM with reality, it was necessary to rethink and rewrite a wider layer of Physics at the modern mathematical level. And because it is directly linked to these theoretical sections in ELEMENTARY MODELS. And because this is how it was possible to understand why “to the wrong steppe” - the developers in “smart” mathematical calculations actually drowned the Ideas of Planck-Einstein, and, at the same time, and Mat. Heaviside physics.

So the completion of the article “Fundamentals of Quantization” required compliance with Einstein’s NECESSARY condition: “Some equations of classical mechanics can be rewritten in operator form”, i.e. rigor was also required in the classical equations used for rewriting.

The completion of this work required a rethinking of what was actually put by Planck in the Basics of Quantization, the fascination with the waves of HIS matter - the Heaviside’s impedance (himself) pushed also far? As well as his Electromagnetic Theory of Gravity.

This required a strict account of both in Classical Mechanics and in the Heaviside Impedance of the Irreversibility of Time.

And the latter is already directly related to Thermodynamics, which since the time of Boltzmann has so far remained uncombed, since it uses a traditional frame, not an orthogonal one.

But combing both the Fundamentals of Thermostatics (which was mistakenly called Thermodynamics) and the Fundamentals of Thermodynamics proper, the Linear Approximation of which was called Nonequilibrium Thermodynamics, is a big independent work. So far, I have limited myself only to the refinement in the description of Thermoelectric Processes on the basis of the traditional thermodynamic reference.

And this phenomenological examination was enough to understand:

1) The traditional Onsager-Ioffe Theory of Thermoelectricity describes only diffuse processes, which Ioffe used for heavily doped semiconductors.

And this alone turned out to be enough to show that modern thermoelectric technology has reached the diffuse limit of the efficiency of the thermoelectric devices being developed.

2) And the lightly doped semiconductors, which dropped out of consideration, are barrier structures that make it possible to dramatically increase the efficiency.

But the high-voltage thermoelectric power discovered back in the fifties of the last century by Tauts in its first transistors, since they did not fit into the phenomenology of thermoelectricity, were classified as “anomalous”, and the estimates by Richardson’s formula of currents above the potential barrier gave such small values that they were practically referred to UNMEASURABLE.

2. Experimental, Results and Discussion

2.1 Semiconductor Barriers

Initially, research was carried out on the contacts of various semiconductors. But later, most of the results discussed in this article were obtained on structures grown on silicon substrates and on aluminum nitride substrates.

And experiments have shown that the local thermopower of a micron p-n junction prevails over the diffuse thermopower of a 300 micron silicon substrate.

Figure 1. The thermopower of a silicon structure with a micron layer of inverse conductivity measured by the direct contact method gives a total voltage determined by the polarity of the n-n junction and exceeding the thermopower of a silicon substrate (silicon wafer) by an order of magnitude.

And the inertness of academic science, which did not recognize the “immeasurable” effects, which already significantly surpassed analogues based not only on diffuse thermolectric effects, but also on the basis of the photoelectric effect, naturally slowed down the introduction of devices based on Local Thermo-EMF.

But, as they say, everything in the world is interconnected. The Quantum Theory of Solids, despite the errors in the Basics of Quantization, methodically in calculations has advanced much further than the dense
formulas of Richardson and Langmuir. But their analysis within the framework of the Quantum Solid State Theory helped to advance in the very understanding of the Basics of Quantization - Spatial Quantum Transitions.

The laws of conservation of energy and momentum rule both the classical and the quantum world. In quantum calculations, they are methodically used in the space of (quasi) momenta. Those zone patterns are constructed for ALLOWED states and transitions between them, in fact, in the velocity space. And strictly speaking, only transitions to UNRESOLVED states are forbidden, which give a low probability and UNMEASURABLE currents. So the real MEASURABLE currents above the potential barrier (which in practice have long been used in electronics, but not in thermoelectricity), it was just necessary to honestly count the transitions between the ALLOWED states on the emitter and collector. But for such calculations, it is necessary to take into account the polarity of the kinetic energy of electrons relative to the electric field in the region of the potential barrier.

2.2 Vacuum Barrier (Brief Historical Background)

The giant differences in currents through semiconductor potential barriers from those predicted by theory and, all the more, the high detectivity of detectors based on thermoelectric barrier effects prompted a thorough experimental analysis of the properties of the vacuum barrier, which served as the basis for calculating semiconductor barriers.

Initially, the Langmuir and Richardson formulas were constructed for thermionic emission [11],

$$ J = \frac{\sqrt{2}}{9\pi} \sqrt{\frac{e}{m}} \frac{1}{d^3/2} U^{3/2}, \quad J_e = (1-r) A T_e^{3/2} \exp \left( \frac{e \phi}{k T_h} \right) $$

(1)

Where in the Langmuir formula $d$ false is the barrier thickness, and $U$ false is the potential difference across it and where $A$ false - the Richardson constant, $\phi$ false and $T$ false - the work function and temperature (of the cathode, in thermal emission), respectively, and $r$ false - the average value of the reflection coefficient of electrons at the boundary, which is small and, in the analysis, we will further assume that the first bracket is equal to 1.

These well-known formulas for the electron flux, both Langmuir and Richardon, were grossly grounded at the microscopic level as well [12], Langmuir’s formula - under the assumption of the initial zero velocity of all electrons above the barrier and its increment due to the electric field. And Richardson’s formula - when taking into account (in the Brillouin zone) only those electrons whose velocity vector is directed towards the interface. In fact, the Richardson model took into account only the difference between the electron concentrations at the emitter and collector above the maximum of the potential barrier, which arises when the field is applied, multiplied by the average thermal velocity of the electrons.

$$ \int_{0}^{\infty} \int_{0}^{\infty} \int_{0}^{\infty} v_x n_0^* e^{-\frac{m}{2k T} \left( v_x^2 + v_y^2 + v_z^2 \right)} \frac{eU}{k T} \, dv_x \, dv_y \, dv_z $$

$$ = n_0^* 2\pi \left( \frac{k T}{m} \right)^2 \cdot e^{\frac{eU}{k T}} $$

(2)

which corresponds to the average thermal velocity along one coordinate $\bar{v} = \sqrt{\frac{2}{\pi}} \left( \frac{k T}{m} \right)^{1/2}$ (the root mean square is equal to $\sqrt{\frac{k T}{m}}$ multiplied by the electron concentration in half of the Brillouin zone $n_0^* = \frac{1}{2} n_0 \left( \frac{2\pi}{k T} \right)^{1/2}$).

For a frequently used one-dimensional view, Formula 2 is simplified:

$$ \int (v_x) n_0^* e^{-\left( \frac{m}{2k T} \left( v_x^2 + v_y^2 + v_z^2 \right) \right)} \frac{eU}{k T} \, dv_x $$

$$ \Rightarrow \quad J_2 = n_0^* \frac{k T}{m} e^{-eU} $$

(3)

Due to the roughness of the original Richardson model, the theoretical does not correspond to the experimental, adjustable values, even in order of magnitude. And neither Langmuir nor Richardson’s formula (2) even gives a qualitative description of the experimental current-voltage characteristics of barriers in a sufficiently wide range, even for an “ideal” vacuum barrier [13] (Figure 2). Therefore, they can be used only when adjusting the $1 – V$ characteristic in a narrow voltage range.

![Figure 2. Experimental and Langmuir – Richardson I – V characteristics for a vacuum barrier.](image)

Nevertheless, it was the estimates by the Richardson formula [13,14] that imposed a “ban” on the experimentally observed large thermopower, transferring them to the category of anomalies [15].

3. Theory

3.1 Fragmented Description of Spatial Transitions

To obtain a rough dependence of current on voltage, one
usually takes the difference between the Richardson saturation currents from two plates of the barrier\cite{16,17} (Figure 3a).

\begin{equation}
\Delta I_{R} = e(n_{v_{+}} - n_{v_{-}}) = en_{b}\pi 2\pi \left(\frac{kT}{m}\right)^{2} \left(1 - e^{-\frac{\phi}{kT}}\right)
\end{equation}

\begin{align}
\Delta I_{R}(U) &= (1 - r)AT\left(1 - e^{-\frac{\phi}{kT}}\right) = J_{e}^{\infty}\left(1 - e^{-\frac{\phi}{kT}}\right) = eU' \cdot J_{e} \quad (4)
\end{align}

But, strictly speaking, according to the Richardson formula, only one generalized independent force is phenomenologically taken into account - the concentration force, which ensures the emission of electrons from the material into vacuum if the material is not charged.

In this case, the difference current of the Richardson electrons was calculated with an error. This is a standard phenomenological error, which, unfortunately, has passed both through the macroscopic theory of thermoelectricity (Ioffe)\cite{16,17} and through the theory of p-n junction\cite{18,19}.

And when considering the barrier currents, one cannot in any way throw out the generalized electric force itself from the model. So, when considering the total current over the potential barrier, it is fundamentally important to take into account not only the Richardson concentration current, but also the addition to it, determined by the electric current.

First, for clarity, we will consider the energy region above the barrier, denoted in Figure 3a as R. In addition to formula (4), we will expand the consideration of the electron current taken into account by the Richardson model - we will take into account in the one-dimensional case the increase in the positive velocities of the emitter electrons due to the difference potentials\cite{20} (Figure 3b, red arrows of spatial transitions):

\begin{equation}
\int_{0}^{\infty} \int_{0}^{\infty} eU \cdot J_{e} = \frac{e}{c} \cdot \frac{m}{\pi} \cdot \pi^{2} v_{+}^{2} e^{-\frac{\phi}{kT}} dv_{v_{+}}
\end{equation}

\begin{align}
J_{R1} &= n_{b}\frac{kT}{m} \sqrt{\pi} \text{Hypergeometric}\left[-\frac{1}{2}, 0, eU'\right] \quad (5)
\end{align}

\begin{align}
J_{R2} &= J_{R1} + \Delta J_{K} = n_{b}\frac{kT}{m} \sqrt{\pi} \text{Hypergeometric}\left[-\frac{1}{2}, 0, eU'\right] \quad (6)
\end{align}

So, in the one-dimensional case, the purely concentration Richardson current of the emitter and, accordingly, the first ballistic addition to it are equal:

\begin{align}
J_{R1} = n_{b}\frac{kT}{m} \Rightarrow \Delta J_{K} = n_{b}\frac{kT}{m} \left(-1 + \sqrt{eU'}\right) \quad (7)
\end{align}

And we obtain the same addition to the positive initial velocities of electrons by direct integration of the velocity increment:

\begin{align}
\int_{0}^{\infty} \int_{0}^{\infty} eU \cdot J_{e} = \frac{e}{c} \cdot \frac{m}{\pi} \cdot \pi^{2} v_{+}^{2} e^{-\frac{\phi}{kT}} dv_{v_{+}}
\end{align}

\begin{align}
\Rightarrow \Delta J_{I} = \left\{n_{b}\frac{kT}{m} \sqrt{\pi} \text{Hypergeometric}\left[-\frac{1}{2}, 0, eU' - 1\right]\right\} \quad (8)
\end{align}
The Richardson model takes into account only electrons with positive initial velocities. So the obtained first addition to the emitter current is not taken into account that when the current passes through the barrier boundary, the momentum and energy shift affects all electrons of the parabolic zone. However, it is obvious that electrons with low negative velocities can also change the sign of the velocity to a positive one. Therefore, we will consider one more addition to the more refined Richardson current from the energy range denoted in Figure 3a as $A_1$. The sum of the partial contributions of these electrons also gives a positive (second and not small) addition to the total current:

$$\Delta J_{\text{Ele}} = n_e \frac{kT}{m} \left[ 1 + \frac{e}{\sqrt{2}} \right] BesselI \left( 0, \frac{eU}{2} \right) \cdot e^{-eU/eT} $$

(9)

But electrons with large negative starting velocities due to the electric field at the barrier also have a positive addition to the velocity, which leads to a positive (third) addition to the emitter current:

$$\Delta J_{\text{E2}} = n_e \frac{kT}{m} \left( e^{-eU/eT} \right) \cdot \text{MeijerG}\left( \{ 1, \{ 1 \} \}, \{ \{ 0, 1 \}, 1 \}, eU \right)$$

(10)

So the total emitter - the modified Richardson current (formula 5), will include the total addition

$$J_{\text{RI1}} = J_{\text{R1}} + \Delta J_{\text{E1}} + \Delta J_{\text{E2}} + \Delta J_{\text{E3}} = J_{\text{R1}} + \Delta J_{\text{E}}$$

(11)

Figure 4. Ballistic additives to the Richardson current: emitter - solid colored lines, collector - dotted lines corresponding to the emitter lines of the color, purple dotted line - full addition to the Richardson differential current (to the black line).

As shown in Figure 4, when the potential difference across the barrier is greater than the average thermal energy of electrons ($eU > kT/2$), the first and second ballistic additives significantly exceed the Richardson saturation current. Moreover, the second addition due to electrons with small negative starting velocities, the speed of which changes sign due to the electric field, even exceeds the first addition of accelerated electrons without changing the sign of their velocity. But all these 3 additives, both separately and naturally - total, as will be further shown below, and at low voltages significantly exceed the Richardson difference current, which is fundamentally “immeasurable” at low voltages (formula 3).

At low voltages, it is necessary to take into account the partial contributions to the anti-accelerated electrons of the collector (dashed lines in Figure 4), which are opposite in sign to the Richardson current of the collector, but similarly exponentially decrease with increasing voltage:

$$J_{\text{RI2}} = J_{\text{E1}} + \Delta J_{\text{E1}} + \Delta J_{\text{E2}} + \Delta J_{\text{E3}} = (J_{\text{R1}} + \Delta J_{\text{E}}) \cdot e^{-eU/eT}$$

(12)

The ballistic additives obtained in the calculation of the spatial transition, referred to the differential saturation current of Richardson, are shown in Figure 5. For clarity of this conclusion, the total ballistic weighting and the Richardson differential current are shown in a wide range of potential differences on a double logarithmic scale.

Figure 5. Comparison of the total ballistic addition to the barrier current (purple dashed curve) with the Richardson differential current (black curve).

Thus, taking into account the ballistic additions to the Richardson current shows that, on the one hand, the initial portions of the $I – V$ characteristic have significantly large measurable currents, and on the other hand, it shows that the actually observed saturation of the $I – V$ characteristic at high currents (Figure 5, 6) is related to not with the complete depletion of the electronic zone of the emitter, but with the rate at which electrons enter it into its surface layer, i.e. in fact, with resistance, volumetric and surface [18-20].

Figure 6. The relative increase in the total current due to ballistic effects.

The ratio of the resulting increment of the total current due to ballistic additions to the “immeasurable” at low voltages at the Richardson differential current barrier,
determined only by the concentration force, tends to infinity as the voltage tends to zero:

$$\frac{\Delta J_{Ec} + \Delta J_{Sc}}{\Delta J_R} = \frac{\Delta J_{Ec}}{eU_{0}} \rightarrow \infty$$

\(13\)

We emphasize that the calculation of the current must also take into account those electrons whose velocities are directed away from the barrier, but which, as shown in Figure 3, are able to overcome it according to the law of conservation of energy. This is due to the fact that in the case of chaotic wanderings and collisions of thermal electrons, the laws of conservation of their energy and momentum are also observed. So in momentum space the electrons “swing in the parabolic zones shown in the figures. Therefore, we will consider the spatial transitions of electrons indicated in Figure 2b by green lines.

**3.2 Generalized Description of Spatial Transitions**

The detailed analysis carried out already implicitly took into account the fact that when calculating spatial transitions, it is necessary to take into account the polarity of the kinetic energy (Figure 7). So its record in general:

$$\dot{e}_{c}^{*} = \text{Sign}[V_s] \cdot \frac{mV_{s}^{2}}{2}$$

\(14\)

**Figure 7.** Electronic transitions under the action of an electric field when considered in the framework of: standard (left) and taking into account polarity (right) dispersion law.

In Figure 7 on the right: 1 - the initial dispersion law, 2 - the dispersion law, shifted only in energy, 3 - the dispersion law, shifted both in energy and velocity, 4 - a decrease in the potential energy of the obtained dispersion law by an amount equal to an increase in the kinetic energy, 5 - demonstration of the displacement of curve 2 by a fixed speed value.

In this case, in contrast to the generally accepted approach \([18,19]\), the record of the total energy is transformed (Figure 7, right):

$$\varepsilon_{c}^{*}[x] = \text{Sign}[V_s] \cdot \frac{mV_{s}^{2}}{2} + eEx$$

\(15\)

And, as shown in Figure 6 (on the right), expression (14) also gives ballistic transitions with negative initial velocities, also with conservation of total energy - horizontal lines.

Having solved equation (14) in general form, we obtain an expression for the final velocity of electrons:

$$V_{F} = \text{Sign}[\text{Sign}[V_s]V_{s}^{2} + A] \sqrt{\text{Abs}[\text{Sign}[V_s]V_{s}^{2} + A]}$$

\(16\)

Where \(A = \frac{2eEx}{m} - \frac{2kT}{m} \cdot eEx = b \cdot eU^{*}\)

In this case, we obtain the final electron velocity \(V_{F}\) false with a significant addition for small initial electron velocities (Figure 8) and an increase in the flux in the 1 – V characteristic.

**Figure 8.** Dependences of the final velocity of electrons \(V_{F}\) false (a) on their initial thermal velocity \(V_{s}\) false for the emitter and collector. The potential difference changes by a factor of 2 (the black dotted line qualitatively shows the distribution of Boltzmann electrons over the initial velocities).

The resulting expression for the final velocities \(V_{F}\) false (15) gives an analytical zero crossing, both in the initial velocity and in the stress applied to the barrier (Figure 4). It makes it possible to analyze in detail the contributions of electrons with different initial velocities \(V_{s}\) false to the total electric current.

The plots presented in Figure 8 demonstrate that there is a singularity in the law of addition of velocities near the zero initial velocity of electrons in the parabolic zone. This feature is a consequence of the root dependence of the sum of squares, taking into account the sign of the velocity.

Taking into account the Boltzmann distribution shown by the wide dotted line in Figure 8 for the one-dimensional case, one can obtain \([20]\) the partial contributions of changes in the electron velocities to the total electron flux (Figure 9):

$$dQ^{0} = e \left( \frac{x^2}{b^2} \right) \left( \text{Sign}[x] \cdot x^2 + beU^{*} \right) \left( \text{Abs}[x] \cdot x + beU^{*} \right)$$

\(17\)

\(x = V_{s}\)
Integration of all these partial contributions for the emitter and collector and their summation gives all the ballistic additions obtained above (f. 15 and 16,) as areas under the curves shown in Figure 9.

And, at the same time, as can be seen from Figure 9, the singularity in the change / increments of the final velocity near zero initial velocities is additionally enhanced by the concentration maximum of the Boltzmann distribution.

**Figure 9.** Partial contributions of changes in the initial velocities of the emitter and collector electrons

Integration of partial contributions over the entire range of initial electron velocities brings us back to the formula for the total current (11, 12) with the contributions strictly described by formulas (7-10).

Further refinement of the obtained analytical expressions for the electron fluxes over the barrier requires additional analysis of the shift of the center of gravity of the Boltzmann distribution over the initial electron velocities. A complete simulation of this shift, requiring both the density and free allowed states, will not be carried out in this work, but this qualitatively increases the partial contribution of electrons that were discarded by Richardson from consideration. Will mark only the main thing. The Richardson differential current describing the macroscopic experiments was actually diffuse - an increment due to the field of the average diffuse velocity was used. Whereas the rigorous calculation carried out gives ballistic additions to the current, which are an order of magnitude higher than the diffuse Richardson current. And as can be seen from the above analysis - the maximum additions due to the acceleration of electrons ejected earlier from consideration with negative velocities.

### 3.3 Allowed Spatial Transitions in the p-n Junction

When analyzing and calculating currents above the barrier, it is necessary to take into account not only the electric force, but also the concentration force arising at the boundary [21]. Without taking it into account, even a rough description of the work of the p-n junction cannot be built.

But, as experiments have confirmed, it is also required to take into account the temperature force that gives the Local Thermal EMF of the barrier. With the traditional Richardson approach to calculating currents, even the Richardson constant could not be used for quantitative estimates and was actually chosen from fitting a small portion of the I – V characteristic, and the I – V characteristic based on the Richardson difference current did not agree well with the experimentally observed one.

For the three-dimensional case, the resulting total fluxes (10, 11) do not change fundamentally - they have only an additional factor, like the three-dimensional Richardson current. In other words, the excess of the three-dimensional ballistic current in relation to the three-dimensional Richardson current remains, which removes the “ban” on the MEASURABILITY of Local Thermal EMF, arising, in particular, in the n-n junction (Figure 10).

**Figure 10.** Scheme of the photoelectric effect and the longitudinal thermoelectric effect in the p-n junction

At the same time, as shown in Figure 10, in the n-n junction, along with the photo-EMF (green arrows), the opposite sign, but almost equal in magnitude, Local Thermo-EMF, independent, in contrast to the Seebeck coefficient, of the direction sign heat flow..

And the values of local thermoelectric currents not only provide MEASURABILITY of “anomalous effects” [22,23], but also give a higher efficiency of energy conversion [24].

Along with the longitudinal, with respect to the heat flux propagating through the n-n junction, the local thermoelectric effect is also observed the so-called transverse local thermoelectric effect [25]. In this case, the appearance of a voltage at the n-n junction during the flow of heat along the boundary of layers with an inverse type of conductivity. This local thermoelectric effect in-phase photoelectric effect gives a significant excess of sensitivity and signal-to-noise ratio in comparison with...
standard photodetectors (Figure 11).

![Figure 11](image_url)

**Figure 11.** Comparison of sensitivity of the thermal receiver (detector) on transversal (N,ThED) Local Thermo-EMF in p-n junction with the reference photodetector – 10 are used nanosecond impulse of green light.

Thus, both local thermoelectric effects in p-n junction, both longitudinal and transverse, demonstrate not only MEASURABILITY, but their high efficiency.

### 4. Instead of a Conclusion

Removal of the Richardson-Langmuir Ban made it possible to explain the experimentally observed high signal-to-noise ratio in thermal detectors based on Local Thermo-EMF (Figure 11), which is directly related to their high conversion efficiency (Figure 12).

![Figure 12](image_url)

**Figure 12.** Elements imbalance energy in p-n junction: consumption - «+», generation - «-»

As shown in Figure 12, Local Thermo-EMF allows, in principle, to go from the low-voltage maximum Ioffe efficiency for diffuse semiconductors, the theoretical limit of which is less than 16% (practical - less than 12%) to the high-voltage maximum efficiency, which, for local Thermo-EMF, in principle, can exceed 36%.

For generators based on Local Thermo-EMF, the efficiency, like any heat engine, increases with an increase in the operating temperature drop. Therefore, for generators, multilayer structures of nn junctions are required and, preferably, with an increase in the band gap from the radiator to the heater, a number of conjugated nn junctions are needed: Ge-Si-GaAs-GaN [26]. In principle, it is possible to use polar superstructures that are stable in the operating temperature range based on incommensurate crystals of higher manganese silicide [27], doped with iron (to reduce their electrical conductivity), or on the basis of silicon carbide polytypes [28,29]. But superstructures must be polarized under current and at temperatures below their thermodynamic decomposition, but above the maximum operating temperature of the generator.

### References


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ARTICLE

Tailoring the Optical Properties of Polymers Blend Nanocomposites

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ABSTRACT

The presented work deals with the structural and optical properties of chemically synthesized TiO₂ nanoparticles filled PC/PS blend nanocomposites. A series of PC/PS (100/0, 50/50, 0/100 wt%/wt %) - TiO₂ (1, 2, 3 wt %) blend nanocomposites have been prepared by solution casting method. Prepared blend nanocomposites have been subjected to XRD, SEM and FTIR for structural analysis. Optical constants have been analyzed using UV-Vis spectroscopy. The XRD, SEM and FTIR spectrum confirms the formation of PC/PS-TiO₂ blend nanocomposites. Results reveal the decrease in band gap and enhancement in optical constants like, extinction coefficient, refractive index and dielectric constants of blend nanocomposites with nanofiller TiO₂ content.

1. Introduction

Polymers, due to their versatility and wide variety of applications, have been creating a worldwide demand. Common polymers used in many applications as raw material are acrylics, acrylonitrile, polyethylene, polypropylene, polystyrene and polycarbonates [1-3]. Among these polymers polycarbonate (PC) has attracted considerable attention, since polycarbonate is amorphous, transparent, fully recyclable, made from natural resources and one of the most widely used engineering polymers. It can withstand all sorts of extreme and adverse environmental conditions. It is also helpful in minimizing the carbon footprint. It shows very good thermal and mechanical properties [4,5]. Moreover, amorphous materials have a lot of useful potential applications concerned with their electrical and optical properties. Many electronic equipment is made up of Polycarbonates like CDs and DVDs, automobile parts, sports safety equipment, reusable water bottles, containers for food-storage due to its toughness and heat resistance [6,7]. Polystyrene (PS), a versatile thermoplastic polymer, is one of the commercial polymers widely used in various industrial fields, packaging and biomedical applications. When combined with various colorants, additives or other plastics, polystyrene (PS) is used to make appliances, electronic, automobile parts, toys etc. [8,9].

In the large field of nanotechnology, combining the properties of the polymer matrix and the inorganic filler provides a new economic way to obtain tailored high-performance materials, as they can provide the necessary stability and easy process-ability with interesting optical

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properties\cite{9-12}. Polymer nanocomposites possess unique material properties which make them suitable for optical applications. The addition of nanoparticles into a polymer matrix makes it wear and scratches resistant. The large surface-to-volume ratio of nanoparticles allows significant improvement and modification of material properties\cite{11-19}. Inorganic filler titanium dioxide (TiO$_2$) has drawn enormous attention in recent years due to its importance in a variety of practical applications: photo catalysis, optics, sensing, optical-interference coatings and electric devices such as varistors, in paints (as a pigment). TiO$_2$ is biologically and chemically inert, non-toxic, abundantly available and cheap\cite{20-24}.

TiO$_2$ is the promising material as semiconductor having high photochemical stability and low cost\cite{25}. A great deal of research effort has been focused on both synthesis of nanocomposites and their linear and nonlinear optical properties. M. T. Ramesan et.al\cite{21} has reported about conductivity studies of copper sulphide nanoparticles incorporated polypyrrole (PPy)/polyvinyl alcohol (PVA) blend by in situ chemical oxidative polymerization. Thin films of polystyrene and polystyrene-TiO$_2$ nanocomposites have been prepared by spin coating and exposed to UV irradiation, the reduced values of optical band gap have been found in the range from 4.54 eV in pure PS to 4.45 eV for PS-TiO$_2$ nanocomposites prior to irradiation\cite{26}. Ruchuan Liu et. al\cite{27} has reviewed recent progress on hybrid photovoltaic systems of inorganic semiconductors and organic conducting polymers.

The measurement of the optical absorption coefficient, particularly near the fundamental absorption edge, provides a standard method for investigation of optically induced electronic transitions. This also provides some ideas about the band structure and energy gap in both crystalline and non-crystalline materials\cite{28-30}. The work described in this paper is concerned with the structural and optical properties of PC/PS-TiO$_2$ blend nanocomposites.

2. Experimental

The polycarbonate, Polystyrene (in granular form), Titanium III Chloride (TiCl$_3$) (mw~154.2) and Ammonium Hydroxide (NH$_3$OH) have been procured from Sigma Aldrich (USA). Di-ChloroMethane (DCM) (density=1.325) has been procured from Merck Pvt Ltd (India).

The chemical precipitation method has been employed to synthesize TiO$_2$ nanoparticles. In this method, solution mixture of TiCl$_3$ solution and NH$_3$OH aqueous solution in a volume ratio 1:6, has been stirred for 48 hrs at room temperature. Then, solution has been centrifuged and white precipitate has been further washed in isopropyl alcohol. White powdered TiO$_2$ nanoparticles have been obtained after drying precipitate at room temperature\cite{31}.

PC and PS have been used as precursor. PC and PS have been taken in 100/0, 50/50, 0/100 weight ratio and dissolved in solvent (DCM). TiO$_2$ nanoparticles, with 1, 2 and 3 wt %, have been added in this solution and is sonicated for 10 min. Resultant solution has been cast and dried on to the glass Petri dish. Self-sustainable film has been peeled off from Petri dish and used for characterization.

3. Theory

The optical absorption coefficient ($\alpha$), can be calculated from the optical absorbance spectra using the relation\cite{32,33}

$$\log \left( \frac{I}{I_0} \right) = 2.303 A = \alpha t$$

(1)

Where, $I$ be the intensity of incident beam, $I_0$ be the intensity of the transmitted beam, $A$ be the optical absorbance, and $t$ be the film thickness.

The transmission coefficient (T) can be calculated using the relation\cite{33},

$$T = 10^{(-A)}$$

(2)

While, the values of reflectance have been obtained from absorbance and transmission coefficient using the relation;

$$R = 1 - (A + T)$$

(3)

The absorption edge for transitions can be obtained according to the model proposed by Tauc\cite{34,10} as,

$$\alpha h\nu = C (h\nu - E_g^{opt})^n$$

(4)

Where, $h\nu$ be the energy, which is independent constant related to the properties of the valance and conduction bands, ($h\nu$) be the photon energy, be the optical energy band gap of the material. The value of ‘$n’ for allowed direct transition is taken as $\frac{1}{2}$\cite{9}. The variation of ($\alpha h\nu$) against ($h\nu$) yields a good straight line fit to the absorption edge and the extrapolated ($h\nu$) for ($\alpha h\nu$) = 0 provides the $E_g^{opt}$.

The extinction coefficient $k$ can be obtained from the relation\cite{35} as

$$k = \frac{\alpha \lambda}{4\pi}$$

(5)

Where, $\lambda$ be the wavelength of light.

The variation of the refractive index ‘$n’ can be calculated by\cite{36},

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}$$

(6)

Refractive index ‘$n’ determines how reflective and refractive a film made from this material will be\cite{37}.

The real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the dielectric constant have been given by the following equations\cite{38},

$$\varepsilon_r = n^2 - k^2$$

(7)

$$\varepsilon_i = 2nk$$

(8)
4. Results and Discussion

4.1 X-Ray Diffraction (XRD)

X-Ray Diffraction of prepared TiO$_2$ nanoparticles and TiO$_2$-PC/PS blend nanocomposites have been recorded, using Bruker D8 Advance with Cu (Kα) radiation ($\lambda=1.54 \text{ Å}$), in the range of $2\theta = 20^\circ-70^\circ$. Figure 1 shows X-ray diffractogram of TiO$_2$ nanoparticles and a representative XRD pattern of PC50%/PS50% and its TiO$_2$ blend nanocomposites.

The appearance of sharp crystalline reflections indicates the high purity and crystallinity of the nanoparticles. Their average crystallite size has been estimated, according to the Scherrer equation $^{[39]}$, as ~19 nm. On the other hand, the diffractogram of PC50% / PS50% shows broad reflections indicative of its amorphous character. These wide peaks in the diffractograms of the blend nanocomposites, together with those characteristics of the nanoparticles, confirm that the crystalline structure of the nanoparticles is maintained in the blend nanocomposites.

4.2 Fourier Transform Infrared (FTIR)

A Fourier transform infrared spectrum has been employed for structural characterization of blend nanocomposites. FTIR spectroscopy is one of the powerful tools for identifying and investigating the presence of various functional groups in polymers. FTIR has been performed in transmission mode using Bruker Alpha-T spectrometer. The spectra have been recorded in the wave number range of 500-4250 cm$^{-1}$.

Figure 2 shows the FTIR spectra of PC 50%/ PS 50% (wt/wt) with TiO$_2$ (1, 2, 3 wt %) nanoparticles as a representative case. The absorption bands of PC, PS and TiO$_2$ have been observed in IR spectrum. Table 1 lists the absorption band modes observed in FTIR spectra.

### Table 1. Observed bands and modes in FTIR spectra

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Mode</th>
<th>Wavenumber (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C=O stretching band</td>
<td>1773</td>
</tr>
<tr>
<td>2</td>
<td>ring (C-C) vibrational mode</td>
<td>1507</td>
</tr>
<tr>
<td>3</td>
<td>O-C-O stretching vibrational mode</td>
<td>1013</td>
</tr>
<tr>
<td>4</td>
<td>aromatic C-H stretching</td>
<td>3026</td>
</tr>
<tr>
<td>5</td>
<td>aliphatic C-H stretching</td>
<td>2849</td>
</tr>
<tr>
<td>6</td>
<td>aromatic C=C stretching</td>
<td>1601, 1493</td>
</tr>
<tr>
<td>7</td>
<td>C-H deformation vibration band of benzene ring</td>
<td>758</td>
</tr>
<tr>
<td>8</td>
<td>Ring deformation vibration</td>
<td>700</td>
</tr>
<tr>
<td>9</td>
<td>Ti-O vibrational group</td>
<td>547, 551, 593</td>
</tr>
</tbody>
</table>

Figure 2. FTIR spectra of PC50%/PS50% and its TiO$_2$ blend nanocomposites

Figure 3. SEM images of (a) PC100%+2% TiO$_2$ (b) PC50%/PS50%+2% TiO$_2$ + (c) PS100% +2% TiO$_2$ blend nanocomposites
4.3 Scanning Electron Microscopy (SEM)

SEM provides very useful information about the particle size and location of filler on the surface of the material. Zeiss EVO 18, Scanning Electron Microscopy machine, has been employed to investigate the dispersion of nanoparticles in the polymer blend matrix. Figure 3 shows the SEM images of PC 100%, PC50%/PS50% and PS100% embedded with 2 wt% TiO$_2$ as representative cases. TiO$_2$ nanoparticles have tendency to agglomerate due to very high surface energy. Random and homogeneous TiO$_2$ distributions have been observed in polymer blend nanocomposites.

4.4 UV-Vis Spectroscopy

Perkin Elmer LAMBDA-750 UV/Vis/NIR spectrophotometer has been employed to record the absorption spectra in the wavelength range of 250-800 nm. Figure 4 shows the absorption spectra of blend nanocomposites under test. Red shift i.e. higher absorption has been observed in TiO$_2$ blend nanocomposites as compared to pure polymer matrix.

Absorption increases as TiO$_2$ content increase due to absorbance of the incident light by the free charge carriers. These absorption spectra have been used to calculate band gap using Tauc relation (eq.-4). Figure 5 shows the variation of $(\alpha h\nu)^2$ against $(h\nu)$ and calculation of band gap according to Tauc relation and the values of band gap have been listed in Table 2. A decreasing trend in the values of optical band gap is observed with the increase in TiO$_2$ wt% in the polymer blend samples under test. The lowest band gap (4.22 eV) has been found for PC50%/PS50% with 3% TiO$_2$ content.

Table 2. Values of band gap for PC/PS-TiO$_2$ blend nanocomposites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pure</th>
<th>1% TiO$_2$</th>
<th>2% TiO$_2$</th>
<th>3% TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC100%</td>
<td>4.38</td>
<td>4.36</td>
<td>4.35</td>
<td>4.34</td>
</tr>
<tr>
<td>PC50%/PS50%</td>
<td>4.26</td>
<td>4.24</td>
<td>4.23</td>
<td>4.22</td>
</tr>
<tr>
<td>PS100%</td>
<td>4.40</td>
<td>4.37</td>
<td>4.36</td>
<td>4.35</td>
</tr>
</tbody>
</table>

$k$, the extinction coefficient, has been calculated using equation (5). Figure 6 shows the dependence of $k$ on $\lambda$ for polymer blend nanocomposites. Results reveal that behaviour of $k$ is nearly similar to corresponding absorption spectra (Figure 4) as, $k$ is directly proportional to $\alpha$. It has also been observed that values of $k$ increase with increasing TiO$_2$ wt%.

The values of reflectance $R$ have been obtained by
Figure 5. Band gap calculation for TiO$_2$ blend nanocomposites of (a) PC100% (b) PC50%/PS50% (c) PS100%

Figure 6. Variation of $k$ with respect to $\lambda$ for TiO$_2$ blend nanocomposites of (a) PC100% (b) PC50%/PS50% (c) PS100%
Figure 7. Variation of $n$ with respect to $\lambda$ for PC50%/PS50% and its TiO$_2$ blend nanocomposites

The real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the dielectric constant have been calculated using equation (7) and (8). Figure 8 shows the variation of real and imaginary parts of the dielectric constant of PC50%/PS50% and its TiO$_2$ blend nanocomposites, as a representative case. The real part of the dielectric constant increases on increasing TiO$_2$ wt%. Furthermore, nearly equal values of real part of dielectric constant have been observed for high (2 & 3wt %) TiO$_2$ content. It has been concluded that the variation of $\varepsilon_r$ mainly depends on ($n^2$) because of small values of ($k^2$), while $\varepsilon_i$ mainly depends on the ($k$) values which are related to the variation of absorption coefficients.

Keen observation of all optical properties leads an interesting inference that PC50%PS50%-TiO$_2$ blend nanocomposites have the modified optical properties in comparison of pure polymer matrix. Such type of polymer blend nanocomposites can be useful for photovoltaic devices, solar cells etc. [41,42].

5. Conclusions

The discussion of the results obtained in present work leads to the following conclusions.

A series of PC/PS-TiO$_2$ blend nanocomposites have been prepared by solution casting method. The average crystallite size of chemically synthesized TiO$_2$ nanoparticles has been estimated using Scherrer equation and it comes out to be ~19 mm.

X-ray diffractograms of PC50%/PS50% and its TiO$_2$ blend nanocomposites show that the nanoparticles remain in nano-regime during blend nanocomposites preparation process. FTIR spectra shows the presence of various functional groups in blend nanocomposites, which confirms the formation of polymer blends and nanocomposites. SEM analysis provides the information about homogeneous distribution of TiO$_2$ in polymer blend nanocomposites.
Increase in absorption has been observed by increasing TiO2 content in PC/PS matrix. Optical band gap decreases with increase in TiO2 wt% in the polymer blend system. The lowest band gap (4.22 eV) has been found for PC50%/PS50% with 3% TiO2 content. The enhancement in extinction coefficient, refractive index and dielectric constants of blend nanocomposites has also been observed. Such blend nanocomposites of PC/PS with modified optical constants are useful for photovoltaic applications.

References
