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Influence ofcorrection factor on nearest neighbour hopping parameter in energy dispersion relationofGraphene nanoribbon

Asif Hassan

Khulna University of Engineering & Technology,Khulna-9203, **BANGLADESH**

Email: hassanstrong_08@hotmail.com

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ABSTRACT

We investigated on energy dispersion relation (E-KR) of graphene nanoribbon (GNR) considering its two prototypical shapes named as armchair GNR (AGNR) and zigzag GNR (ZGNR) but specially of AGNR in nearest neighbor interactions.Two parts $\frac{\Delta}{2}$ *and* $(\hbar\gamma_s)^2$*of E-KR relation have different characteristics independently expresses their importance. A correction factor* Δ_{γ_1} *is used for hopping between two edge carbon atoms to count edge relaxation. Influence of this factor on hopping parameter exemplifies the edge bond relaxation effect in AGNR and ZGNR.*

Keywords: Energy dispersion relation, graphene nanoribbon, nearest neighbor interactions, ballistic performance, correction factor, edge relaxation.

INTRODUCTION

Carbon nanomaterial reveals different outstanding properties subject to their geometrical structures. Nanoscale strips of single layer graphene named as GNRs have recently been the focus on widespread efforts in theoretical and practical field [1]. There is a confinement of carriers in two directions so GNRs are a one dimension (1D) structure with [2]GNRs are expected to have electronic properties as like as in those of Carbon nanotubes(CNTs) that can be unwrapped into GNRs as there is structural similarity with compared to CNTs and effects in quantum confinement[3]. Today's theoretical statistics indicates that characteristics such like metallic or semiconducting behavior in GNRs unlike from that in CNTs [4, 5]. Two prototypical edge shapes are formed by cutting graphene sheet along a straight line named as the armchair edge and the zigzag edge between the two edge orientations with a difference of 30° in the axial direction [6]. Either one of these two "ideal" shapes or more complex geometries composed of a mixture of armchair and zigzag shaped fragments is formed depending on the cutting direction, the edges of the GNRs [7]. GNRs are classified by the number of dimer lines (zigzag lines) named as armchair (zigzag) edges on both sides across the ribbon width [8,9]. GNRs are semiconducting due to the edge effects for all sub-10 nm make more attractive for electronic device applications [10].The electronic band structure of AGNRs are found to play an important role in the edge bond relaxation and the 3NN interactions [11, 12, 13,14] that are not prominent in CNTs. Using the NEGF formalism atomistic simulations of GNRFETs have also been described [15,16,17.18]. But they are expensive so we have

examined by MATLAB simulation of the influence of correction factor on nearest neighbor of hopping parameter in AGNR. GNRs semiconducting properties can be guessed through its geometrical nature where width is [19, 20, 21, 22] rely on N [21, 23] in which this properties occur in GNRs when m = 3p or m = 3p+1, where p is an integer [24].At first we have calculated the main energy dispersion than without considering the correction factor we measured the energy dispersion from which we calculate the percentage of deviation or error on energy.

MATERIALS AND METHODS

simulation model : with a view to following the standard gnr literature convention —"armchair" and —"zigzag" denote to the shape of the edge in the transport direction of the gnr and, that is contrasting to the cnt convention [25]. an armchair ribbon is cut so that the edge looks as if it consists of repeated armchairs. the width of an armchair ribbon can be defined in terms of the number of dimer lines (n): [26]

W_{ac}= (m-1) $\frac{\sqrt{3}}{2}$a Eq.(A.1)

Again we can write from the above equation

m=$\frac{2w_{ac}+2\sqrt{3}a}{\sqrt{3}a}$ Eq.(A.2)

Where a=1.42A° the nearest neighbor distance and

And m = 3p or m = 3p+1 or m=3p+2.

Now to observe the ballistic performance along with the band structures in the energy range of interest of AGNR where

E-k dispersion parameter is given by: [10]

$\frac{\Delta}{2} = \gamma_1(2s\, cos\frac{p\pi}{m+1} + 1) + \gamma_3\,(2s\, cos\,\frac{2p\pi}{m+1} + 1) + 4(\frac{\gamma_1+\Delta_{\gamma_1}}{m+1})sin^2\,\frac{p\pi}{m+1}$ Eq.(A.3)

Where p=m/3 or (m-1)/3 or (m-2)/3 and s=0.129 indicates overlapping integral.

Here for convenient to understand say m=3p or 3p+1 or 3p+2.

Also [10]

$(\hbar\gamma_s)^2=$
$(3d)^2\left\{-\frac{1}{2}\,\gamma_1 s\, cos\,\frac{p\pi}{m+1}\times\left[\gamma_1 + \gamma_3\left(2cos\,\frac{2p\pi}{m+1}+1\right) + 4\left(\frac{\gamma_3+\Delta_{\gamma_1}}{m+1}\right)sin^2\,\frac{p\pi}{m+1}\right] - \gamma_3\left(\gamma_1 + 2\gamma_3 cos\,\frac{2p\pi}{m+1} + 4\left(\frac{\gamma_3+\Delta_{\gamma_1}}{m+1}\right)sin^2\,\frac{p\pi}{m+1}\right)\right\}$ Eq.(A.4)

Where γ_1=-3.2eV indicates first nearest neighbor hopping parameters, γ_3=-0.3eVthird nearest neighbor hopping parameters and

Δ_{γ_1}=-0.2eVis the correction of γ_1 for the bonds due to the edge bond relaxation and ħ is the reduced Planck constant. [11].

The main goal of our investigation is the 'term' which causes an error of correction factor in energy dispersion relation is

$\frac{\Delta_e}{2} = \gamma_1(2s\, cos\frac{p\pi}{m+1} + 1) + \gamma_3\,(2s\, cos\,\frac{2p\pi}{m+1} + 1)$ Eq.(A.5)

$(\hbar\gamma_s)^2{}_e=(3d)^2\left\{-\frac{1}{2}\,\gamma_1 s\, cos\,\frac{p\pi}{m+1}\times\left[\gamma_1 + \gamma_3\left(2cos\,\frac{2p\pi}{m+1}+1\right)\right] - \gamma_3\left(\gamma_1 + 2\gamma_3 cos\,\frac{2p\pi}{m+1}\right)\right\}$ Eq.(A.6)

So the final energy dispersion equation become which has ± value denoted as [10]

$$E=\sqrt{\left(\left(\frac{\Delta}{2}\right)^2+(\hbar\gamma_s)^2\right)} \quad \text{Eq.(A.7)}$$

$$E_e=\sqrt{\left(\left(\frac{\Delta_e}{2}\right)^2+(\hbar\gamma_s)^2\right)} \quad \text{Eq.(B.1)}$$

$$\text{Or } E_e=\sqrt{\left(\left(\frac{\Delta}{2}\right)^2+(\hbar\gamma_s)^2{}_e\right)} \quad \text{Eq.(B.2)}$$

$$\text{Or } E_e=\sqrt{\left(\left(\frac{\Delta_e}{2}\right)^2+(\hbar\gamma_s)^2{}_e\right)} \quad \text{Eq.(B.3)}$$

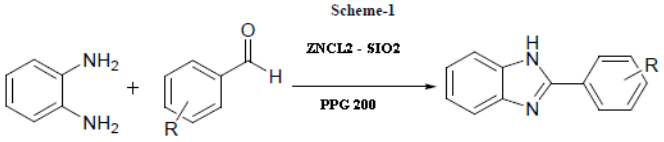
To check the influence of correction factor of γ1 we have omitted the Δ_{ce}term from equation (3), (4) for this corresponding value of E is obtained as E_e.Based on this value the percentage of error can be calculated.

$$e_r=\frac{(\text{actual value of E}-\text{ error value of E}(E_e))}{actual\ value\ of\ E}\times 100\% \quad \text{Eq.(A.8)}$$

RESULTS AND DISCUSSION

In continuation of our efforts on developing green methodologies for biologically active 29 organic compounds, we reported here a $ZnCl_2$ catalysed procedure for the synthesis of benzimidazole derivatives in PPG at 50°C. Initially, a blank reaction was carried out using 1equiv. each of o-phenylenediamine and benzaldehyde. These were stirred at ambient temperature in ethanol for 12 h and only 65% of the expected product was obtained. The same reaction was then carried out using PPG 200 as the reaction medium under similar conditions. Surprisingly, a significant improvement was observed and the yield of product was dramatically increased to 85% for 10 h. Further to improve the yield and also to explore the catalytic activity of $ZnCl_2$ the reaction was carried out with same amount of reactants in PPG (5 mL) we restirred at 50°C in the presence of 2 mol% of $ZnCl_2$ for 5 h, a good improvement was observed and the reaction yield is 90% benzimidazole (scheme 1). With this optimistic result in hand, we further investigated the best reaction condition by using different amounts of $ZnCl_2$. An increase in the quantity of $ZnCl_2$ from 2 mol% to 5 mol%, not only decreased the reaction time from 5 h to 2 h but also increased the product yield from 90to 92.

Scheme-1



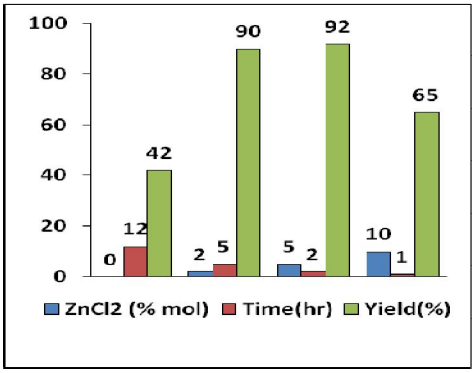


Figure 1. Catalytic activity evaluation for benzimidazoles. Reaction conditions: o-phenylenediamine (1 mmol), benzaldehyde(1 mmol); solvent PPG200 . temperature 50°C.Isolated yields.

Table 1. Synthesis of 2-phenyl benzimidazole derivatives by using $ZnCl_2$-PPG 200 system.

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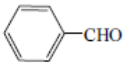
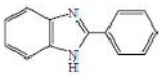
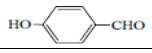
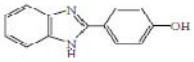
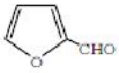
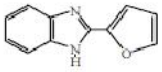
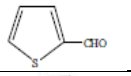
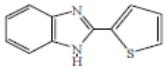
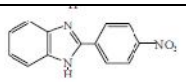
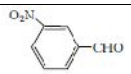
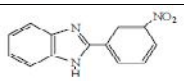
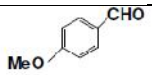
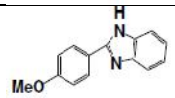
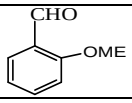
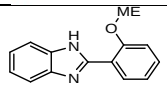
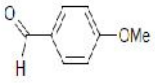
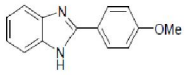
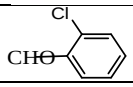
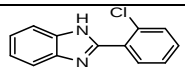
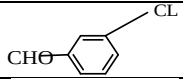
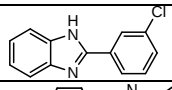
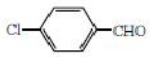
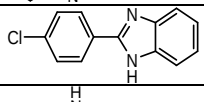
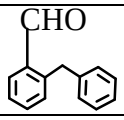
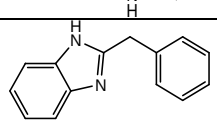
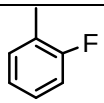
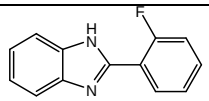
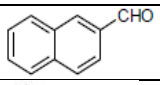
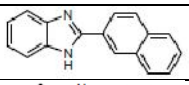
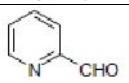
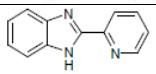
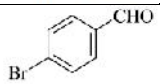
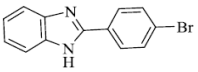
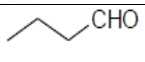
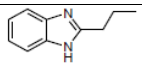
1			98
2			92
3			90
4			91
5			96
6			98
7			96
8			95
9			92
10			92
11			85
12			96
13			93

14			96
15			94
16			95
17			94
18			96

Reaction conditions: o-phenylenediamine (1 mmol), aldehydes (1 mmol), $ZnCl_2$ (5 mol%); solvent PPG 200; temperature 50°C Isolated yields.

Although the use of 10 mol% of $ZnCl_2$ permitted the reaction time to be decreased to 1h, the yield unexpectedly decreased to 65%. A possible explanation for the low product yields is that the starting material or the product may have been destroyed during the reaction when excess amount (10 mol%) of $ZnCl_2$ was used in the reaction. It appears that a concentration of 5 mol% of $ZnCl_2$ is the suitable choice for an optimum yield of benzimidazoles (figure 1). In order to study the generality of this procedure, the applicability of the PPG 200 with $ZnCl_2$ system was then examined for the reaction of a series of aromatic aldehydes with o-phenylenediamine under the optimized reaction conditions (table 1). As shown, a variety of substituted aromatic aldehydes, bearing either electron-donating or electron-withdrawing substituents, afforded the products in excellent yields and high purities. In addition, heterocyclic aldehydes could also be used for efficient preparation of various heterocyclic-benzimidazoles (table 1, entry 3 and 4). It was interesting to observe the remarkable stability of a variety of functional groups such as ether, nitro, hydroxyl, halides, and formyl under the reaction conditions. The nature of reaction media has an important role in the synthesis of benzimidazoles in the presence of $ZnCl_2$ (5 mol%). Almost all solvents afforded products in excellent yield with a variation in reaction time. Therefore we used only PPG 200 as a solvent because it is recyclable, non-toxic and thermally stable (figure 2)

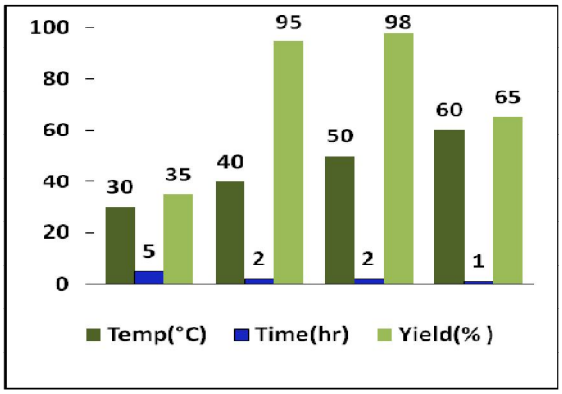


Figure 2: $ZnCl_2$ catalyze Benzimidazoles reaction in various solvents. Reaction conditions: o-phenylenediamine(1 mmol), benzaldehyde (1 mmol); solvent PPG 200; temperature 50°C. Isolated yields.

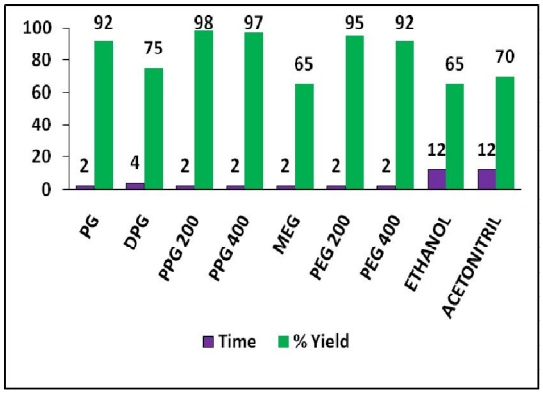


Figure 3. Effect of Temperature. Reaction conditions: o-phenylenediamine (1 mmol), benzaldehyde (1 mmol), $ZnCl_2$ (5 mol%); solvent PG 400; temperature 50°C. Isolated yields.

The effect of temperature was also studied. Faster reactions occurred on raising the temperature but the yield of product decreased at higher temperature possibly because one of the reactants (aldehydes) oxidizes at high temperature in presence of $ZnCl_2$ (figure 3).In order to prove that the use of PPG as solvent is also practical, it was recycled with minimum loss and decomposition. Since poly PPG is immiscible with solvent ether, the desired product may be extracted with it and remaining PPG phase may be used. The solvent phase was recycled with no change in reactivity for three cycles but approximately 5% weight loss of PPG was observed from cycle to cycle (figure 4). Overall this methodology offers the competitive advantages of recyclability of the solvents which could be used without further purification and without any additions. It also requires less loading of the catalyst and has broad substrate applicability with ease and improved yields. In addition low cost, recyclable solvent system and ready availability of catalyst, an environmentally benign procedure makes this methodology a useful contribution to the existing procedures available for the synthesis of benzimidazole derivatives.

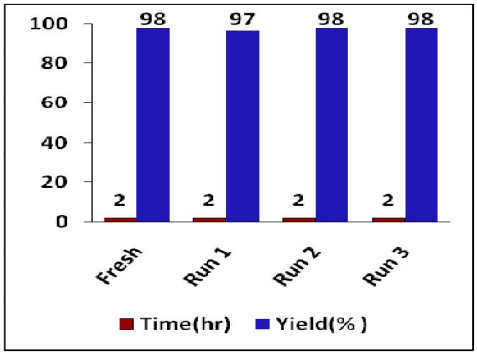


Figure 4. Recycling yields. Reaction conditions o-phenylenediamine (1 mmol), aldehyde (1 mmol), $ZnCl_2$ (5 mol%); solvent PPG 200; temperature 50°C. Isolated yields

APPLICATIONS

These methods involve use of solvent free method or use of recyclable organic solvents. The low cost, recyclable solvent system and ready availability of catalyst, an environmentally benign procedure makes this methodology, a useful contribution to the existing procedures available for the synthesis of benzimidazole derivatives.

CONCLUSIONS

In conclusion, the PPG has been employed as a novel, mild and highly efficient solvent system for the convenient preparation of benzimidazoles in excellent yields from o-phenyldiamine and a wide variety of aryl aldehydes using $ZnCl_2$ as catalyst. In addition low cost, recyclable solvent system and ready availability of catalyst, an environmentally benign procedure makes this methodology a useful contribution to the existing procedures available for the synthesis of benzimidazole derivatives.

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