Junchen Zhao

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Education

09/2014- Present Suzhou Industrial Park Xinghai Experimental Middle School
GPA : 4.0/4.0
SAT: 1450/1600   TOEFL: 107

Research Experience

1. **2017** ***Math Expectation of the Number of Suits in N Pokers***
   —Use combinatorics and computer science to analyze a random process
   —See the attached Research on Math Expectation of the Number of Suits in N Cards (Page 3-10)

2. **2017** ***Experiments and report on Enhanced Photoelectrochemical Performance in Reduced Graphene Oxide/$BiFeO_3$ Heterostructure*** **at Soochow University**
   —Perform experiment to fabricate $BiFeO_3$ heterostructure
   —Report and review the deficiencies of this experiment
   —See the attached Report and Retrospect on Experiments (Page 11-14) and Enhanced Photoelectrochemical Performance (Page 15-30)

Projects

1. **2016-2017   A Robot to Solve Rubik's Cubes**
   —Use C++ to generate solution in cube state and Use Arduino to control steppers to execute solution
   —Write code independently according to algorithm and documentation online
   —Self-design and combine the robot structure and components together
   —Solve a Rubik's Cube in 5 seconds
   —See the video at https://m.weibo.cn/status/4169240011431230
   —View the code at https://github.com/g20150120/cubot
   —Visit http://alexanderzhao.info#resume for more information

2. **2017 Pocket College**
   —Build a platform for students in US colleges to share experiences and information
   —View the code at https://github.com/g20150120/pocketcollege

3. **2017 Weibo Spide**r
   —Design a web crawler to do data mining in the most popular social media in China
   —Increase efficiency by at least 1400% with the creative code
   —View the code at https://github.com/g20150120/weibospider

4. **2017 Smart Classroom System**
   —Code the program and combine the components in an innovation competition
   —Design the system that regulates temperature and humidity by controlling fans and ACs connected to sensors and clean blackboard automatically

5. **2016 iOS9 Development**
   —Program and implement applications to present texts, images, and videos for iPhone
   —Perform function to change background and text colors

Summer Program

1. **2017 Stanford Pre-Collegiate Studies**
   —Study the fundamentals of *Web Technologies*, including both front end (HTML, Javascript, and CSS) and back end (Node with Express and MongoDB).
   —Build an online platform to assist applicants in their American College applications

2. 2017 Harvard Summit for Young Leaders in China

—Receive rigorous training in scholarship, entrepreneurship, leadership and citizenship via taking courses: Practical Electronics,The Mosaic of Self and Struggle, Introduction to Privacy & Technology, Randomness in Science and Literature, China Thinks Big

—Get GPA 3.82/4.0

3. 2016 Olympiad in Informatics Summer Camp

—Enrich the knowledge about the algorithms and data structures

—Win the Third Prize in Jiangsu (Provincial)

Honors and Awards

1. Online Physics Brawl: Top 180 teams worldwide (International)
2. Geography and Technology Competition: Second Prize (National)
3. Electrical Engineers Recognition for Teenagers: First Prize in Jiangsu (Provincial)
4. Junior High School Mathematics and Culture Festival: First Prize in Jiangsu (Provincial)
5. Olympiad of Informatics: Third Prize in Jiangsu (Provincial)
6. Olympiad of Chemistry: Second Prize in Suzhou (Municipal)
7. China Youth Business League Suzhou Regional: Fifth Place Team (Municipal)

Computer Skills

1. C++ with STL: used in algorithm and data structure competition and basic needs
2. Python: used in web crawler development and simple data or image analysis
3. Node with Express, jade, and MongoDB: used in web server to handle requests and so on
4. HTML, Javascript, and CSS: used in webpage development
5. Swift: used in iOS development
6. Mathematica: used in math calculation, plotting and so on.
7. C: used to control single chip computers

Sports

1. Basketball (starts at 12): made Grade Team in sophomore year and junior year
2. Frisbee (starts at 16): proficient in backhand, forehand; good at chasing and catching
3. Swimming (starts at 11): free stroke (Personal Best: 50m in 42s) and breast stroke
4. Ping Pong (training between 7 and 10)
5. Sprint: 100m second, 200m third at school sports meeting
6. Board Jump: second at school sports meeting
7. Chess, Chinese Chess, and Gobang
8. Pocket Cube, Rubik’s Cube (PB 25’’), Rubik’s Revenge (PB 2’06’’), and Pyramid

Voluntary Work

1. 2016-2017 Volunteer for students’ mental health in the school
2. 2016-2017 Volunteer for Suzhou Industrial Park Bo’ai School
3. 2016 Volunteer for National High School Debate League of China
4. 2015-2016 Volunteer for the school library

For more information, please visit http://alexanderzhao.info/

Research on Math Expectation of the Number of Suits in N Cards

Junchen Zhao, Hao Zhou

1. Abstract

In this paper, we aim to design an algorithm to calculate the expectation associated with card at a stochastic process. Techniques used include combinatorics, probability, and statistics. Code in C++ using a recursive function is also provided to substantiate our theory.

2. Introduction

We are inspired by a board game called “Killers of Three Kingdoms”. In this board game, a hero’s spell is defined by taking cards with different suits among the first five cards on the card pile. (For example, when two spades, two diamonds, and one heart are taken, one spade, one diamond, and one heart are obtained by the player.) We want to calculate the math expectation of the cards obtained according to this spell, further getting a formula to express the number of suits in n cards taken from an infinite card pile. Our research is aimed at getting a deeper understanding of combinatorics and solving real-life problems using knowledge learned in class. Three independent tools are employed to analyze this process to calculate the math expectation: combinatorics, exhaustive algorithm, and recursion relation analysis; they all give out the same result. In our essay, the new concepts of “similarity” and “dissimilarity” are defined.

3. Method employed

A. In this essay, the method such as (1+4) and (1+1+3) is used to analyze suit combinations. For example, (1+4) means a total of 5 cards, where there are two groups, one of which has one card in a suit, the other of which has four cards in another suit; (1+1+3) means a total of 5 cards, where there are three groups, which have 1, 1, 3 cards in different suits respectively.

B. When allocating suits to cards, the number of combinations (C) is used to calculate “similar” cards, and the number of permutations (P) is used to calculate “dissimilar” cards. For example, there are three conditions when 6 cards with 2 suits are drawn from the card pile, two of which are (2+4) and (3+3). For (2+4), “2” and “4” are “dissimilar”, so the formula to allocate suits is P_4^2 , which means to assign suits (picking 2 from 4 suits regardless of their permutation) to each group of cards. For (3+3), “3” and “3” are “similar”, so the formula to allocate suits is C_4^2 , which means to assign suits (picking 2 from 4 suits only considering combination) to each group of cards. That’s because when considering the arrangements of the cards, the reverse of “3” and “3” has already been included. If the reverse is considered again, one condition will be recorded once again, so the number of combinations (C) is used to calculate the suit-distribution conditions.

C. According to the Multiplication Rule, the number of cases satisfying the respective condition is obtained by multiplying the arrangement of cards and combination of suits. ***[1]***

4. Combinatorics analysis

4-1. Analysis of taking 5 cards

When there are 5 cards, the number of total conditions is $4^5 = 1024$.

Get 1 card

Obviously, if only 1 card is obtained, each card must be of the same suit. So there are 4 conditions. The possibility is $P_1 = \dfrac{4}{1024}$.

Get 2 cards

If 2 cards are obtained, the suit combinations of 5 cards are (1+4) or (2+3).

i. The total number of (1+4) is $C_5^1 \times C_4^4 \times P_4^2 = 60$. C_5^1 means the number of arrangements of "1" in 5 cards; C_4^4 means the number of arrangements of the remaining 4 cards; P_4^2 means the number of suit combinations regardless of their permutation.
ii. For the same reason, the total number of (2+3) is $C_5^2 \times C_3^3 \times P_4^2 = 120$.

In summary, the possibility of getting 2 cards in 5 cards is $P_2 = \dfrac{180}{1024}$.

Get 3 cards

If 3 cards are obtained, the suit combinations of 5 cards are (1+2+2) or (1+1+3).

i. The total number of (1+2+2) is $C_5^1 \times C_4^2 \times C_2^2 \times C_4^2 \times 2 = 360$. C_5^1 means the number of arrangements of "1" in 5 cards. C_4^2 means the number of arrangements of a "2" in the remaining 4 cards. C_2^2 means the number of arrangements of the last "2". The final C_4^2 means the number of suit combinations of two "similar" "2". The last factor 2 means the two possibilities of the suit of "1".
ii. For the same reason, the total number of (1+1+3) is $C_5^1 \times C_4^1 \times C_3^3 \times C_4^2 \times 2 = 240$.

In summary, the possibility of getting 3 cards in 5 cards is $P_3 = \dfrac{600}{1024}$.

Get 4 cards

If 4 cards are obtained, the suit combination of 5 cards is (1+1+1+2).

Same as the condition of getting 3 cards, the total number of (1+1+1+2) is $C_5^1 \times C_4^1 \times C_3^1 \times C_2^2 \times C_4^3 \times 1 = 240$. So the possibility is $P_4 = \dfrac{240}{1024}$.

Combining all the above analysis of taking 5 cards, we could get the math expectation:

$$E(5) = 1 \times P_1 + 2 \times P_2 + 3 \times P_3 + 4 \times P_4 = 3.05078$$

4-2. Analysis of taking 6 cards

When there are 6 cards, the number of total conditions is $4^6 = 4096$.

Get 1 card

Same as the case of 5 cards, the possibility here is $P_1 = \frac{4}{4096}$.

Get 2 cards

If 2 cards are obtained, the suit combinations of 6 cards are (1+5), (2+4), or (3+3).

i. When it is (1+5), the formula is $C_6^1 \times C_5^5 \times P_4^2 = 72$.
ii. When it is (2+4), the formula is $C_6^2 \times C_4^4 \times P_4^2 = 180$.
iii. When it is (3+3), the formula is $C_6^3 \times C_3^3 \times C_4^2 = 120$.

In summary, the possibility of getting 2 cards in 6 cards is $P_2 = \frac{372}{4096}$.

Get 3 cards

If 3 cards are obtained, the suit combinations of 6 cards are (1+1+4), (1+2+3), and (2+2+2).

i. When it is (1+1+4), the formula is $C_6^1 \times C_5^1 \times C_4^4 \times C_4^2 \times 2 = 360$.
ii. When it is (1+2+3), the formula is $C_6^1 \times C_5^2 \times C_3^3 \times P_4^3 = 1440$.
iii. When it is (2+2+2), the formula is $C_6^2 \times C_4^2 \times C_2^2 \times C_4^3 = 360$.

In summary, the possibility of getting 3 cards in 6 cards is $P_3 = \frac{2160}{4096}$.

Get 4 cards

If 4 cards are obtained, the suit combinations of 6 cards are (1+1+1+3) and (1+1+2+2).

i. When it is (1+1+1+3), the formula is $C_6^1 \times C_5^1 \times C_4^1 \times C_3^3 \times C_4^3 \times 1 = 480$.
ii. When it is (1+1+2+2), the formula is $C_6^1 \times C_5^1 \times C_4^2 \times C_2^2 \times C_4^2 \times 1 = 1080$.

In summary, the possibility of getting 4 cards in 6 cards is $P_4 = \frac{1560}{4096}$.

Combining all the analysis above, we could get the math expectation:
$$E(6) = 1 \times P_1 + 2 \times P_2 + 3 \times P_3 + 4 \times P_4 = 3.28809$$

4-3. Analysis of taking 7 cards:

When 7 cards are taken, the number of all possible situations is $4^7 = 16384$.

Same as the method above, we can easily conclude that P_1, the probability of obtaining 1 card, equals $\frac{4}{16384}$; P_2 equals $\frac{756}{16384}$; P_3 equals $\frac{7224}{16384}$; and P_4 equals $\frac{8400}{16384}$.

According to these results, E(7), the math expectation of the number of suits in 7 cards, equals 3.46606.

5. Verification by exhaustive algorithm in computer science *[2]*

In order to verify the results, a piece of C++ code using exhaustive algorithm is designed to enumerate all possible situations.

($P_i(n)$ below represents the probability of obtaining i cards when n cards are taken from the card pile.)

n	P_1(n)	P_2(n)	P_3(n)	P_4(n)	Math expectation
5	0.003906250	0.175781250	0.585937500	0.234375000	3.050781250
6	0.000976562	0.090820312	0.527343750	0.380859375	3.288085938
7	0.000244141	0.046142578	0.440917969	0.512695312	3.466064453
8	0.000061035	0.023254395	0.353759766	0.622924805	3.599548340
9	0.000015259	0.011672974	0.276947021	0.711364746	3.699661255
10	0.000003815	0.005847931	0.213546753	0.780601501	3.774745941

6. Formula obtained by recursion relation analysis

E(n), the math expectation of cards obtained when n cards are taken from the card pile, is calculated by recursion relation analysis.

We can conclude: $E(n) = 1 \times P_1(n) + 2 \times P_2(n) + 3 \times P_3(n) + 4 \times P_4(n)$

$P_i(n) \times 4^n$ is firstly calculated to get the number of all the situations when i cards are obtained by taking n cards from the card pile. Subsequently, we determine whether the suit of the $(n+1)^{th}$ card occurred or not, therefore confirming the overall number of suits in these (n+1) cards. Finally, these situations are re-classified according to current number of suits, and then divided by current sum of situations, 4^{n+1}, to get $P_i(n+1)$.

The deduction of the recursion relation of $P_i(n)$:

When i=1, the $(n+1)^{th}$ card taken must be the same as the suit of previous n cards, so its suit is certain:

$$P_1(n+1) = \frac{P_1(n) \times 4^n \times 1}{4^{n+1}}$$

When i=2, there are two possibilities: there are 2 suits in previous n cards, the suit of the $(n+1)^{th}$ card taken is the same as one of them (2 cases); there is 1 suit in previous n cards, the suit of the $(n+1)^{th}$ card taken is different from either one of them (3 cases):

$$P_2(n+1) = \frac{P_2(n) \times 4^n \times 2 + P_1(n) \times 4^n \times 3}{4^{n+1}}$$

When i=3, there are two possibilities: there are 3 suits in previous n cards, the suit of the $(n+1)^{th}$ card taken is the same as one of them (3 cases); there are 2 suits in previous n cards, the suit of the $(n+1)^{th}$ card taken is different from either one of them (2 cases):

$$P_3(n+1) = \frac{P_3(n) \times 4^n \times 3 + P_2(n) \times 4^n \times 2}{4^{n+1}}$$

When i=4, there are two possibilities: there are 4 suits in previous n cards, the suit of the $(n+1)^{th}$ card taken is the same as one of them (4 case); there are 3 suits in previous n cards, the suit of the $(n+1)^{th}$ card taken is different from either one of them (1 case):

$$P_4(n+1) = \frac{P_4(n) \times 4^n \times 4 + P_3(n) \times 4^n \times 1}{4^{n+1}}$$

In order to obtain a general formula, n=1 is used as the initial condition. Obviously, only one suit will be obtained if there is only 1 card taken from the card pile, so:

$$P_1(1) = 1,\ P_2(1) = 0,\ P_3(1) = 0,\ P_4(1) = 0,\ E(1) = 1.$$

Finally, the 5 equations above, with initial condition, are solved as a set of simultaneous equations:

$$E(n) = 4 \times [1 - (\frac{3}{4})^n],\ n > 0$$

7. Conclusion

Three independent methods give out the same result respectively, therefore proving their validity. The problem is also furthered to calculate the math expectation of the number of suits in n cards. By analyzing the impact of taking the $(n+1)^{th}$ card, the recursive formula of $P_i(n)$ is deduced, and the general formula of E(n) is solved subsequently.

8. Acknowledgements

Firstly we would like to appreciate Ms. Y. Chen; her ideas about researching mathematics inspired us to pick up this problem associated with cards, further extending it to “n dimensions” to do deeper research. We are also very grateful to Mr. J. Lu; he not only inspired us to use recursion relation analysis, but also helped us revise this paper very carefully.

[1]:

We assume each suit is represented by one specific shape:

(2+4) is represented by OOXXXX. The permutation of O and X is determined first, which is given by $C_6^2 \times C_4^4$ (firstly select 2 positions for O in all 6 positions; then select 4 positions for X in the remaining 4 positions); then different suits are assigned to O and X: …… O<—spade, X<—diamond……O<—diamond, X<—spade……; later, the total number of suit-assignment is calculated, which is given by P_4^2.

(3+3) is represented by OOOXXX. If we continue our analysis according to the method above, the permutation of O and X counted will be $C_6^3 \times C_3^3$, and the total number of suit-assignment will be P_4^2. All the possibilities considered is $C_6^3 \times C_3^3 \times P_4^2$, as is shown in the table below:

	o=spade x=diamond	o=diamond x=spade
ooxoxx	I	II
xxoxoo	III	IV

However, it is obvious that I&IV (II&III) are the same situation but counted twice, which is in contrast with reality.
Therefore, when two groups are “similar”, P should not be used to count the suit-assignment after their permutation is determined by C. Instead, C, which does not take permutation into account, should be employed. So the total possibilities are given by $C_6^3 \times C_3^3 \times C_4^2$ to avoid over-counting, as is shown in the table below:

	o=spade x=diamond	o=heart x=diamond
ooxoxx	I	II
xxoxoo	III	IV

[2]:

All the results given by our recursive function in C++ are shown in the table below:

n	$P_1(n)$	$P_2(n)$	$P_3(n)$	$P_4(n)$	Math expectation
1	1.000000000	0.000000000	0.000000000	0.000000000	1.000000000
2	0.250000000	0.750000000	0.000000000	0.000000000	1.750000000
3	0.062500000	0.562500000	0.375000000	0.000000000	2.312500000
4	0.015625000	0.328125000	0.562500000	0.093750000	2.734375000

5	0.003906250	0.175781250	0.585937500	0.234375000	3.050781250
6	0.000976562	0.090820312	0.527343750	0.380859375	3.288085938
7	0.000244141	0.046142578	0.440917969	0.512695312	3.466064453
8	0.000061035	0.023254395	0.353759766	0.622924805	3.599548340
9	0.000015259	0.011672974	0.276947021	0.711364746	3.699661255
10	0.000003815	0.005847931	0.213546753	0.780601501	3.774745941
11	0.000000954	0.002926826	0.163084030	0.833988190	3.831059456
12	0.000000238	0.001464128	0.123776436	0.874759197	3.873294592
13	0.000000060	0.000732243	0.093564391	0.905703306	3.904970944
14	0.000000015	0.000366166	0.070539415	0.929094404	3.928728208
15	0.000000004	0.000183094	0.053087644	0.946729258	3.946546156
16	0.000000001	0.000091550	0.039907280	0.960001169	3.959909617

And here is our code:

```
#include <cstdio>
#include <iostream>
using namespace std;

const int maxn=100;
long long a[maxn],u[maxn],res[maxn];
//a[0--n-1] represent n cards, each of which has value in {1,2,3,4}, representing 4 suits
//u[i in range[1,4]] represent whether or not suit i has occurred, each of which has value 0 or 1
//res[i in range[1,4]] represents the time i suits has occurred

int N; //the number of cards taken

void check()
{
    //count the number of suits occurred and add to res[]
    int ans=0;
    for(int i=1;i<=4;i++)
        if(u[i])
            ans++;
    res[ans]++;
    return;
}
void work(int n)
{
```

```
    //generate all situations by recursion
    if(n==N)
    {
        //check suits when n cards generated
        check();
        return;
    }

   //generate cards and record suits at the same time to increase efficiency
    for(int i=1;i<=4;i++)
    {
        a[n]=i;
        u[i]++;
        work(n+1);
        u[i]--;
    }
    return;
}

int main()
{
    //run with n from 1 to 10
    for(N=1;N<=16;N++)
    {
        cout<<endl<<endl<<"When "<<N<<" cards are taken from the card
            pile:"<<endl;

        //initialize arrays
        for(int i=0;i<maxn;i++)
            a[i]=u[i]=res[i]=0;

        //generate all possibilities and count
        work(0);

        double sum=0;   //record all possibilities
        for(int i=1;i<=4;i++)
        {
            sum+=res[i];
        }

        for(int i=1;i<=4;i++)
        {
            cout<<"The chance occurring "<<i<<" suits: ";
            printf("%.9lf\n",(double)res[i]/sum);
        }

        double n=0;
        for(int i=1;i<=4;i++)
            n+=1.0*i*res[i]/sum;
        printf("The math expectation is: %.9lf",n);
    }
    cout<<endl<<endl;
    return 0;
}
```

Report and Retrospect on Experiments on Enhanced PEC Performance in BFO Heterostructure

Junchen Zhao

Gel Configuration

To study enhanced photoelectrochemical performance in BFO heterostructure, the BFO thin films are prepared by the sol–gel method; consequently, BFO gel (25mL in volume and 0.2mol/L in concentration) is needed.

In the gel, Bi comes from $Bi(NO_3)_3{\cdot}5H_2O$ and Fe comes from $Fe(NO_3)_3{\cdot}9H_2O$. It is shown that 0.005mol of each substance is required, which means 2.42535g of $Bi(NO_3)_3{\cdot}5H_2O$ and 2.02005g of $Fe(NO_3)_3{\cdot}9H_2O$ respectively. In addition, 25mL of 2-methoxyethanol is needed as solvent.

Step 1:

2-methoxyethanol is measured with a syringe and pour into a beaker. In this case, a 5mL syringe is used 5 times to measure 25mL 2-methoxyethanol.

Step 2:

Firstly, a piece of paper is folded by diagonal and put onto a electrical balance. Then $Bi(NO_3)_3{\cdot}5H_2O$ crystals are measured accurate to ten thousandth gram. Such measurement should be as quick as possible since the crystal deliquesces very easily when exposed in the air.

Step 3:

Firstly, those crystals are poured into the beaker carefully to prevent the solvent from splashing. Then the beaker is covered with preservative film to reduce the loss of evaporation. Later the beaker is put onto the magnetic stirrer with a proper mixing speed until all of the crystals dissolve.

Step 4:

Same as step 2, $Fe(NO_3)_3{\cdot}9H_2O$ crystals are measured and poured into the beaker. Then 0.01mol (2.1014g) citric acid is added.

Step 5:

Same as step 3, the beaker is put onto the magnetic stirrer for 1h.

Gel Spin-Coating

Prepared gel was spin-coated onto Pt substrate for later PEC measurement.

Step 1:

Syringe is used to draw 5 mL BFO gel for later operations. Then Pt substrate is taken out from Acetic acid solution with tweezers.

Step 2:

Pt substrate is put onto the centrifuge; button 'Vacuum' is pressed to fix the substrate. Dust is firstly blown from its surface; q-tips are later used to absorb acetic acid to further clean its surface, during which blow drier is used to increase evaporation rate.

Step 3:

When the Pt substrate is completely cleared, the gel is slowly dropped, until the substrate, including 4 corners, is covered by an even and relatively thick layer of BFO gel. Any air bubble in this gel layer should be punctured by the needle, which should, at the same time, be kept from touching the surface of Pt substrate.

Step 4:

Subsequently, the centrifuge, which is initialized to spin at 1000rpm for 5s followed by spinning at 5000rpm for 30s, is activated. After such centrifugation, whether the gel left on the the Pt substrate is even in color and surface and is without air bubbles should be examined carefully.

Step 5:

The gel should be completely removed from the Pt substrate, ***restarting from step 2*** exactly as is described above, if there is any deficiencies. If there is not, one selected corner of the Pt substrate should be cleared completely using a clean q-tip in order to leave a small arc region at one corner for later photocurrent measurement.

Step 6:

Button 'Vacuum' is pressed to de-fix the substrate. Then, the wet Pt film is transferred onto the evaporating dish, which is later covered with a small piece of paper to separate dusts. They are dried on a electrothermal furnace at 150 degrees centigrade for 2.5min. When finished, the paper is uncovered to check whether the film is even in both surface and color. If not, the gel should be completely removed from the film, ***restarting from step 2***. Otherwise, the evaporating dish, along with the film in it, is put into another electrothermal furnace at 600 degrees centigrade for 5min.

Repeat step 2 to 6 for 9 times.

Film Annealing

Step 1:

The film is put into a electrothermal furnace at 620 degrees centigrade for 2h and later cooled to room temperature naturally.

Film Sealing

Step 1:

Firstly, a piece of wire is cut off from a copper coil. Its both ends (approximately 5cm) are later burned in the alcohol burner until black copper oxide is formed, after which they are polished with abrasive paper.

Step 2:

One end of the copper wire is curved to a circle (in order to increase contact area) and clung onto the corner of the film that is not covered with BFO. Meanwhile, copper foil is used to keep them close.

Step 3:

Glue is used to seal the film. It is mixed first and smeared on the edges of the film, around the face covered with BFO, and completely on the face without BFO. It should also be smeared to the place where the wire is polished and where the wire and the film are connected to each other in order to prevent photocurrent leakage.

PEC Performance Measuring

Photocurrent density is measured by electrochemical analyzer. The light source was a 300 W Xe lamp with tunable light intensity. The Nyquist plot was obtained using an AC voltage of 10 mV with a frequency range of 0.01 Hz to 10 MHz.

Step 1:

The film is put into 0.1 M Na_2SO_4 aqueous solution and connected to PEC workstation, which consists of equipment as mentioned above.

Analysis, Conclusion, and Retrospect

The film I made during the experimentation has a relatively inferior PEC performance during PEC measurements in that there is a tiny difference between photocurrent and dark current.

Factors that have an impact on the results of the experimentation are omnifarious. First, the ratio between the solutes and the solvent should be very accurate when configuring the gel. Additionally, the air temperature and humidity are significantly influential to the film when the gel is spin-coated. Also during 9 times of spin-coating, any unevenness at any time of the procedure, any difference in thickness of each BFO layer, and any dust on the Pt substrate will all affect the final outcome. Meanwhile, it is important to control the time of pre-heating at 150 degrees centigrade and the time of annealing. Insufficient contact between the copper wire and the film and deficiencies in the sealing process will cause photocurrent leakage and reduce PEC performance.

This experience in the laboratory in Soochow University gives me the opportunity to explore something unknown and the difficulty of experiments and research. Failure is quite common especially when any seemingly insignificant factor all has an effect on the final result.

Enhanced Photoelectrochemical Performance in Reduced Graphene Oxide/$BiFeO_3$ Heterostructures

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- Current $BiFeO_3$(BFO)-based ferroelectric could be used as visible-light-driven photoelectrodes for oxygen production; however, its photoelectrochemical performance is inferior, and its fabrication process is expensive.

- In comparison to current BFO-based ferroelectric, newly developed reduced graphene oxide (RGO)/BFO composite film exhibits a 600% improvement of the short-circuit photocurrent density and threefold enhancement of incident photon-to-current efficiency; it also outperforms the noble-metal/BFO cells under the same reaction conditions. The optimized RGO/BFO composite film is also cheap to produce, so it could be used as a potential material for ferroelectric photoelectrodes.

Introduction

- How to convert light energy into chemical and electrical energies triggered intensive research. The efficiency of photoeletrochemical(PEC) cells are limited by the PEC performance of semiconductor photoelectrodes. Recent goal is to fabricate narrow-bandgap ferroelectrics for the photoelectrodes of PEC cells.

- There are a few advantages: switchable photovoltaic outputs, above-bandgap photovoltage, and above Shockley-Queisser-limit efficiency.

- However, the microscopic mechanism of the ferroelectric photovoltaic effect has not been clarified yet; some deficiencies(oxygen vacancies) and their effects remain enigmatic.

- There are two advantages in Multiferroic BiFeO3 (BFO): robust room-temperature ferroelectricity and a band gap within the visible light range.

- BFO will show different physical and chemical properties when in different crystal structures, resulting in different PEC performances. Joint effort has been paid to find a microscopic structure that best optimizes the PEC performance.

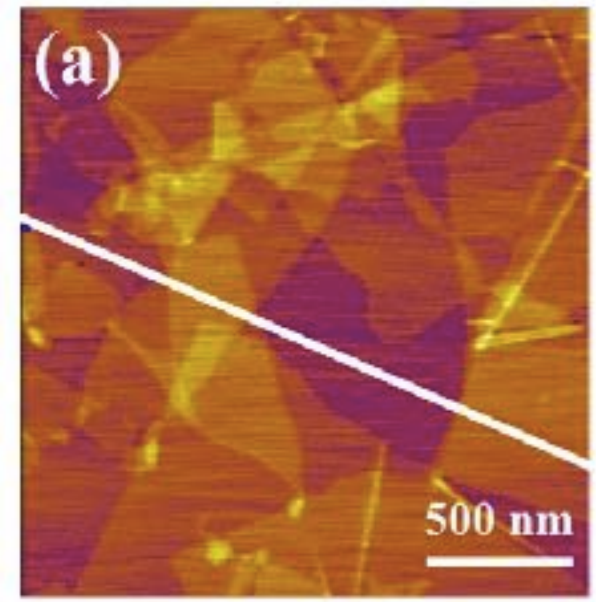
- It has been demonstrated that **by decorating the BFO surface with appropriate amount of Ag nanoparticles, the maximum short-circuit photocurrent density could be doubled**. It has also been proposed, by research into the crystal structure and physical and chemical properties, that **RGO(as an intermediate state) offers an opportunity to fabricate composite photoelectrodes**.

- According to these studies and analysis, composite films are produced for photoelectrodes; the mutual impact of RGO and BFO are systematically analyzed.

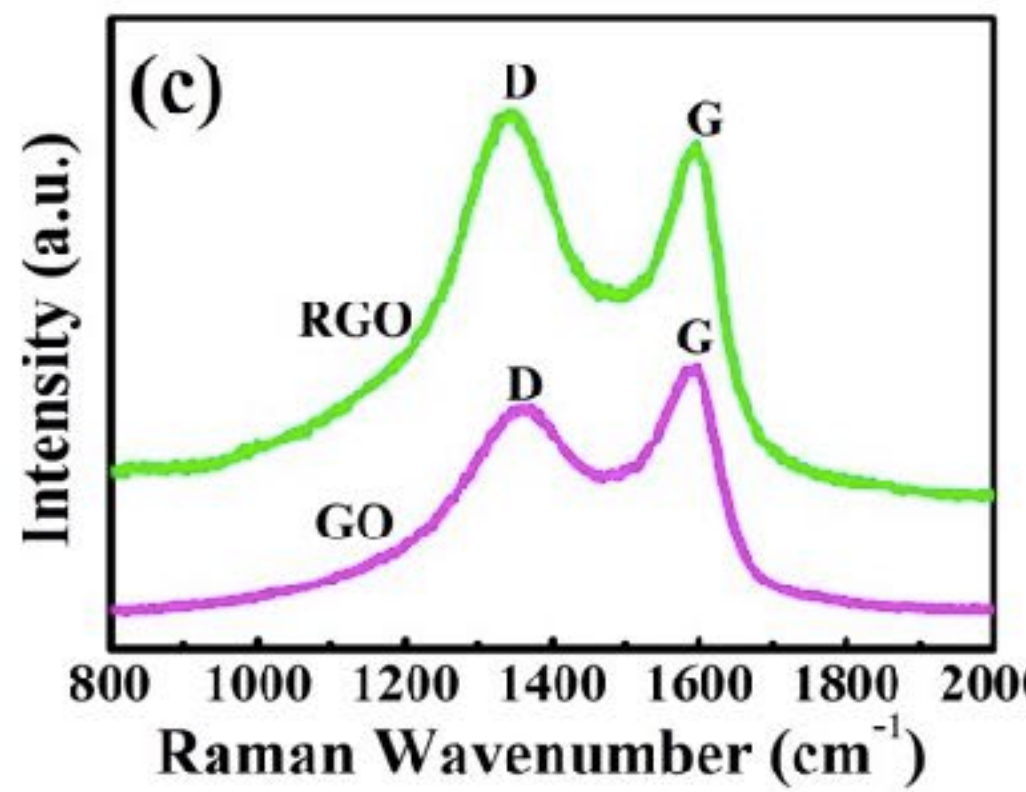
- Subsequently, a mechanism for PEC reaction in the RGO/BFO system has been proposed, opening up a brand new pathway for further study in improving the PEC effect of ferroelectric films.

Results and Discussion

- The morphologies and the thicknesses of the RGO nanosheets are measured by atomic force microscopy (AFM).



- The Raman spectra of RGO is later compared with that of GO; it is revealed that the D/G intensity ratio of RGO is higher than that of GO because of the restoration of sp^2-hybridized carbon during the reduction reaction.



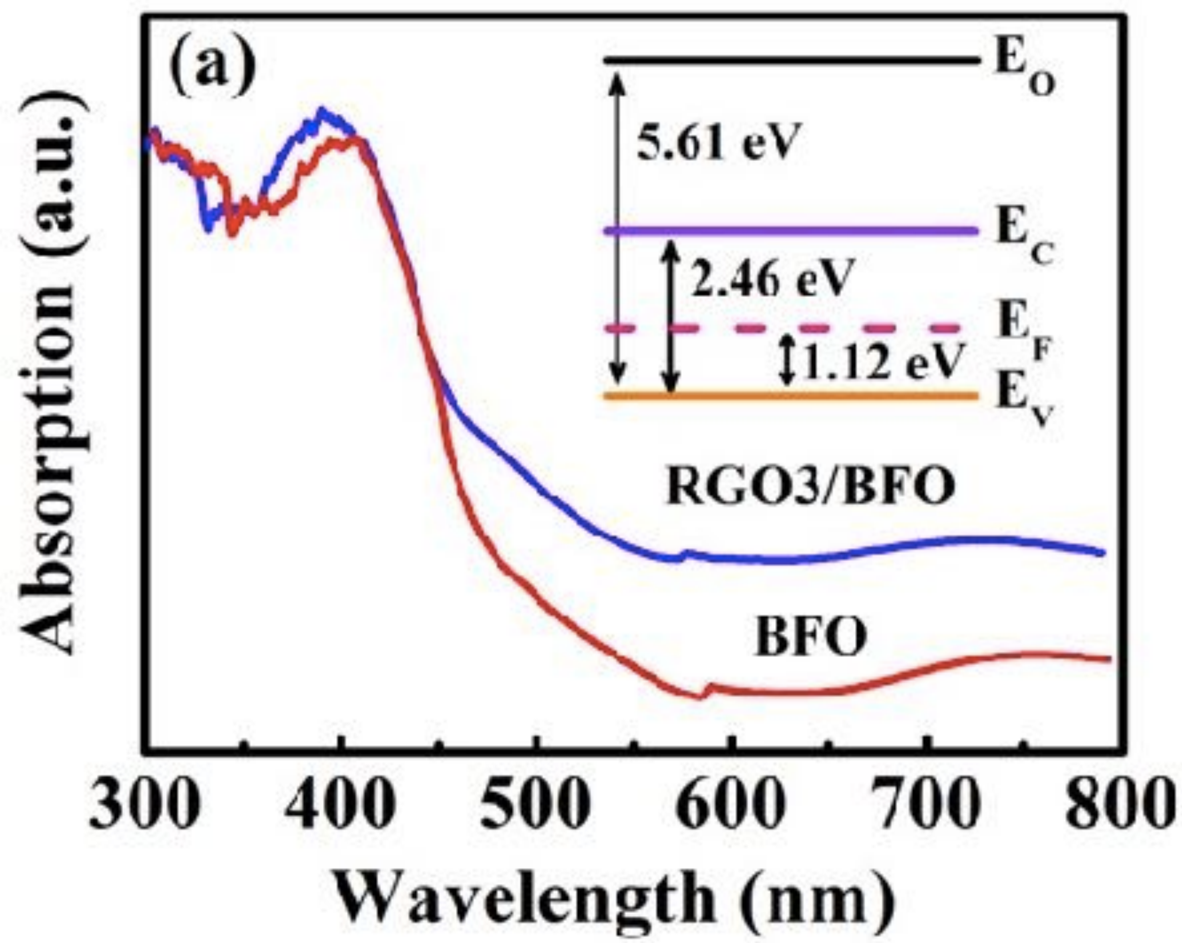
- The crystal structures of the BFO thin film before and after RGO decoration were measured by X-ray diffraction (XRD).

- The microscopic ferroelectric properties of the BFO film is verified by piezoresponse force microscopy (PFM). Later, Raman spectroscopy is used to confirm the existence of RGO.

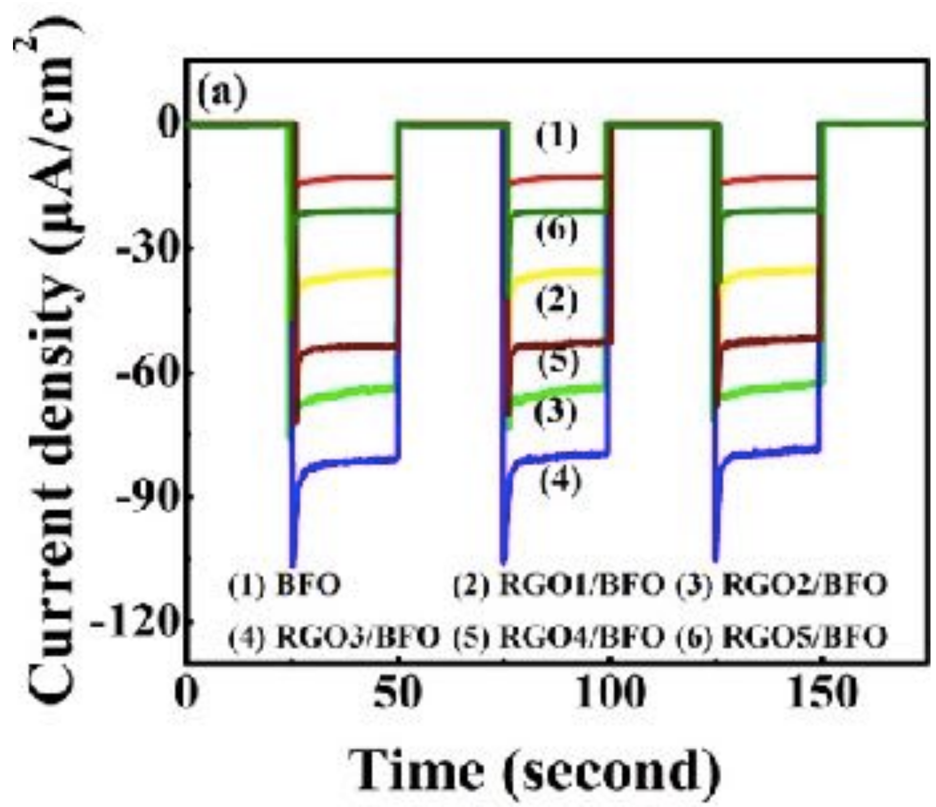
- The results observed match the ideas before perfectly. Desired RGO/BFO composite films have been achieved.

- The absorption spectra of the BFO before and after decorated with the RGO nanosheets is measured: the RGO3/BFO sample shows better light absorption capability in the whole visible-light range because of the existence of RGO.

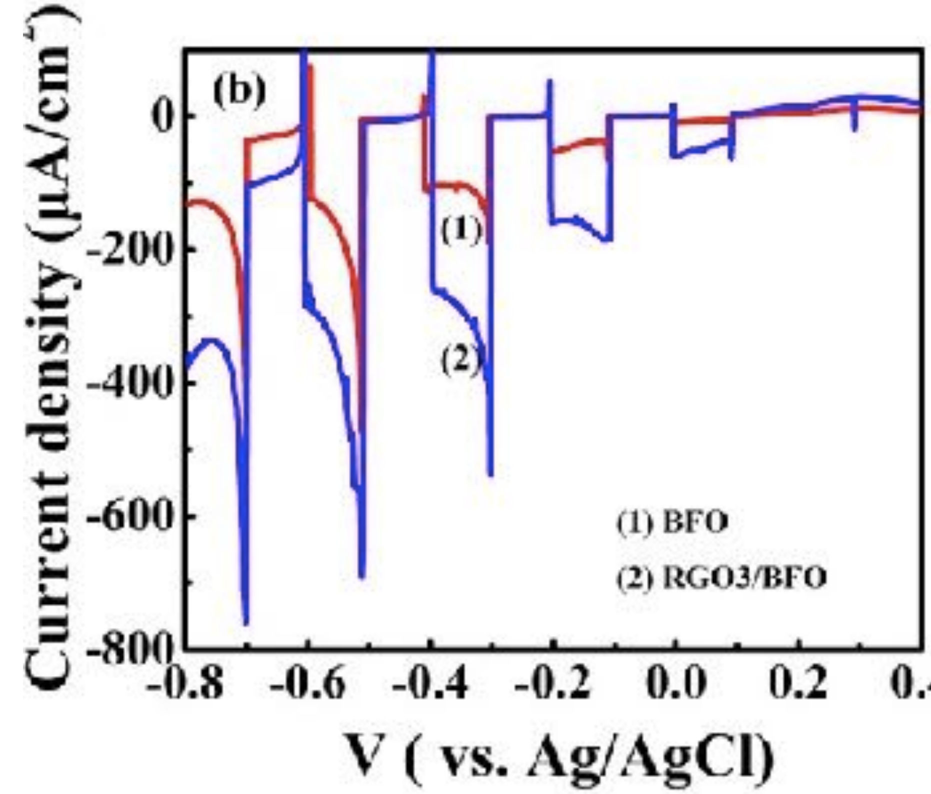
- It is also demonstrated that the BFO film in this study could be considered as a P-type conductor by calculating the work function and the energy level of $E_F - E_V$.



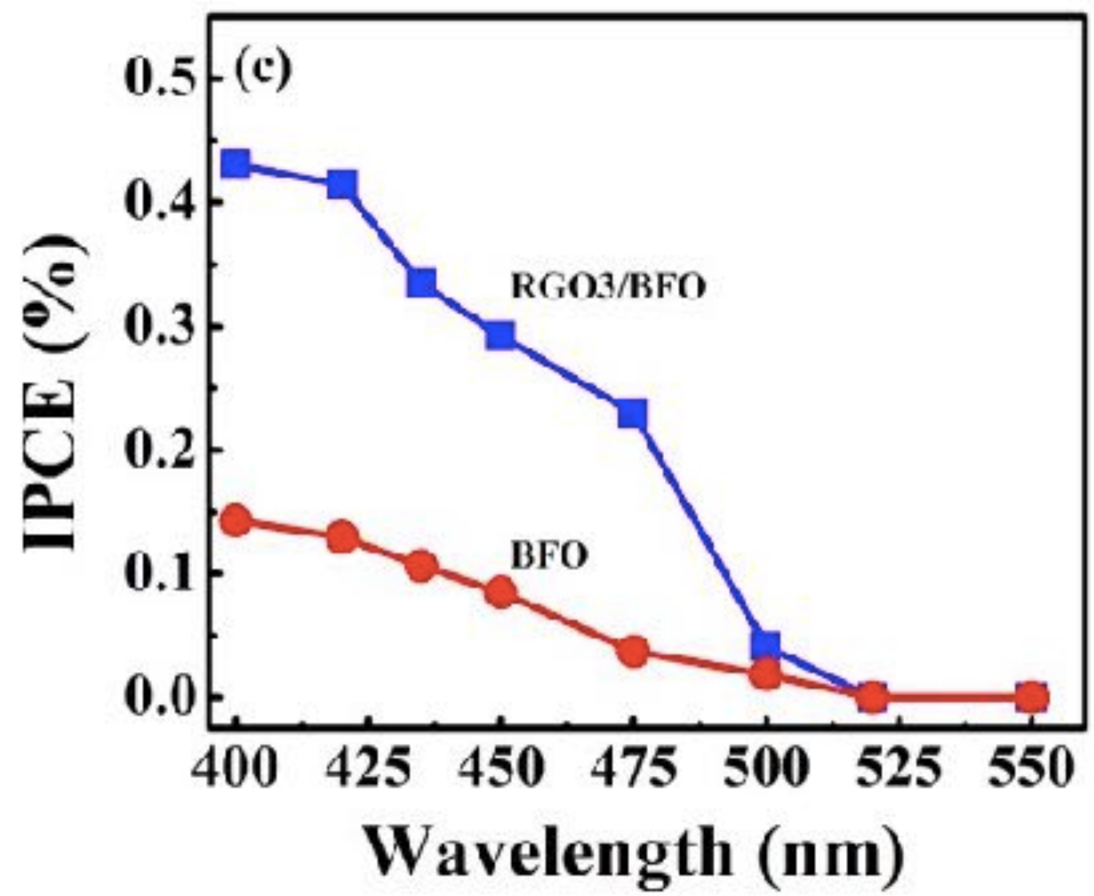
- The photocurrent density of the composite film when decorated with different quantities of RGO nanosheets is analyzed: the initial increase of photocurrent density can be ascribed to the increased content of RGO nanosheets, which enhances the separation of photogenerated carriers.
- However, the higher coverage of RGO nanosheets reduces the surface area of BFO in direct contact with the electrolyte, and decreases the intensity of light absorbed by the BFO film.



- The figure shows that there is a steady increase in photocurrent density with increasing applied potential, and that BFO and RGO3/BFO have a fast photocurrent response during every switch on and switch off event.
- It is also proved that the RGO3/BFO sample outperforms BFO in photoenergy conversion.
- In conclusion, RGO/BFO composite photoelectrodes not only show superior PEC performance, but also exhibit the advantage of the low-cost and simple fabrication process.



- The incident photo-to-current conversion efficiency (IPCE) is measured to verify the advantage of adding RGO nanosheets.
- The IPCE value of the pure BFO lm is 0.15% (at 400 nm), whereas the IPCE response shows a remarkable enhancement to 0.43% when RGO is incorporated.
- The relationship between the PEC performance and the ferroelectric polarization is also investigated; experimental date is analyzed and explanations are made.



- The electrochemical impedance spectroscopy(EIS) is used to study the charge-transfer process of the PEC cell: surface charge-transfer process dominates the PEC reaction.

- Because the arc radius of the RGO3/BFO sample is smaller than that of pure BFO sample, the interfacial charge transfer between RGO3/BFO photoelectrodes is faster; therefore the separation of photogenerated carries is more efficient.

- It could be concluded that **the photocarrier separation and the charge-transfer process play a more important role compared to the light absorption** in this system.

- A mechanism is proposed on the basis of these physical and electrochemical characterizations to explain RGO/BFO-enhanced photoelectrochemical properties.

- Besides **the light absorption, the charge transportation and separation** were also considered to be key factors on improving the photoelectronchemical activity. These factors are all derived from **the unique delocalized conjugated structure and superior electrical conductivity**.

- In conclusion, higher photocurrent density results from **the combination of photoactive ferroelectrics and electrically benign 2D materials**, which will become the new focus in PEC field.

Conclusion

- The RGO/BFO composite material greatly enhances the photocurrent density and IPCE in the hybrid PEC cells due to its **unique microscopic structure and superior electrical conductivity**.

- A simple and efficient method is found to improve the PEC performance of ferroelectric photoelectrodes: **add 2D materials**.

Experimental Section

- The fabrication process of the RGO/BFO composite material and its characteristics are introduced.

Thanks!