A NOVEL METHOD FOR PREPARATION OF GRAPHENE AND STUDY OF MECHANISM OF IT'S REDUCTION

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Introduction:

Graphene, the two dimensional nanosheet, has wide applications in the field of electrochemistry (1), electronics (2), biomedicines (3), gas storage (4) and composite for its enormous mechanical strength. Graphene has been synthesized by different methods, but the common reducing agent for conversion of graphene oxide (GO) to graphene (RGO) is only hydrazine which is very specific. We have developed a simple method of preparation of GO using dichromate and conversion of GO to RGO has been performed by dithionite or hypophosphite in presence of $-NH_2$ containing compounds. We have studied the reduction in presence of various reagents to understand the mechanism of reduction.

Experimental:

Apparatus and Procedures

GO was prepared by the oxidation of pristine graphite with dichromate and sulphuric acid (5). After preparation of GO, it was dispersed in water in presence of aniline and was reduced by sodium hypophosphite by stirring for 24hr at 25^0C. After reduction, ethanol was added to precipitate the reduced GO and washed with ethanol. Finally the product was dried in a vaccum oven.

FT-IR spectroscopy was the most essential technique to predict the functionalization of the products.

We performed the reduction with various combinations of nucleophillic reagents (amines and thiols) and reducing agents. The list is given in the table 1.

Results and Discussion:

The oxidations of graphite by powerful oxidizing agents first disintegrate into smaller graphite sheet along with various oxidized functional groups. Those are carboxylic acid, quinonoid structure, phenolic group, epoxy group, cis dihydroxy group on the basal plane. Reduction with hydrazine removes quinoid structure and hydroxyl groups from the basal plane (this will be termed as si-OH).

It is interesting to note that the removal of si-OH is very effective with hydrazine in absence of any other reagents. The reduction has been attempted with $NaBH_4$, dithionite, even with hypophosphite individually only. But surprisingly none of these reagents are capable to remove si-OH. The most interesting point was noted that all common reducing agents are effective to reduce oxidized pristine graphene only in presence of a nucleophile like aniline and glycine. Table 1 shows the summery of reactions.

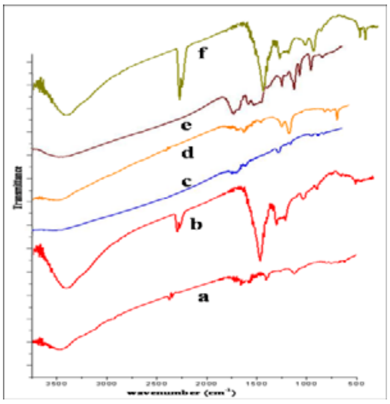


Fig. 1 FTIR spectra of reduced graphene oxide in presence of (a) aniline, (b) hypophosphite (c) aniline and hypophosphite, (d) aniline and dithionite, (e) aniline and borohydride and (f) dithionite.

It is also observed that such types of experiments are completely failure for MGO sheets. But in presence of catalyst (Pt-C), the MGO sheets are completely reduced by the aniline and hypophosphite. This is probably due to the less amount of oxygenated group (~ 23%) is present for CGO sheets in comparison to the MGO sheets (~ 30%).

Table 1 Results for effective reductions.

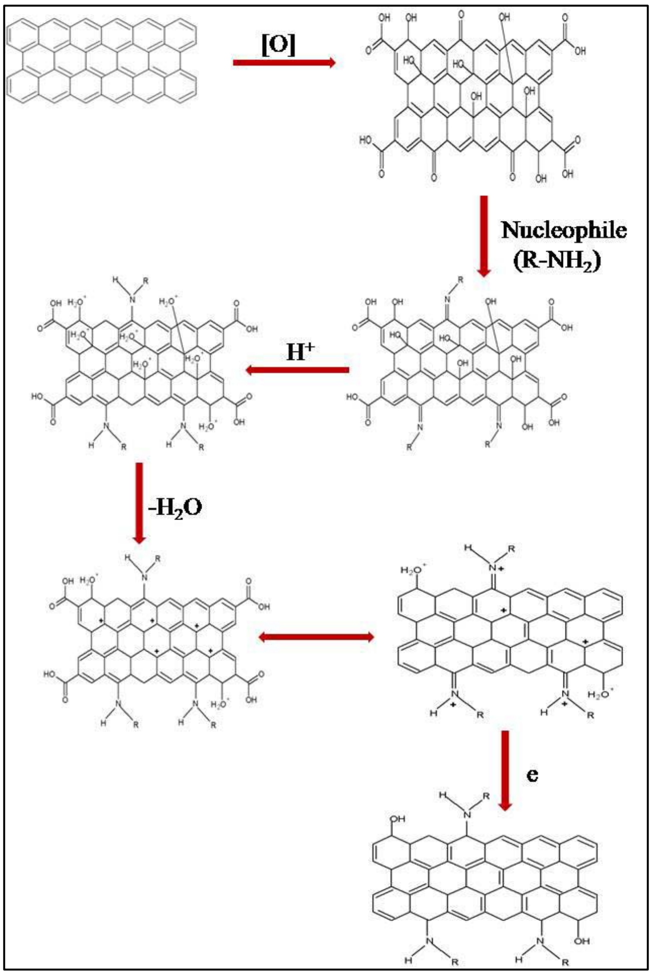
No.	Nuclophile	Reducing agent	Result (removal of si-OH)
1	nil	Borohydride	No action
2	nil	Hypophosphite	No action
3	nil	Dithionite	No action
4	NH3	Nil	No action
5	Glycine	nil	No action
6	4-amino benzoic acid	nil	No action
7	p-aminophenol	nil	No action
8	Thioglycolic acid	nil	No action
9	4-thiol benzoic acid	nil	No action
10	NH3	Borohydride	No action
11	NH3	Hypophosphite	No action
12	NH3	dithionite	No action
13	Glycine	Borohydride	Removed
14	Glycine	Hypophosphite	Removed
15	4-amino benzoic acid	Borohydride	Removed
16	4-amino benzoic acid	Hypophosphite	Removed
17	p-aminophenol	Borohydride	Removed
18	p-aminophenol	Hypophosphite	Removed
19	Thioglycolic acid	Borohydride	No action
20	Thioglycolic acid	Hypophosphite	No action
21	4-thiol benzoic acid	Borohydride	No action
22	4-thiol benzoic acid	Hypophosphite	No action
23	Semicarbazide	Borohydride	Removed
24	Semicarbazide	Hypophosphite	Removed

Conclusion:

The oxidation of graphite by dichromate produces graphine oxide with less amount epoxy and hydroxy groups on the basal plane. Reducing agents are only effective when primary amine forms schiff-base or =C=N- group. This group after reduction in first step produces amino derivative of poly-cyclic aromatic compound. Then removal of hydroxy-group from basal plane is facilatated through the formation of carbonium ion in the basal plane which is resonance stabilised by amine group produced in the first step. Finally the carbonium forms quinoid structure and is reduced by reducing agent.

In the case of hydrazine, all the reactions are peformed alone by it due to fulfillment of requirements of chemical-properties needed for all the steps.

Sodium hypophosphite is very suitable for the reduction of graphene-oxide in presence of any primary amine contaning compounds.



Scheme 1 Mechanism of the reduction of GO.

References

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