SYNTHESIS OF POLYANILINE HYBRIDS OF GRAPHENE/MWNT FOR PHOTOCURRENT GENERATION AND OPTICAL LIMITING APPLICATIONS

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REMYAMOL T.

Department of Chemistry

INDIAN INSTITUTE OF SPACE SCIENCE AND TECHNOLOGY

THIRUVANANTHAPURAM

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ABSTRACT

In the last few years polyaniline, an environmentally and thermally stable, easily processable conducting polymer, in nano regime attracted enormous interest of the researchers owing to its lightweight, flexibility, ease of device fabrication in large areas and control over electrical and optical properties. Also there has been a notable enthusiasm in graphene research since the discovery of graphene in 2004 by the mechanical exfoliation of graphite using scotch tape. The combination of polyaniline and graphene/carbon nanotubes offers an attractive way for the generation of new hybrid materials that find a range of applications such as photovoltaics, optical limiters, sensors, actuators, transistors, etc.

This thesis focuses on the synthesis, characterization and property evaluation of polyaniline in nano dimensions and its hybrids with graphene and multiwalled carbon nanotubes. Polyaniline nanostructures with cube-like morphology are synthesized by a novel inverse microemulsion polymerization technique using ammonium oleate as the surfactant and toluene sulphonic acid as the dopant. The formation mechanism of cube-like nanostructures by the self assembly of polyaniline nanorods inside the inverse micelles of ammonium oleate in the paraffin–oil water system is proposed with the support of experimental techniques. The suitability of cube-like polyaniline for optical limiting and photocurrent generation applications are studied (This part of the work is published in *Synthetic Metals* 2013). The optical limiting device applications require easy fabrication of films of nonlinear optical materials in a transparent host. In this respect, films of cube-like polyaniline in transparent polymer matrix (polymethyl methacrylate) are fabricated by *in situ* free radical polymerization of methyl methacrylate in the presence of cube-like polyaniline. Detailed studies on the nonlinear optical properties of the films are carried out using open aperture Z scan technique by varying the polyaniline loading and also by varying the laser energy. A switchover from saturable absorption to reverse saturable absorption is observed in the film (0.1 wt % polyaniline loading in the monomer) as the energy of laser beam increases from 5 μJ to 100 μJ (This part of the work is published in *Materials Chemistry and Physics* 2014).

Both applications (optical limiting and photocurrent generation) under study can be improved by the combination of electron donating polyaniline with an electron acceptor material. Stable carbon allotropes like carbon nanotubes and graphene are well known electron acceptor materials and photoinduced electron transfer from conjugated polymer to these materials are already reported. To initiate the study, polyaniline is hybridized with graphite oxide by *in situ* polymerization of aniline in the presence of synthesized graphite oxide. The hybrid shows photoluminescence quenching compared to pure polyaniline. The hybrid also shows strong optical limiting (high nonlinear absorption coefficient, β=19 cm/GW and low saturation intensity, I_{sat}=0.4 GW/cm^2) than individual components due to the photoinduced electron transfer between polyaniline and graphite oxide and the synergetic combination of reverse saturable absorption of polyaniline and nonlinear scattering of graphite oxide. The hybrid shows stable photocurrent cycles upon repetitive switching (on/off) of illumination with white

light for 30 second duration (intensity of light is 100 mW/cm^2). The photocurrent generated by this class of hybrid (9.1 µA) is higher than that of pristine polyaniline (4.6 µA) and it increases as the graphite oxide loading increases (published in *Materials Research Express 2014*).

With the aim of improving the properties of polyaniline/graphite oxide hybrid through covalent connection, phenylene diamine functionalized reduced graphene oxide is synthesized. By this modification of graphite oxide, significant reduction and exfoliation is achieved and aniline monomer is introduced on the reduced graphene oxide layers. The presence of phenylene diamine groups on reduced graphene oxide results in the formation of hybrids with covalent connections during the *in situ* polymerization of aniline. Photoluminescence quenching is more significant in this hybrid compared to unfunctionalized graphite oxide-polyaniline hybrid, revealing better electron transfer through the direct covalent linkage between polyaniline and reduced graphene oxide. This covalently connected hybrid shows better optical limiting (β=25 cm/GW, I_{sat}=0.2 GW/cm^2) compared to pristine polyaniline (β=5.8 cm/GW, I_{sat}=2.5 GW/cm^2) and polyaniline-graphite oxide hybrid (published in *Carbon* 2013). The hybrid also shows dc conductivity (6.3 S/cm), 200 times higher than that of polyaniline-graphite oxide hybrid (0.03 S/cm). Moreover, this hybrid shows a photocurrent of 29 µA, while the corresponding polyaniline-graphite oxide hybrid and pristine polyaniline shows only 9.1 and 4.6 µA, respectively. This large improvement in dc conductivity and photocurrent is attributed to the formation of direct conducting pathways by the covalent connection and may be due to the photoinduced electron transfer from polyaniline to reduced graphene oxide (Published in *RSC Advances 2014*).

To study the optical limiting and photocurrent generation properties of polyaniline/carbon nanotube hybrids, polyaniline-phenylene diamine functionalized multiwalled carbon nanotube hybrids through covalent connections are synthesized by the same methodology adopted for polyaniline-phenylene diamine functionalized reduced graphene oxide hybrid. This hybrid also shows photoluminescence quenching, improved optical limiting (β=23 cm/GW, I_{sat}=0.3 GW/cm^2) and photocurrent generation (10 µA) compared to pristine polyaniline.

Finally, the synthesized cube-like polyaniline is grafted on reduced graphene oxide layers by utilizing acylation chemistry of graphite oxide followed by amide bond forming reaction between amine groups of polyaniline and acid chlorides of graphite oxide. Significant reduction and exfoliation of graphite oxide is achieved in the hybrid and the cube-like morphology of pristine polyaniline is disturbed by the weakening of the interaction between polyaniline nanorods due to the introduction of reduced graphene oxide layers (published in *Synthetic Metals* 2013). The hybrid shows a dc conductivity of 6.6 S/cm. Considerable quenching of the photoluminescence of cube-like polyaniline is observed after covalent grafting on reduced graphene oxide layers due to the photoinduced electron transfer between polyaniline and reduced graphene oxide. The cube-like polyaniline grafted reduced graphene oxide hybrid shows improved optical limiting (β=20 cm/GW, I_{sat}=0.25 GW/cm^2) and photocurrent generation (31 µA) compared to pristine cube-like polyaniline (4.5 µA). The films of this hybrid in polymethyl methacrylate matrix are also fabricated and studied the nonlinear optical properties in comparison with cube-like polyaniline-polymethyl methacrylate film with the same linear transmittance. The hybrid film shows significant contribution of reverse saturable absorption at laser energy of 5 μJ, while cube-like polyaniline film shows only saturable absorption at the same laser energy. At 45 μJ, both the films show reverse saturable absorption, but large improvement in optical limiting behaviour is observed in the hybrid film (β=320 cm/GW, I_{sat}=0.2 GW/cm^2) compared to pristine cube-like polyaniline film ((β=70 cm/GW, I_{sat}=3 GW/cm^2).

In conclusion, this thesis gives an insight into the synthesis strategies, properties, and fabrication methods which can be used for utilizing polyaniline hybrids in various applications like optical limiting devices and photovoltaics.