
**SIMULTANEOUS REDUCTION OF GRAPHENE OXIDE AND POLYANILINE:
DOPING ASSISTED FORMATION OF A SOLID STATE
CHARGE-TRANSFER COMPLEX**

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Graphene, a single-atom-thick sheet of hexagonally arranged sp²-hybridized carbon atoms, owing to its high electrical and thermal conductivities, great mechanical strengths and large specific surface area is a promising constituent for various types of applications ranging from nanoelectronics, to advanced composites and novel electrode materials for flexible electronic devices [1]. Solution based strategies involving the exfoliation and reduction of graphite oxide are of relevance not only for high volume production of single-layered graphene (reduced graphene oxide) sheets, but also offer a versatile assembly and processing of functional graphene-based composite materials [2]. In the focus here are establishing favorable interactions between graphene's highly conjugated structure and delocalized electron system by using for example aromatic molecules [3] or conjugated polymers [4].

Polyaniline [5], as a member of the family of intrinsically conducting polymers, is a promising candidate for developing highly functional graphene-based composite materials. Of relevance is PANI's extended π conjugated structure, the presence of highly delocalized charge carriers in its doped, electrically conducting and hydrophilic state (emeraldine salt state, ES) and, moreover, its unique ability to undergo reversible doping processes as efficient means for controllable switching between neutral and charged states. Combining PANI with graphene (reduced graphene oxide) thus should lead to significant performances and processing improvements.

Recently, graphene-PANI composites were developed as (flexible) electrode material for energy storage devices showing increase electrochemical performance [6]. Typically in situ polymerization processes involving GO in the presence of aniline were applied followed by posterior reduction and oxidation processes to enhance performance of the devices. While the focus in these works clearly lies on performance improvement, the important issue of PANI's chemistry commonly is underestimated or not fully addressed when synthesizing graphene-PANI composites. Having a closer look at this important point will open opportunities for exploring further specific non-covalent interactions and broadening up the application spectrum for graphene-PANI composites.

Here, we provide a conceptual description of unprecedented interactions between graphene and PANI. We demonstrate the formation of a solid state charge-transfer complex upon simultaneous reduction of a graphene oxide polyaniline (GO-PANI) composite consisting of GO sheets coated by a thin layer of PANI as confirmed by SEM, TEM analyses. Controlling the reduction conditions and morphology of (GO-PANI) we synthesized a reduced R(GOPANI) product, which exhibited an unprecedented donor-acceptor interaction between reduced graphene oxide (RGO) and PANI in the solid state confirmed by UV-Vis, Raman, FTIR and XPS spectroscopy as well as by cyclovoltammetry [7]. Here RGO plays a dual role as electron acceptor of reduced PANI (leucoemeraldine, LE) and as stable counterion of the doped state of PANI (emeraldine salt, ES). Hence the doping assisted charge-transfer leads to a partial redox doping of PANI by RGO stabilizing PANI in an atypical intermediate oxidation state between LE and ES. In addition, charge-transfer in R(GO-PANI) is responsible for improved material properties including enhanced conductivity, superior thermal and redox stability, and a remarkably high water dispersibility. These results may enable opportunities for the development of novel functional materials based on graphene and intrinsically conducting polymers through improved processing routes of interest for applications in flexible plastic and wearable electronics.

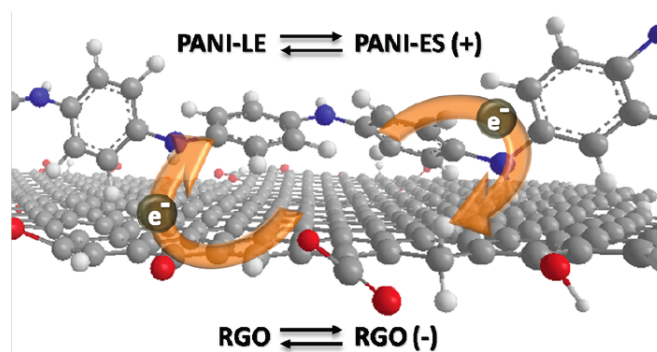


Figure 1: Donor-acceptor interactions in reduced (GO-PANI) charge transfer complex



Figure 2: Water soluble reduced (GO-PANI)

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