

Supporting Information

Simultaneous Reduction of Graphene Oxide and Polyaniline: Doping-Assisted Formation of a Solid-State Charge-Transfer Complex

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S1. Polyaniline: Structure and oxidation states

Polyaniline (PANI)¹ is a mixed oxidation state polymer (Figure S1) with three different oxidation states in the neutral form: the completely reduced polymer ($x=1$) called leucoemeraldine (LE), the “half-oxidized” polymer ($x=0.5$) called emeraldine base (EB), and the completely oxidized polymer ($x=0$) called pernigraniline base (PB). Intermediate oxidation states at molecular level are known to exist only at mixtures of the aforementioned states.¹ The conducting or 'doped' state of PANI is associated with a protonated form of the half-oxidized state EB, called emeraldine salt (ES) (Figure S1). It is characterized by a backbone structure containing polysemiquinone radical cation stabilized by corresponding 'dopant' counterions. In the very special case of PANI doping can be carried out by two completely different processes: redox reactions and

non-redox protonation reactions.¹ Thus, the conducting ES form of PANI can be obtained either by oxidation of LE or by protonation of imine nitrogen atoms of EB (Figure S1). Doping is reversible and provides efficient means for controllable switching between the conducting and various non-conducting states.

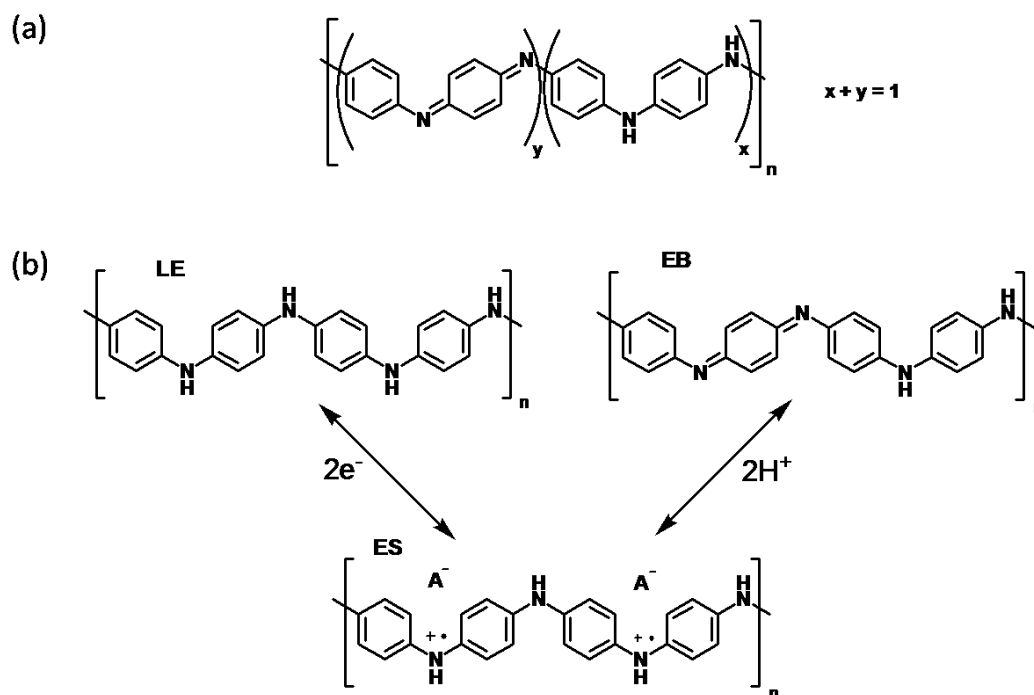


Figure S1. (a) Generalized composition of PANI. The oxidation state is indicated by y which varies from 0 to 1. (b) Reversible doping and dedoping of PANI by i) redox processes between non-conducting leucoemeraldine (LE) and conducting emeraldine salt (ES), and ii) protonation reactions between non-conducting EB and ES. A^- denotes the dopant counterion in ES.

S2. Characterization of materials

S2.1. Elemental Analyses

GO-PANI and R(GO-PANI) gave the following elemental compositions:

Table S1.

	Carbon	Hydrogen	Nitrogen	Sulphur
R(GO-PANI)	60.09 %	3.26 %	5.18 %	0.06 %
GO-PANI	54.64 %	2.88 %	4.26 %	0.06 %

The tentative approach for an estimative calculation of the PANI/graphene weight proportions involved the following assumptions:

- All the nitrogen content of the samples belongs to PANI, with the defined composition of ES (or LE) state.
- Once the weight proportion of PANI chains is calculated, all the remaining carbon content belongs to graphene species.
- The oxygen and hydrogen content of graphene species is ignored (since it is unknown) and hence the weight ratio is calculated dividing the calculated weight percentage of PANI chains by the calculated carbon weight of graphene species.

S2.2. X-ray photoelectron spectroscopy (XPS)

The deconvolution of the N(1s) core level spectrum for GO-PANI and R(GO-PANI) is shown in Figure S1.

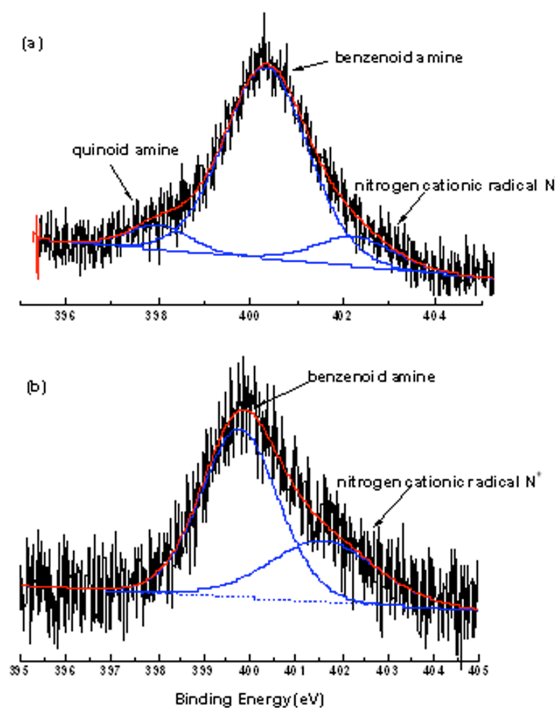


Figure S2. N1s core-level XPS spectra of GO-PANI (a) and R(GO-PANI) (b).

For GO-PANI the N1s core-level signal can be decomposed into three components corresponding to three different kinds of nitrogen atoms². The 'quinoid' imine nitrogen atoms show a binding energy of 398.3 eV. The component peak of 'benzenoid' amine groups can be found at a binding energy of 399.7 eV. The nitrogen cationic radical component appears with a binding energy of 401.1 eV.

In R(GO-PANI) N1s core-level spectrum apparently only two components are present, corresponding to secondary amine and radical cation nitrogen atoms, this last component with an increased relative contribution compared to GO-PANI. The absence of the quinoid component is indicative of low number of bipolarons in the PANI chain (that is, $-\text{NH}^{+}=\text{Q}=\text{NH}^{+}-$ groups). During the reduction of ES to LE state there is a

relative increase in the number of radical cations (that is, polarons or $\text{-NH}^+\cdot\text{-B-NH-}$ 'semiquinoid' groups); this has been proven by the increase in the EPR signal during the reduction of ES or the oxidation of LE³. The lower number of bipolarons and higher number of polarons is hence characteristic of an intermediate oxidation state between ES and LE. The relative increase in the radical cation N1s component in XPS has also been observed in complexes of LE and electron acceptors such as o-chloranil, o-bromanil⁴ or iodine^{2b}, which supports the hypothesis that in R(GO-PANI), RGO acts as an effective electron acceptor and LE acts as an electron donor forming a solid-state charge transfer complex.

S2.3. Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were performed with a Setaram TG-DTA 92 thermobalance using an air flow of 100 ml min^{-1} at a heating rate of $10^\circ\text{C min}^{-1}$ of the powder materials GO-PANI and R(GO-PANI).

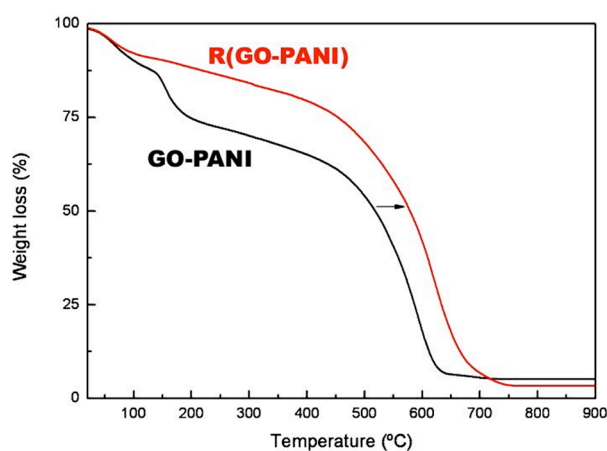


Figure S3. Comparison of the TGA plots of GO-PANI and R(GO-PANI) nanocomposites.

S3. References

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