Preparation of coke-based graphenes and their application in batteries and catalysis

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Graphene materials have recently attracted increasing interest due to the excellent physico-chemical properties that they can exhibit.[1] One interesting application is as electrodes in vanadium redox flow batteries (VRFBs). These are promising large-scale energy storage devices in which the electrodes must be carefully selected since they support the chemical reactions necessary for the operation of the battery. In this regard, graphenes obtained by thermal treatment of graphite oxide exhibited an excellent performance due to their high electrical conductivity and a high mechanical stability.[2]

The use of graphene at industrial scale in conventional applications is however conditioned by the amounts required and the associated cost.[3] We have recently reported the possibility to replace the graphite by coke as precursor in the preparation of graphene oxides by chemical methods. Furthermore, the characteristics of the materials obtained from coke and from graphite were comparable. The advantages of the procedure proposed lie mainly in the possibility to use a product (coke) which is largely available and cheaper than synthetic graphite, which requires temperatures above 2000 º C for its preparation.

Following with these investigations, the main objectives of this work are to obtain thermally reduced graphenes from cokes and to demonstrate that their performance in VRFB devices is equivalent to that obtained for graphenes.

In the present study, a commercial carbochemical coke (C), graphitizable, with a well-developed microtexture of large anisotropic domains is used as the raw material for graphene oxide and graphene preparation. For comparative purposes, graphene-like materials were also prepared from (i) the graphite obtained after treating the same coke C at 2000°C (CG) and (ii) from a commercial graphite (SG, ALDRICH).

Coke oxide and graphene oxides are prepared by a modified Hummers method. Graphenes were then produced by thermal exfoliation/reduction of the coke oxide and the graphite oxides at 1000ºC in a single step, yielding TRG-C, TRG-CG and TRG-SG from coke C and graphites CG and SG, respectively. It is worth mentioning that, in the case of the samples from coke, a slightly larger amount of KMnO₄ was required during the oxidation step, to facilitate the subsequent thermal exfoliation.

TEM studies of the TRGs evidenced the presence of monolayers in all cases (Figure 1), with the typical wrinkled structure currently observed for this kind of graphenes.

The reconstruction of the Csp2 structure after the thermal treatment was observed in all cases, the atomic C/O ratio increasing from ≈ 2.2 in the GOs up to ≈ 22 in the TRGs, as determined by XPS. The Csp2 content raises in the three cases to values above 77 % (Figure 2), well in the range of the values obtained for this type of materials in the literature.

All these results also confirm the similarities among samples independently of their origin (cokes or graphites) and confirm that cokes can be excellent candidates to prepare graphenes with standard characteristics and avoiding the use of high temperatures.

In order to confirm the suitability of graphenes from cokes as other standard graphenes, TRG-C was therefore used as active electrode material in the positive half-cell of a VRFB. This material exhibits a similar performance to those graphenes obtained from graphites. Thus, the CVs recorded on the CRBTR1000 electrode display similar electrochemical activity and kinetic reversibility towards the vanadium redox reactions.
The catalytic activity of these coke-based graphenes was also tested in catalysis. For that we developed a covalent bonding of organometallic complexes (Iridium N-heterocyclic carbenes (NHC)) to the graphenes through their OH-groups. Our proposed strategy proceeds, in a first step, with the functionalization of the GO via the formation of carbonate groups, from the surface hydroxyl groups with p-nitrophenyldichloroformate. Those p-nitro groups can be easily displaced in a second step by another nucleophilic center such as the OH-ending of the imidazolium salt (1) producing p-nitrophenol. To the best of our knowledge, this strategy has not been employed before with carbonaceous supports, and proceeds with similar reactivity and selectivity in the case of using graphenes form cokes or from graphites. The catalytic activity of the supported catalyst was tested in hydrogen transfer reactions.

References

Figures:

Figure 1: TEM images of TRGs from a) coke (TRG-C), b) carbochemical graphite TRG-CG and c) commercial graphite (TRG-SG).

Figure 2: XPS C1s spectra and deconvoluted curves of TRGs from a) coke (TRG-C), b) carbochemical graphite (TRG-CG) and c) commercial graphite (TRG-SG).