Study on magnetism of defective reduced graphene oxides

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The origin of magnetism in graphene-based materials has been determined to be related with the presence of defects in their sheets.[1–3] A graphene-derived material that has a significant amount of defects is reduced graphene oxide (rGO). The magnetic state of rGO has been reported to vary depending on the defect state and, thus, on the preparation history. Paramagnetic,[4] super-paramagnetic,[5] and even room-temperature ferromagnetic states[1,2] have been reported to coexist in rGO.[6] A magnetic ordering is expected to appear in the presence of a sufficient amount of defects in rGO.[3] In this study, we investigate the presence of possible room-temperature magnetic ordering in rGO prepared using the green-synthesized method[7] by means of muon-spin relaxation (μSR).

The investigation of the Raman spectra of the synthesized rGO revealed the presence of a significant amount of defects and that the amount of defects can be enhanced by thermal reduction.[7] In addition to sp^2 carbon hybridization (C = C), the main functional group, the presence of different types of oxygen functionalities was observed in the synthesized rGO.[7,8] The magnetization at 300 K was found to increase with an increasing amount of defects, and the enhancement was not attributed to magnetic impurities.[7] Moreover, a divergence in $\chi(T)$ was observed under field cooling (FC) and zero-field cooling (ZFC) conditions, which might indicate that the blocking temperature is noticeable at 300 K. Thus, the μSR experiment was subsequently performed to microscopically investigate magnetism in rGO at 300 K.

The inset in Fig. 1 shows the zero-field (ZF) time spectrum of the synthesized rGO at 300 K. An appreciable muon-spin precession on top of the decaying signal was observed in the spectrum, which is somehow similar to that observed in as-prepared graphene.[9] The spectrum can be well fitted by a single precession component and a Lorentzian decay. The fitting results in a hyperfine field of about 6 G. Such coherent muon-spin precession could indicate the presence of long-range magnetic ordering and/or the formation of a muonium (Mu)-H entangled state.[9] Meanwhile, the Lorentzian decay signifies muon diffusion through a carbon surface.[10] Under the assumption of the Mu-H dipolar interaction, a dipolar field of approximately 5 G is obtained which is equal to a Mu-H internuclear distance of 1.344 ± 0.005 . Furthermore, a longitudinal-field (LF) was applied to decouple the muon spin from the electron spin. The LF dependence of the muon-spin repolarization fraction is displayed in Fig. 1, which can be well fitted by a simple model for isotropic muonium with the function described in Eq. (1).[10]

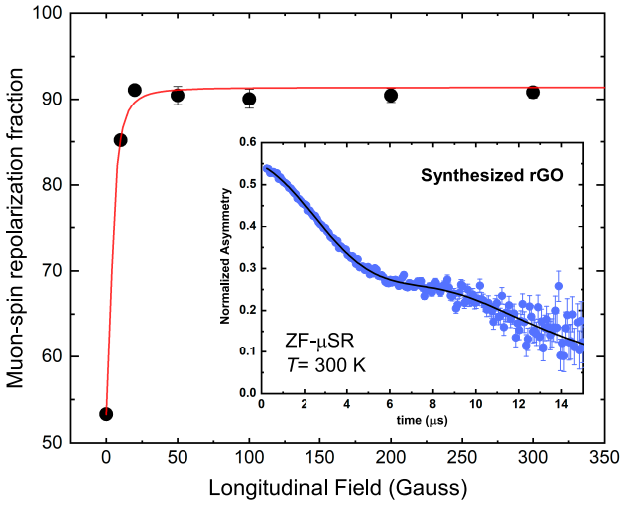

Fig. 1. Field dependence of the muon-spin repolarization fraction of the synthesized rGO at 300 K fitted by a simple model for the muonium radical (Eq. (1)). Inset: zero-field (ZF) μSR spectrum (at 300 K) of the synthesized rGO fitted by the summation of Lorentzian decay and a single precession component, as described in the text.

$$P_{exp} = P_{dia} + A_{rad}[x^2/(x^2+1)], \quad (1)$$

where $x = B/B_{hyp}$. B_{hyp} is the hyperfine field for free muonium. P_{dia} and A_{rad} are the diamagnetic fraction and the amplitude of the radical fraction, respectively. The obtained B_{hyp} is about 4.35 ± 0.24 G, which is almost as large as that procured from the ZF spectrum. This B_{hyp} value corresponds to a hyperfine frequency of 12(1) MHz, which is close to the instrument cut-off of 13 MHz. This can be the reason why ∼45% of the implanted muons were not observed in the ZF spectrum. Furthermore, a more detailed analysis in conjunction with first-principles calculations is required to confirm that the observed muon-spin precession originates from Mu-H interaction to form the CHMu group as suggested for hydrogenated graphene.[9]

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