

Electrochemical modification of graphene to enhance its electronic and vibrational properties

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Abstract

Chemical functionalization of graphene allows for a judicious engineering of the physical and chemical properties of graphene. Among the various schemes electrochemical modification [1] presents a versatile and straightforward strategy to fine tune the properties of graphene for a specific application, of which two examples will be presented here. On the one hand it allows us to improve the electronic and electrochemical performance, while on the other it provides us with a handle to continuously tune the extent of Raman scattering.

In the first part, we show that trace metal impurities present on graphene have a significant impact on its physical and chemical properties. This observation has recently been made in a number of CVD-grown and graphite-derived graphene samples. This is analogous to the case of carbon nanotubes where trace metals were found to have a strong effect on the electrocatalytic properties of the material. We observe by direct electroanalysis that even after the usual copper etching process, trace copper impurities still remain on transferred CVD graphene. We devise an electrochemical etching procedure [2] using which we successfully eliminate at least 90% of these impurities with a clear improvement in both the electrochemical and electronic transport properties of monolayer graphene.

In the second part we present an electrochemical deposition route to attach gold nanoparticles (AuNPs) controllably on to a graphene surface. Raman scattering in graphene can be significantly enhanced through the coupling of metal nanostructures. Many of the reported approaches utilize physical vapor deposition requiring patterning of graphene or the underlying substrate. A major limitation is the inability to measure the Raman enhancement at the same location as a function of variation in particle size and / or density. Moreover, there is no direct possibility to tune the strength of enhancement after the structures are fabricated. Using our electrodeposition route, the size or density of the nanoparticles and thereby the Raman enhancement can be continuously increased through appropriate choice of electrochemical parameters. [3] We clearly show that the strength of Raman enhancement varies as a function of the frequency of the vibrational mode (*D*, *G* or *2D* of graphene) and may be correlated with the plasmonic fingerprint of the attached AuNPs. An additional chemical contribution can be also deciphered through charge transfer from AuNPs on to graphene. Subsequently, we show that these devices can be efficiently utilized as SERS substrates for the detection of specifically bound non-resonant analyte molecules.

[1] R.S. Sundaram, et al., *Adv. Mater.* **20**, 3050 (2008)

[2] R.M. Iost et al., *ChemElectroChem* **Early View** DOI: 10.1002/celec.201402325

[3] L. Zuccaro, et al., *Adv. Funct. Mater.* **24**, 6348 (2014).