Charge Transfer Dynamics in Graphene-Inorganic 'hybrids' with Transition Metal Oxides Using In-Situ Raman Spectroelectrochemistry

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Abstract

We report on the electrochemical assembled two- and three-dimensional graphene variants with nanostructured cobalt oxide (CoO and Co_3O_4) polymorphs that synthesize hybrids with optimal loading and chemical attachment of cobalt oxides micro/nano particles on the functionalized graphene surface, creating tailored interfaces crucial to electrochemical property enhancement. In-situ Raman spectroscopy integrated with electrochemistry was employed to investigate ion transport and charge transfer dynamics and to determine the concomitant electrochemical tuning of Fermi level. The variation of structural bonding in these hybrids dipped in aqueous alkaline electrolyte (*e.g.* KOH) with electrochemical biasing was monitored. It is because Raman spectroscopy can detect changes in graphene/metal and graphene/metal oxide bond through various spectral features. Two of the transverse optical phonons and corresponding longitudinal optical (LO) phonons of Co_3O_4 (and CoO) above 500 cm^{-1} are observed depending on the surface morphology and particle size as well as carbon-carbon bonding via G and 2D bands at 1590 cm^{-1} and 2670 cm^{-1}, respectively. Consistent reversible and substantial variations in Raman intensity and band positions of these modes induced by electrode potential point at the fine and continuous tuning, indicative of emptying/depleting or filling of the specific bonding and antibonding states which become electroactive. The results were explained in terms of changes in the electron density of states arising due to alterations in the overlap integral of bonds between the s and p (and d) orbitals of the adjacent carbon and metal oxide atoms. We estimated the extent of variation of the absolute potential of the Fermi level and overlap integral between the nearest-neighbor atoms from modeling the electrochemical potential dependence of Raman intensity thus corroborating the synergistic coupling of graphene and cobalt oxide polymorphs. The interplay of heterogeneous basal and edge plane sites graphene and crystalline spinel cobalt oxides reinforce density of states in the vicinity of Fermi level and efficient interfacial electron transfer. We acknowledge KY NSF EPSCOR RSP, WKU Research Foundation and Graduate School internal awards in parts for financial support.