Chapter 12
Extraction of Preformed Mixed Phase Graphene Sheets from Graphitized Coal by Fungal Leaching

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ABSTRACT

The potential use of coal as source of carbon nano structure is seldom investigated. Herein we report a facile fungal solubilization method to extract mixed phase carbon structure from low grade coal. Coal had been used as a primary source for the production of carbon nanostructure with novel property, in addition to its main utility as a fuel. The major hurdle in its application is the inherent mineral embedded in it. An environmentally benign demineralization procedure make coal as a widely accepted precursor for the novel carbon materials. With Aspergiilus niger leaching, the randomly oriented preformed crystalline mixed phase nanocarbon in coal can be extracted. Raman studies revealed the presence of E_2g scattering mode of graphite. The sp^3 domains at ~1355 cm^{-1} (D band) is an indication of diamond like structure with disorder or defect. In the 2D region, multilayer stacking of graphene layers is noticed. The ratio of the defect to graphitic bands was found to be decreasing with increasing rank of coal. Bio leaching of coal enhances the carbon content in coal while eliminating the associated minerals in it. These defected carbon is an ideal material for graphene quantum dots and carbon dots, which are useful in drug delivery and bio imaging applications.

INTRODUCTION

Coal is extensively used as solid fuel across the world and has sizeable share in the global fossil fuel reserve. Utilization of this resource generate excess spoil and low grade waste to the environment. Solubilization of minerals in coal has the potential to elevate this inherently dirty solid fuel to a source of value-added products like graphene, graphene quantum dots or carbon nanotubes (Manoj, 2014; Ruquan et al, 2013). Microorganisms have the ability to breakdown while beneficiating the low grade coal.

DOI: 10.4018/978-1-5225-2325-3.ch012

Bioremediation technologies have unfortunately not been realized for obtaining value added products from coal. Currently the application of bioremediation in controlling and eradicating mineral pollution has generated great interest. Alternatively bio-sorption, which exploits resources of biological origin, like bacteria, fungi, yeast, algae, are also gaining momentum. These microorganisms have the property to sequester metal-and decrease them to *ppb* level. It can effectively and quickly sequester metal ions out of complex molecule and is an ideal candidate for the treatment of industrial waste (Wang, & Chen, 2006; Volesky, 2001; Lin et al., 2006). The bio-sorbent materials like algae, fungi and bacteria have the ability to bind on metal elements and is considered from the toxicological point of view. This biomass can passively bind on metallic ions or organic compounds through various physico-chemical mechanisms (Wang, & Chen, 2006). The challenge is the proper selection of biomass from a large pool of readily available biomaterial, which has high mineral/metal binding property. In recent past, extensive research is being carried out on the bio-sorption phenomena, particularly on the demineralization or leaching of minerals to enhance the quality of ore (Wang, & Chen, 2006; Volesky, 2001, 2007).

Graphene is sp^2 hybridized form of carbon, appear in many forms like graphite, nanotubes or fullerenes (Manoj, 2014; Manoj, & Kunjomana, 2014). With the recent advances in nano carbon research, its synthesis plentiful natural source like coal has gained momentum (Elcey, & Manoj, 2016; Raquan et al., 2013). Coal or black carbon is a solid product formed by the partial combustion or anaerobic digestion of vegetation. It comprises of crystalline carbon with turbostratic structure with highly disordered amorphous addends on the edges (Elcey, & Manoj, 2010; 2013; 2014; Dong et al., 2014). Nano domain in coal consist of about 3-4 stacked carbon layers, with lateral dimension and interlayer spacing of 3nm and ~ 0.35 nm respectively. The amorphous realms constituted of polycyclic aromatic compounds, which are graphene sheets having irregular onion-like arrangement along with other organic constituents. The main hindrance in the structural characterization of coal is the inherent minerals present in it. Being inherently low quality due to the mineral matter and ash, leaching of coal is need for any application. Generally chemical leaching with mineral acids or alkalis are used for the demineralization of coal. Even though mineral matter could be removed, the disposal of the used chemical in safe manner is a serious concern. These chemicals generally corrode the environment and generates serious environmental pollution. In this scenario, a facile, ecofriendly demineralization technique of coal is worthwhile problem to be investigated.

Direct application of organic acids may affect mineral weathering rates by at least 3 mechanisms: by changing the dissolution rate far from equilibrium through decreasing solution pH or through forming complexes with cations at the mineral surface or affecting the saturation state of the solution with respect to the mineral (Elcey, & Manoj, 2010; 2013). Use of mineral acids in demineralization not only modifies the surface morphology and deteriorates the carbon structure, but also reduces the calorific value. These acids have strong oxidizing power and the safe disposal of the spent liquid is a major environmental concern. For commercial utility of coal bio-demineralization, fungal leaching is an ideal eco-friendly method. These mild organic acid partially removes the minerals in coal without much modification to the stacking structure. Coal being amorphous in nature, the ordering of carbon in it happens only with a strong acid.

In the present work, efficacy of the fungus *Aspergillus niger* in leaching coal and its effect on nano carbon layer stacking is discussed. It is a green extraction of preformed carbon structure from low rank coal. Changes in the stacking structure, nature of defect, degree of graphitization and change surface morphology with bioleaching is also highlighted. The mechanism of demineralization with carboxylic acid secreted by *Aspergillus niger* was elaborated.