Graphene oxide reduction activity of seaweed polymer derivative: efficient bio-based alternative

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The present study demonstrates utilization of functionalized seaweed polysaccharide, namely agarose–gallate (Ag–GA_{Est}) for the preparation of reduced graphene oxide (rGO) under mild reaction conditions. Ag–GA_{Est} obtained with the lowest degree of substitution (degree of substitution (DS) = 0.45; with 1 : 0.5 w/w agarose : gallic acid) shows excellent performance compared to its high DS (1.1; with 1 : 2.0 w/w agarose : gallic acid) ester derivatives. Further, the formation of rGO was confirmed using UV–Vis, TEM, FTIR, Raman spectroscopy, elemental and XRD analysis. This study describes a new application of seaweed-derived polysaccharides.

Keywords: Agarose–gallate, biomaterials, green approach, graphene oxide, reduction activity.

GRAPHENE is the thinnest aromatic sheet of sp^2 hybridized carbon atom organized in the two-dimensional chicken wire pattern. It is also the strongest material known with excellent electronic properties like ballistic transport[1,2]. Graphene and graphene-based materials are important in hydrogen storage[3], organic photovoltaic devices[4], organic solar cell[5], lithium-ion batteries[6], flexible field emission cathodes[7], etc. In addition, its exceptional properties such as high surface area and flexibility have an important role in cell growth and differentiation[8]. Graphene is also used in the preparation of biomaterials for biosensors, therapeutics as well as tissue engineering applications[8]. Researchers and technologists are continuously working towards the development of an improved process for the preparation of reduced graphene oxide (rGO) through discovering novel green reducing agents. Graphene oxide (GO) is an exceptional and industrially important material with a large number of carboxylic acid, epoxy and hydroxyl functional groups[1,9]. Nowadays rGO has great application potential due to its excellent properties, e.g. electronic, mechanical, optical and thermal properties[10]. Reduced graphene oxide can be obtained using several reducing agents such as hydrazine, $NaBH_4$, $LiAlH_4$, hydriodic acid (HI), NaOH (ref. 11), ascorbic acid, gallic acid[12] and glucose[13]. It tends to aggregate and precipitate due to its π–π stacking interaction. To overcome this problem, various stabilizers (e.g. lysozyme, porphyrins, pyrene butyric acid) have been developed to enhance rGO dispersion. Most of the reducing agents such as chemical reductants are toxic or explosive in natures, which restricts the use of rGO in the synthesis of biomaterials. Several naturally occurring reductants such as seaweed sap, protein, carbohydrates (glucose, dextran), tannin, gallic acid, dopamine, tea and vitamin C have been reported in the literature[12–14]. Recently, we have successfully tested seaweed polysaccharide agarose derivatives for the preparation of eco-friendly mercury sensor, self-healing and stretchable materials[15–18]. Till date, there is no report on the reduction of GO using agarose derivatives. Hence we explored other novel applications of seaweed polysaccharides.

Here, we report a green approach for reduction of GO using a biopolymer derivative, agarose–gallate (Ag–GA_{Est}). Ethylene glycol was used as a solvent for reduction. This process is green and utilizes bio-based reducing and stabilizing agent during the reaction in a very low concentration compared to pristine gallic acid[12]. The individual agarose polymer and a gallic acid equivalent to agarose–gallate (Ag–GA_{Est}) system were unable to reduce GO up to 3 h. However, Ag–GA_{Est} system having ~100-fold less gallic acid content compared to pristine gallic acid was required for the reduction of GO (ref. 12).

Experimental

Raw materials

The powdered graphite (avg. particle size ~400 nm, CAS no. 7782-42-5) was purchased from Sisco Research Lab (SRL) Chemicals Pvt Ltd, Mumbai. Other chemical reagents used in this study (e.g. AR-grade sodium nitrate,

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