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Preparation of water dispersible and biocompatible nanodiamond-poly (amino acid) composites through the ring-opening polymerization

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ABSTRACT

Nanodiamond (ND) is one of the most fascinating carbon materials that have been extensively investigated for biomedical applications owing to its small size, high specific surface areas, chemical inert and desirable biocompatibility. It has been reported that surface modification of ND with polymers could not only improve the dispersibility of final ND based composites but also endow them novel functions to fulfill the requirement for biomedical applications. Although some strategies have been developed previously, surface modification of ND with poly(amino acid)s has not been reported previously. In this work, poly(amino acid)s functionalized ND composites were fabricated through a ring-opening polymerization of α-amino acid *N*-carboxyanhydrides (NCAs), which was synthesized by conjugation of hydrophilic ethylene glycol with glutamic acid. The successful preparation of ND-GluEG composites was confirmed by a series of characterization techniques. The results suggest that the water dispersibility of final ND-GluEG composites is obviously improved. Moreover, ND-GluEG composites show low toxicity and are of great potential for biomedical applications.

1. Introduction

With the rapid development of nanoscience and nanotechnology, various nanostructured materials with different composition and size have been employed for use in various applications [1–7]. Some of these nanomaterials are designed to be used for bioimaging and drug delivery with great expectation. In particular, carbon nanomaterials with small size, high specific surface area and good biocompatibility have attracted great research interests in medical technology for their remarkable chemical stability and optical properties etc. [8–17] Among them, nanodiamond (ND) from detonation explosives has stand out as one of most promising carbon materials for biomedical applications owing to its small size, low cost, high specific surface areas and biocompatibility [18]. These remarkable features make ND and its composites promising candidates for various biomedical applications [13,14,19–21,23–32,52]. It also has been reported that ND could conjugate with biomolecules, such as proteins, drug or nucleic acids for protein immobilization/separation and drug/gene delivery [7,33–37]. However, the poor dispersibility of ND in aqueous and most organic medium has largely impeded its applications in biomedical applications. To facilitate the practical applications of ND, considerable research efforts have been devoted to developing new surface functionalization approaches for fabrication of ND based composites. Among them, surface modification of ND with polymers through both grafting from and grafting to methods has demonstrated to be the effective and efficient choice [38–41]. For example, we have demonstrated that hydrophilic and biocompatible polymers can be introduced onto ND through both grafting to and grafting from methods relied on the direct conjugation reaction and controlled living polymerization (e.g. surface-initiated atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) polymerization) [38–41]. These ND polymer composites have shown great potential for intracellular delivery of anticancer agents for cancer treatment.

Compared with conventional polymers, biodegradable polymers are highly demand for biomedical applications given their advantages in biocompatibility and biodegradability. A variety of biodegradable polymers including polyesters, poly(amino ester)s and poly(amino acid)s have been widely investigated [42–48]. It is well known that polypeptides exhibit sufficient biocompatibility and can be degraded into innocuous amino acid residues via the cleavage of peptide bonds. In addition, polypeptides have hierarchical self-assembled nanoscale structures that attracted more and more interest [49]. Nonetheless, for

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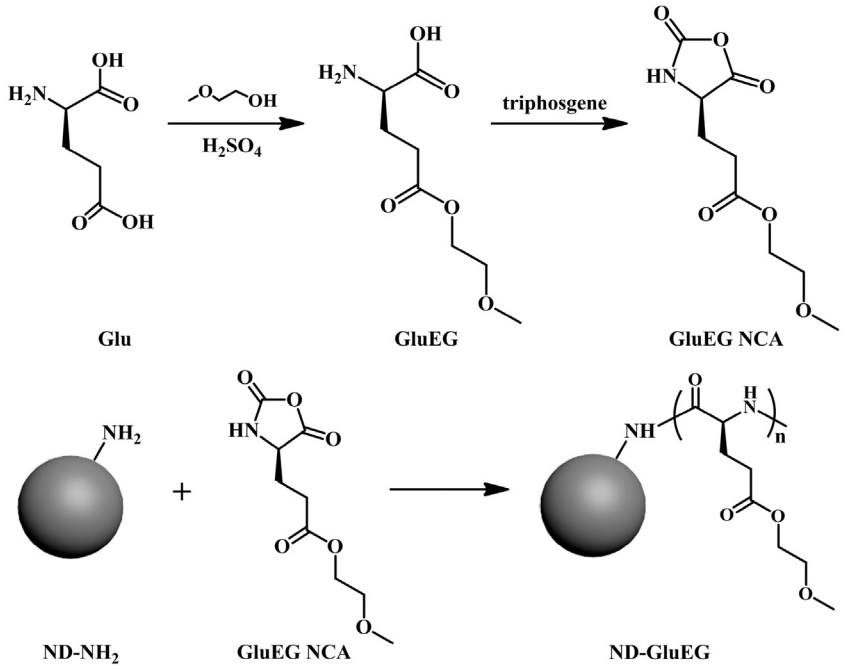

Scheme 1. Schematic showing the experiment procedure for synthesis of GluEG NCA and surface modification of ND with hydrophilic polymers through surface-initiated ring-opening polymerization.

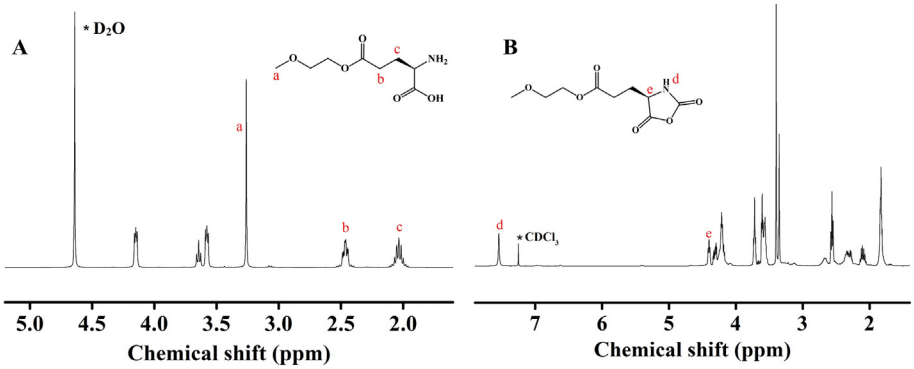

Fig. 1. ^1H NMR spectra of GluEG and GluEG NCAs. The ^1H NMR spectra were obtained using D_2O and $CDCl_3$ as the solvents.

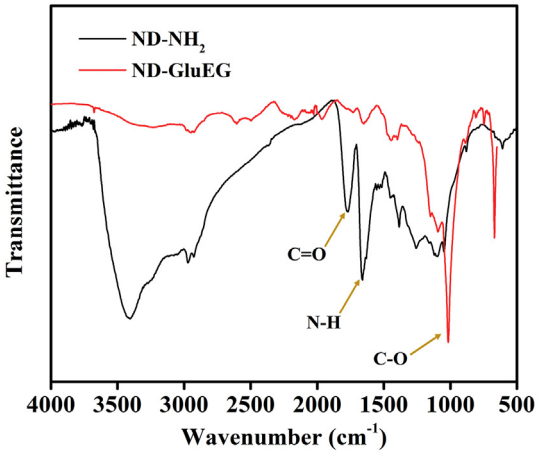

Fig. 2. FT-IR spectrum of $ND-NH_2$ and polypeptides functionalized ND-GluEG.

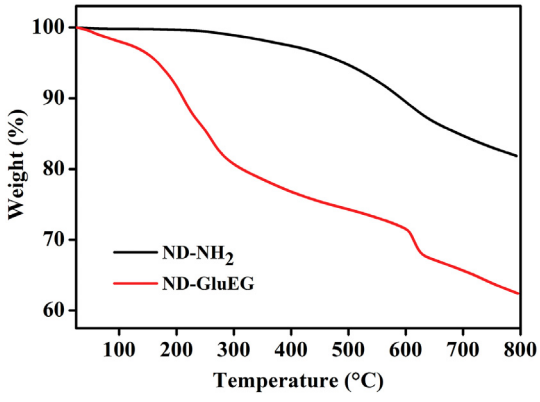

Fig. 3. TGA curves of $ND-NH_2$ and ND-GluEG.

natural polypeptides, majority of water-soluble polypeptides are polyelectrolytes, and have problems with pH dependent solubility and aggregation with oppositely charged biomolecules. Therefore, synthesis and design of nonionic water-soluble polypeptides is an efficient way to conquer this problem. Based on natural amino acids, a variety of side chain functionalized nonionic water soluble amino acids were developed. The general route to synthesize high-molecular weight polypeptides is by amine initiated ring-opening polymerization of the α-amino