Silk fibroin–carbon nanoparticle composite scaffolds: a cost effective supramolecular ‘turn off’ chemiresistor for nitroaromatic explosive vapours†

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The detection of nitroaromatic explosives is a pertinent issue with implications in homeland security, health and environmental monitoring. In this study, the development of a novel supramolecular bionanocomposite material based on Bombyx mori (B. mori) silk fibroin protein scaffold (SF) and carbon nanoparticles (CNPs) has been reported as a sustainable sensing platform for the nitroaromatic explosive vapours 2,4,6-trinitrophenol (TNP) and 2,4,6-trinitrotoluene (TNT). Herein, the sensing material is prepared via a static adsorption strategy involving non-covalent interactions, as evidenced from Fourier transform infrared (FTIR) spectroscopic studies, which demonstrate no change in the characteristic stretching frequencies of the carbon coated silk fibroin scaffold (SFC). Cross-sectional field emission scanning electron microscopy (FESEM) images suggest a thickness of CNPs of around 0.9 μm on the SF scaffolds. Further, Brunauer–Emmett–Teller (BET) analysis indicates multilayer adsorption of CNPs on the SF scaffolds. For sensing studies, carbon coated silk fibroin scaffolds are exposed to the vapours of TNP (SFCP) and TNT (SFCT) respectively followed by in-depth electrical analysis. Impedimetric analysis indicate changes in resistivity of the materials, following the order SF > SFC < SFCP, SFCT. The sensitivity of the biocomposite sensor has been investigated and found to increase by one order and two orders of magnitude when exposed to the vapours of TNP and TNT for 0–3 s, respectively. Further, the chemiresistive sensor is found to exhibit excellent reversibility, which is an important aspect from the point of view of recyclability of the sensor. In a nutshell, the use of low cost precursors, one pot approach for material development, utilization of impedimetric sensing technique, efficient sensitivity, excellent response time and reversibility make the system an ideal choice for sensing applications. Thus, the stated bio-nanocomposite might provide an excellent platform for the development of mechanically deformable and biodegradable systems, which has implications in the development of wearable electronics.

1. Introduction

The detection of ultra-trace amounts of highly energetic nitroaromatic compounds (NACs) viz. 1,3,5-trinitrohydro-1,3,5-triazine (RDX); 2,4,6-trinitrotoluene (TNT); 2,4,6-trinitrophenol (TNP) etc. has recently emerged as an important area of research particularly in the field of material science. It has an important significance in the field of homeland security, environmental monitoring and minimization of health hazards. Among the aforementioned analytes, TNP and TNT vapour sensing requires special attention particularly due to the severe health hazards and environmental effects associated with their exposure.1–5 TNP, commonly known as picric acid, is highly explosive in nature which arises from its chemical composition, very low vapour pressure and high volatility.1 In addition, TNP is highly water soluble, and its large scale use in industries leads to an increase in probability its release to the environment, which in turn results in soil and water pollution.2,3 According to ‘NIOSH Recommendations’, the recommended exposure limits are (10 h time-weighted avg) 0.1 mg m⁻³ (0.0998 ppm) for TNP and 0.5 mg m⁻³ (0.049 ppm) for TNT.4 Exposure to TNP and TNT above the permissible limits gives rise to many medical disorders, particularly strong