One-pot synthesis of magnetite nanorods/graphene composites and its catalytic activity toward electrochemical detection of dopamine

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ABSTRACT

Magnetite (Fe_3O_4) nanorods anchored over reduced graphene oxide (rGO) were synthesized through a one-pot synthesis method, where the reduction of GO and in-situ generation of Fe_3O_4 nanorods occurred concurrently. The average head and tail diameter of Fe_3O_4 nanorods anchored over the rGO matrix are found to be 32 and 11 nm, respectively, and morphology, structure and diameter of bare Fe_3O_4 nanorods were not altered even after the composite formation with rGO. The increased structural disorders and decrement in the sp^2 domains stimulated the high electrical conductivity and extended catalytic active sites for the prepared rGO/Fe_3O_4 nanocomposite. The constructed rGO/Fe_3O_4/GCE sensor exhibited excellent electrocatalytic activity toward the electrooxidation of dopamine (DA) with a quick response time of 6 s, a wide linear range between 0.01 and 100.55 μM, high sensitivity of 3.15 μA μM^{-1} cm^{-2} and a lower detection limit of 7 nM. Furthermore, the fabricated sensor exhibited a practical applicability in the quantification of DA in urine samples with an excellent recovery rate. The excellent electroanalytical performances and straight-forward, surfactant and template free preparation method construct the rGO/Fe_3O_4 composite as an extremely promising material for the diagnosis of DA related diseases in biomedical applications.

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1. Introduction

Dopamine (DA) is a significant catecholamine neurotransmitter present in the mammalian central and peripheral nervous systems, regulating variety of neuronal functions such as emotion, movement, behavior, cognition, attention, learning and memory. In the living systems, transmission of signal messages to the brain domains and other parts of the body is usually controlled by DA (Biji and Patnaik, 2012; Liu et al., 2012a; Palanisamy et al., 2013). It is also useful in tuning the various physiological functions including human metabolism, renal, cardiovascular, central nervous and hormonal systems (Jin et al., 2013; Pivonello et al., 2007). For the proper neurological functions, the concentration level of DA in extracellular fluid of caudate nucleus should be maintained in the

range of 0.01–1 μM. The deficient DA level causes neurological disorders such as Schizophrenia, Parkinson and epilepsy diseases and the higher level of DA in biological system leads to reward, pleasurable feelings and euphoria (Feddersen et al., 2014; Guo et al., 2013). It has sparked great interest in the detection of DA present in the biological as well as chemical systems.

Although number of strategies have been documented for the quantification of DA, certain constrains such as expensive, requiring speculated and large scale instruments, tedious sample pretreatment, multi-step and complicated sample preparations, low sensitivity and selectivity limited their on-site applications, necessitating the development of simple, cost and time efficient, highly sensitive and selective DA sensors (Babaei and Taheri, 2013; Xu et al., 2013). Recently, electrochemical technique has grabbed considerable attention in DA sensors, owing to its rapid detection, simplicity, easier operation, cost and time effectiveness, feasibility for miniaturization, lower detection limit, reliability, high selectivity and sensitivity (Babaei and Taheri, 2013). In addition, the electroactive characteristics of DA increase the competence of

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electrochemical technique in the quantification of DA further. However, the electrochemical detection of DA in physiological conditions is hindered by the co-existence of ascorbic acid (AA) and uric acid (UA), owing to their closer oxidation potential with DA, which leads to the serious interference effect during the determination of DA (Guo et al., 2013). In addition, high over potential, less electron transference, irreversibility behavior of DA and fouling of electrode surface by the DA oxidation products directed toward poor results for the bare electrodes, urging the modification of electrodes with the catalytic nanoparticles (Cheemalapati et al., 2013).

Among the variety of metal and metal oxide nanoparticles used for DA sensors, magnetite nanoparticles (Fe_3O_4) composed of Fe(II) and Fe(III) valence metals have received considerable interest due to their unique properties such as distinctive specific surface area, availability, structural manipulation, magnetic properties, biocompatibility etc., (Comba et al., 2012), which may progressively improve the sensitivity and selectivity toward DA without altering the bioactivity of bio-molecules. However, Fe_3O_4 nanostructures exhibited certain limitations including defects, mechanical instability, weaker electrical conductivity and poor electro catalytic activity, leadings to poor electrochemical performances with limited detection limit, low sensitivity and narrow linear range (Yea et al., 2012).

Most of the aforementioned significant issues can be effectively tackled by anchoring the Fe_3O_4 nanostructures over the active carbon support. Owing to the excellent electrical, thermal and mechanical properties, enlarged specific surface area and distinctive electrical conductivity, graphene has been recognized as one of the most promising futuristic materials in electrochemical sensors (Gnanakumar et al., 2014b). In general, chemical reduction of GO is extensively followed for the preparation of graphene, owing to its low cost, ease of production, free of toxic chemicals, inclination of sophisticated instruments and tedious process conditions (Chu and Pumer, 2014). The synergetic interaction between rGO and nanomaterials effectively determine the unique properties of rGO based nanocomposites (Bai and Shen, 2012).

Few reports such as reduction of hematite by CO/CO_2 (Darken and Gurry, 1946) or H_2 (Osterhout et al., 1975), microwave hydrothermal synthesis (Hu et al., 2011), co-precipitation (Mascolo et al., 2013), template method (Ahmad et al., 2009) and discharge method (Wang et al., 2002) have been reported for the synthesis of Fe_3O_4 nanorods. However, the unique properties of Fe_3O_4 nanorods and its composite and their controllable syntheses are still the great challenges. Fe_3O_4 nanorods prepared with oleic acid are stable only in the oil phase and immiscible with aqueous solution, which restricted their sensor applications. The surfactants used for the synthesis of Fe_3O_4 nanorods stimulated the agglomeration, which has not only decreased the active surface area of nanorods but has also reduced its competence in biological applications (Sun et al., 2012). Furthermore, the preparation of Fe_3O_4/graphene nanocomposite comprised of two steps process, involving the attachment of Fe_3O_4 nanoparticles over the surface of GO sheets and the reduction of GO sheets (Liang et al., 2010). The complicated multi-step process and magnetic properties of magnetite nanostructures led to the non-homogeneous distribution of Fe_3O_4 nanostructures, which limited their practical applications. Therefore, it is essential to develop the surfactant and template free and one-pot facile method for the preparation of Fe_3O_4 nanorods and rGO/Fe_3O_4 composite. This report is aimed at developing the simple, cost and time-efficient, environmentally benign one-pot synthesis for the preparation of Fe_3O_4 nanorods and rGO/Fe_3O_4 composite and evaluates their catalytic activity toward electrochemical detection of DA.

2. Experimental

2.1. Synthesis of Fe_3O_4 nanorods

To the mixture of 0.4165 M $FeCl_3$ and 0.1232 M $FeSO_4 \cdot 7H_2O$, 1 M urea was gradually added and refluxed for 12 h at 90 °C. The resultant solution was centrifuged at 12,000 rpm for 30 min, the resultant precipitate was washed with de-ionized water and dried at 80 °C.

2.2. Synthesis of rGO/Fe_3O_4 composite

GO was prepared according to the modified Hummer's method as described elsewhere (Gnanakumar et al., 2014a). To the GO dispersion (0.5 mg ml^{-1}), the mixture of 0.4165 M $FeCl_3$, 0.1232 M $FeSO_4 \cdot 7H_2O$ and 1 M urea was gradually added and refluxed for 12 h at 90 °C. The resultant composite was collected via centrifugation at 12,000 rpm, washed with de-ionized water and dried at 80 °C.

2.3. Modification of glassy carbon electrode (GCE)

GCE (3 mm dia) was polished sequentially with 1.0, 0.3 and 0.05 μm sized alumina powder and sonicated in de-ionized water, after each stage of polishing. The prepared nanostructures were dispersed in DMF (0.5 mg ml^{-1}) and 10 μl of the above suspension was dropped on the surface of a polished GCE and dried in air. To fix the electrocatalyst, 10 μl Nafion solution was dropped on the electrode surface and dried. Fe_3O_4 and rGO/Fe_3O_4 nanocatalysts modified GCEs were represented as Fe_3O_4/GCE and rGO/Fe_3O_4/GCE, respectively.

2.4. Characterizations

The synthesized nanostructures were characterized by using JEOL-JEM-2010 Transmission Electron Microscopy (TEM), Rigaku X-Ray powder Diffractometer (XRD), Shimadzu-Equinox FT-IR spectrophotometer and HORIBA-LabRAM-HR Raman spectrometer.

2.5. Electrochemical measurements

The electrochemical studies of prepared nanocatalysts were evaluated according to the procedures as described elsewhere (Gnanakumar et al., 2014b). The cyclic voltammograms (CV) of studied electrodes were obtained in 0.1 M PBS at a scan rate of 20 mV s^{-1} in the absence and presence of 100 μM DA. The amperometric experiments were carried out in 0.1 M PBS solution with the successive addition of different concentrations of DA at an applied potential of 0.25 V (vs. Ag/AgCl).

3. Results and discussion

3.1. Morphological properties

The homogeneously distributed needle like nanorod structures were observed for the prepared Fe_3O_4 materials and the average head and tail diameter of the prepared nanorods are found to be 32 and 11 nm, respectively (Fig. 1a–c). The regular contours were observed throughout the surface of nanorods and the average length of nanorods is observed to be 460 nm. The hydroxyl ions were gradually released during the hydrolysis of urea and the released OH^- ions combined with Fe^{3+} and Fe^{2+} ions, resulting $Fe(OH)_3$ and $Fe(OH)_2$, respectively. It is proceeded by the decomposition of $Fe(OH)_3$ into FeOOH nucleates and the growth of $Fe(OH)_2$ on FeOOH nucleates lead to the formation of Fe_3O_4