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Highly sensitive determination of atropine using cobalt oxide nanostructures: Influence of functional groups on the signal sensitivity

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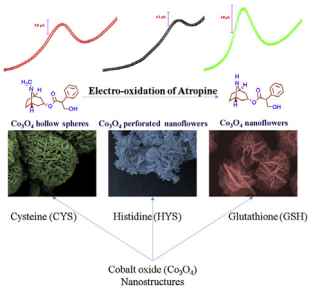
HIGHLIGHTS

- Template-assisted growth of Co_3O_4 nanostructures.
- Shape-dependent electro-catalysis of atropine.
- Effect of functionalisation of signal sensitivity.

GRAPHICAL ABSTRACT



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ABSTRACT

This study describes sensitive determination of atropine using glassy carbon electrodes (GCE) modified with Co_3O_4 nanostructures. The as-synthesised nanostructures were grown using cysteine (CYS), glutathione (GSH) and histidine (HYS) as effective templates under hydrothermal action. The obtained morphologies revealed interesting structural features, including both cavity-based and flower-shaped structures. The as-synthesised morphologies were noted to actively participate in electro-catalysis of atropine (AT) drug where GSH-assisted structures exhibited the best signal response in terms of current density and over-potential value. The study also discusses the influence of functional groups on the signal sensitivity of atropine electro-oxidation. The functionalisation was carried with the amino acids originally used as effective templates for the growth of Co_3O_4 nanostructures. The highest increment was obtained when GSH was used as the surface functionalising agent. The GSH-functionalised Co_3O_4-modified electrode was utilised for the electro-chemical sensing of AT in a concentration range of 0.01 −0.46 μM. The developed sensor exhibited excellent working linearity ($R^2 = 0.999$) and signal sensitivity up to 0.001 μM of AT. The noted high sensitivity of the sensor is associated with the synergy of superb surface architectures and favourable interaction facilitating the electron transfer kinetics for the electro-

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catalytic oxidation of AT. Significantly, the developed sensor demonstrated excellent working capability when used for AT detection in human urine samples with strong anti-interference potential against common co-existing species, such as glucose, fructose, cysteine, uric acid, dopamine and ascorbic acid.

1. Introduction

Recent progress in nanotechnology has led to the development of novel materials with promising applications in almost every scientific area. The excellent characteristics of such materials are attributed both to the size and shape of the nanostructure. In particular, use of nanomaterials in electrochemical sensor systems has revolutionised the field and enabled highly effective quantification of numerous important molecules. Synergy of the electrochemical approach with highly conductive nanomaterials provides an effective platform for widespread electrochemical investigations [1]. Recently, electrochemical sensors based on various architectures (shapes) of nanomaterial and composite materials have gained a lot of research attention [2,3]. Bansal, V., et al. (2010) [4] demonstrated variation in the generated signal for hydrazine reduction with different shapes of Ag nanostructures. Similarly, Soomro, R.A., et al. [5] described the shape effect of CuO nanostructures on the electrochemical quantification of organophosphate pesticides. Unlike solution-based catalysis, the electrochemical reactions are more inclined towards the shape of nanomaterial under investigation. Such dependency has proven to affect both the sensitivity and selectivity of the devised sensors [6,7]. This morphological influence is a consequence of shape-dependent surface free energy, charge density associated with unusual surface architecture and higher surface area of nanostructures. Contrary to metals whose surface energy is associated with the nature of crystal facets, metal oxides tend to behave differently. The associated surface energy for a metal oxide is a complex combination of inherent surface area, shape complexity and curvature-tempered charge concentration at the apex of nanostructures. Recently, Yang, C., et al. (2015) [8] described the shape effect during electrochemical determination of toxic gases with CuO nanoflowers in comparison to sheet-like CuO nanostructures. Despite the higher surface area of sheets, the CuO nanoflowers were found to be highly sensitive towards electrochemical determination of the gases. Similarly, urchin-shaped CuO was reported for its greater sensitive towards H_2 determination in comparison to nanorods and fibres. The observed sensitivity in this case was considered to be the consequence of multi-particle linkages associated with spines of the urchin-shaped CuO nanostructure structures [9].

With the increasing use of pharmaceutical drugs the global pharmaceutical companies, in order to meet the world-wide growing demand, require firm regulations regarding quantitative analysis associated with the drug processing stages. Such strict measures not only ensure the quality and stability but also assure the appropriate formulation of the designed drug [10]. In this context, atropine (AT), an alkaloid-based drug used for treatments of gastrointestinal diseases, cardiopathy and parkinsonism, is an important drug for investigation based on its significance in clinical and forensic toxicology [11]. Atropine is also known to be used as an antidote for the organophosphate cholinesterase inhibitor commonly found in chemical warfare agents such as tabun (GA), sarin (GB) and soman (GD) [12]. Despite its clinical applications, atropine is highly toxic and may result in serve problems for patients previously diagnosed with abnormal kidney function. Since the dosage level of atropine in the associated pharmaceutical is quite low, it requires highly sensitive and selective methods for accurate quantification. The conventional approaches for the determination of AT include chemiluminescence, capillary electrophoresis and liquid- or gas-based chromatographic methods [13,14]. Although sufficient for quantification, these conventional methods are time consuming, expensive, complex and tied to the laboratory. Contrary to this, the electrochemical approach provides faster analysis, simplicity, inexpensiveness and ability for device miniaturisation, which can enable development of lab-to-field sensor systems [15–17]. Although AT is an electro-active molecule, the electrochemical quantification carried out with bare glassy carbon electrodes (GCEs) is quite sluggish [18]. To overcome this restraint, various chemically-modified electrodes (CMEs), including carbon nanotubes, graphite-assisted screen-printed electrodes and multi-wall carbon nanotubes, have been previously adopted [19–21]. The inherent characteristics, such as high surface-to-volume ratio and enhanced conductivity of modifiers, provide higher sensitivity with much lower electron transfer resistance compared to bare GGEs. Recently, Bagheri, H., et al. (2015) [18] demonstrated the use of Co_3O_4 nanostructure assisted reduced graphene oxide modified carbon paste electrodes. The authors attributed the observed current enhancement to the synergetic effect of higher surface area associated with the Co_3O_4 nanostructures and conductivity of graphene oxide.

It is widely accepted that electro-catalysis is largely influenced by the architecture (shape) of the nanomaterials and presence of specific functional groups at the electrode/solution interface can alter the electrochemical generated electrochemical response [20,22]. The present study is designed to explore shape-dependent electro-catalysis and study the variation in electrochemical response with presence of certain functionalities at the electrode/solution interface. Herein, Co_3O_4 nanomaterial is chosen as the electro-catalyst with AT molecules as the target species. The discussed nanostructures were synthesised via a simple hydrothermal approach with the assistance of bio-compatible templates like cysteine (CYS), histidine (HYS) and glutathione (GSH). The as-synthesised nanostructures were then used for the modification of GCEs and were assessed for their behaviour towards oxidation of AT. To further estimate the effect of functional groups on the generated AT oxidation signal, the as-synthesised nanostructures were then functionalised with the same amino acids that were originally used as modifiers. The functionalised nanostructures were then evaluated for AT oxidation in compassion to their unfunctionalised counterparts. Moreover, the developed sensor system was assessed for its practical applicability by detecting AT in human urine samples.

2. Experimental

2.1. Reagents and materials

All the utilised chemicals were analytical grade and used without any prior purification. Cobalt chloride hexahydrate ($CoCl_3.6H_2O$), glutathione ($C_{10}H_{17}N_3O_6S$), cysteine ($C_3H_7NO_2S$), histidine ($C_6H_9N_3O_2$), 35% ammonia solution (NH_3), potassium