A sustainable alternative to synthesis optical sensing receptor for the detection of metal ions

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ABSTRACT

The development of new optical sensing receptors not only need to focus on its sensitivity and selectivity aspects, but should also emphasis on the sustainability of the development as a whole. This report proposed a green synthesis method to produce fluorescent carbon nanoparticles via thermal carbonisation of orange peels. This is a sustainable option since used agricultural waste as starting precursor, involved no excess or toxic chemical reagents, produced low or no waste side product, and employed simple synthesis steps. Parameters governing the precursor conversion into carbon rich residues were investigated and found that the optimum carbonisation occurs at the temperature range of 300–350 °C for an exposure time of 2 h. The carbon residue was then grinded into fine nanoparticles, dispersed in water and followed by sonication to promote better dispersion in water. Colloidal suspension remaining in the aliquot after centrifugation for 15 min at 13,400 rpm was collected and found to show strong fluorescence emission at 435 nm, when excited at the optimum wavelength of 325 nm. This unique optical property has been utilised for sensing application since the fluorescence intensity was significantly quenched in the presence of heavy metal ions. Analytical characteristic was evaluated using standard Stern–Volmer equation and the limit of detection was evaluated to be significantly low that enable the practical utilisation for quantification applications. It can serve as a less toxic fluorophore candidate to replace some of those existing quantum dots or dyes that are less sustainable in nature or in terms of its development approach.

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1. Introduction

Fluorescence technique has been widely employed in bioassays and optical sensors. This mainly due to its capability to achieve extremely low detection limit, where there are increasing examples demonstrating the detection limit down to single-molecule level [1–3]. Besides, the principles underlying fluorescence spectroscopy are well understood, making it easy to be utilised as an analytical probe. Generally, fluorescence technique consists of several main operating components, which include an excitation source, waveguides, fluorophores, and a photo-detector. In a typical working scheme, the interaction of an analyte with the fluorophore will subsequently cause a recordable change in the property of fluorescence emission. The unknown concentration of the analyte can be later evaluated from a standard calibration curve [4]. Usually, the most challenging task in developing a new fluorescence probe is on obtaining a suitable fluorophore that can detect a targeted analyte. The instrumentation of the probe is less of an effort since the electronic and mechanical components are readily available from the market with various specifications and most of them can be directly 'plugged and play' on a computer.

Fluorophores are usually extracted from natural resources such as directly from plants in the early days, but often this has some limitations for sensing tasks due to the lack of specificity. Later, advancement has progressed into the option to synthesis organic fluorescent dyes in laboratories. This gives more flexibility as the engineering of the fluorophores with specific chemical functionalities is now made possible. Cyanine- and azo-based dyes and its respective derivatives are some common examples of fluorophores that have been popularly synthesised in-house for optical sensing applications [5–9]. Although these dyes serve well for sensing with simple sensing mechanism, the synthesis process is often tedious, uses of various reagents and chemicals, and produces side products that some could be toxic and harmful

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to the environment and health. In addition, purification requires large amount of solvent that is costly and non-sustainable. More recently, the discovery of quantum dots has made another alternative for fluorophore. These semiconductor nanoparticles show good photostability, high quantum yield, chemically stable, and having tuneable emission [10], which have been successfully adopted for fluorescent labelling and sensing [11–14]. Although the performance is good, likewise, the synthesis process suffers similar limitations as faced by their dyes counterpart. In addition, there is also concern over its toxicity impact since part of the building blocks is of heavy metal that could leach out during the application stage.

It is clear that current technology could produce various types of fluorophores with specific analytical characteristics, but majority of synthesis processes have neglected the aspect of sustainability. This is associated especially on the use of large amount of chemicals, toxicity of the reagents, and wastes generated from the synthesis that could have negative impact to the environment and living organisms including human. To strike a counterbalance, the synthesis process should also emphasis on minimising or eliminating totally the use of toxic reagents and to eliminate the production of side products from the synthesis. In view of this, the green analytical chemistry approach should be emphasised more, which defined generally as the use of chemistry with the intention for pollution prevention [15]. Go green is one of the most recent trends in community of science and technology in the effort to promote sustainability in ensuring the future generation can enjoy what the world is like today. More and more studies have reported examples of adopting greener approach in their works, for instance in extraction [16], catalyst [17], polymer technology [18], and organic synthesis [19].

In this work, a green approach has been taken to synthesis fluorophore using agricultural waste of orange peels, without producing toxic side products along the process. Orange peels have been chosen since it is considered waste, a renewable source with no other known potential usage, and can be easily obtained all year round from tropical countries including Malaysia. The orange peels were carbonised using simple thermal pyrolysis in an oven before grinded into fine carbon nanoparticles (CNPs) with fluorescence property. The fluorescent CNPs were then employed as luminescent probe for the detection of various metal ions based on its quenching trend. This work is definitely greener since adopting waste as starting precursor, using less synthesis procedure and reagent, simple since using only thermal carbonisation, clean as it produces no toxic or harmful side products, and finally giving comparable sensing characteristic to those dyes and quantum dots. This work serves as one of the novel examples on using sustainable alternative in the area of optical sensor development.

2. Experimental

2.1. Reagents

All chemicals used in this study were of analytical grade unless otherwise stated. Ultrapure water ($\sim$18.2 MΩ, 25 °C) was obtained from a Milipore Mili Q-system and used as solvents throughout the study. Peels of green orange (*Pericarpium Citri Reticulatae Viride*) was obtained from local market at Kuching, Sarawak, which was carefully washed with running water and rinse with double distilled deionised water before used. Stock solutions of metal ions were prepared from its respective salts, ($Cu(NO_3)_2$, $SnCl_2$, $Ni(NO_3)_2$, $Al(NO_3)_3$, $Co(NO_3)_2$, $Pb(NO_3)_2$, and $HgCl_2$) that were purchased from R&M marketing, Malaysia and used without further purification.

2.2. Instrumentation

Fluorescence intensity was recorded using fluorescence spectrofluorometer (CARY Eclipse, Varian) set under fluorescence mode with both the excitation and emission slits of 5 nm. Sample was placed in a 4-sides polished quartz cuvette with the path length of 10 mm. Laboratory furnace (Carbolite ELF 11/14 B) with a maximum setting temperature of 1100 °C was used for carbonisation. Sonicator (Branson 5510 Ultrasonic cleaner) was used for sample dispersion and centrifuge system (Eppendorf Minispin) was used for the separation of bulk residue from the aliquot that was rich in CNPs in the dispersed form. FTIR was recorded using IR spectrometer (Shimadzu).

2.3. Preparation of CNPs

The preparation of the CNPs is mainly divided into two major steps; carbonisation of orange peels via thermal approach and isolation of fine nanoparticles through centrifugation. Fresh orange was obtained from the local market and the skin was carefully peeled and cut into the rough dimension of 10 mm^2. These peels were washed under running water and rinsed with distilled water before left to dry in an oven for overnight. For carbonisation, approximate 5.0 g of the orange peels were placed into a porcelain crucible and place into a furnace. The peels were heated from room temperature to a final pre-set temperature (ranging from 250 °C to 450 °C) and kept at the set temperature for 2 h. Sample was removed from the furnace after that and cooled to room temperature in a desiccator. The black residue obtained was grinded into fine powder using pestle and mortar. In order to separate the fine nanoparticles from the bulkier particles, 0.01 g of the grinded product was dispersed into 10 ml of ultrapure water and homogenised under sonication for an hour. Following that, the mixture was centrifuged at 13,400 rpm for 10 min and the slightly yellowish supernatant was collected, leaving the non-soluble residue at the bottom of the tube. The supernatant was kept inside a sample bottle, sealed and stored at cold dark place for further analyses.

2.4. Optimisation of synthetic and analytical variables

Synthetic parameters affecting the final fluorescence of the CNPs were investigated. The optimum temperature used for carbonisation of the orange peels was determined by altering the temperature of the furnace from 250 to 400 °C and the standing period ranging from 1 to 4 h for each of the fixed temperature. The fluorescence intensities of the final obtained samples were monitored at 435 nm with the excitation wavelength that was set at 325 nm. The effect of time taken for sonication and centrifugation against the fluorescence intensity were also investigated. All standard procedures involved in the optimisation were set at similar condition and setting except the parameter under investigation.

The potential of CNPs as sensing probe for metal ions detection was investigated. Different metal ion solutions (made from $Cu(NO_3)_2$, $SnCl_2$, $Ni(NO_3)_2$, $Co(NO_3)_2$, $Pb(NO_3)_2$, $AgNO_3$ and $HgCl_2$) were added into the CNPs solution and any alteration and change on the emission spectrum will be recorded. To investigate the analytical trend, dependency of the signal change on the alteration of the concentration of the metal ions was studied by adding increasing amount of the metal ions to the CNPs sample. For quantification and data analysis purposes, all intensity data recorded were first normalised against the blank, where the blank consisted only the fluorescent CNPs without addition of metal ions. The limit of detection (LOD) of the CNPs towards different metal ions was evaluated using the standard $3\sigma/s$, where σ is the standard deviation of blank ($n = 6$), while the s is he slope of the calibration of the technique obtained from the plot of intensity versus concentration.