



# Facile synthesis of hexagonal-shaped polypyrrole self-assembled particles for the electrochemical detection of dopamine



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## ABSTRACT

Nanomaterials have been used as an electroactive medium to enhance the efficiency of bio/chemical sensors, primarily when synergy is reached upon mixing different materials. In this study, we report on the facile synthesis of hexagonal-shaped plate-like polypyrrole (PPY-IC) prepared through inclusion polymerization of the host–guest pyrrole monomeric inclusion complex of  $\beta$ -cyclodextrin ( $\beta$ -CD) to be used in the detection of the neurotransmitter dopamine (DA). The amount of the monomer complex plays a crucial role in the fabrication of well-defined hexagonal-shaped PPY-IC through intermolecular interactions such as  $\pi$ – $\pi$  interactions and hydrogen bonding between the  $\beta$ -CD and PPY. The microstructure and morphology of the PPY-IC were examined by using various analytical techniques and a tentative mechanism for the growth process proposed which elucidates the formation of the hierarchical structure of the PPY-IC. Cyclo-voltammetry was performed with a PPY-IC modified glassy carbon electrode (GCE) for the electrochemical detection of DA. The concepts behind the novel architecture of the PPY-IC modified electrodes have potential for the production of materials to be used in electrochemical sensors and biosensors.

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## 1. Introduction

Recognition and sensing of biomolecules play ever more important roles and have an ever-increasing importance in clinical diagnostics, as well as for environmental, agricultural, and industrial monitoring, as well as food safety, and even national security [1]. Biosensors are designed to produce a response toward the target analyte for the detection of bio-species and the identification of genetic abnormalities, enzymes, pathogens, DNA, viruses, toxins and biological markers of diseases. There has been a significant amount of research into the development of biosensors which are sensitive, selective and cost effective which can be produced by adjusting conventional methods such as physical/chemical adsorption, covalent bonding, cross-linking and entrapment in gels or polymer matrices [2,3]. In general, polymer based biosensors have benefits in terms of biosensor applications due to their flexibility, corrosion-resistivity and chemical inertness. Electrically conductive polymers are highly sensitive to environmental changes and

other triggers so have been widely utilized for sensing applications [4,5].

In particular, dopamine detection is crucial in clinical applications, because of its crucial role in the functioning of the central nervous, hormonal, renal and cardiovascular systems, as well as the roles it plays in drug addiction, schizophrenia, and Parkinson's disease [6]. This is why the precise detection of the dopamine concentration in biological systems is of great significance in the field of clinical diagnostics. Simple, sensitive, selective, and reliable electrochemical methods already widely used in the field of analytical chemistry have been adapted for dopamine determination and the development of electrochemical methods for both quantitative and qualitative monitoring [7]. However, there have been challenges that need to be overcome, such as the coexistence of excess ascorbic acid (AA), which has an oxidation potential close that of DA, in human body fluids [8]. With conventional electrodes, the voltammetric response of AA often masks that of dopamine. In order to overcome this problem, electrode surface modification strategies have been developed which cover the surface with various negatively charged materials [9–11].

Thus, isolation of the electrochemical responses of AA and DA has been attained through modification of the electrode

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conducting-polymer [4]. The fabrication of dimensionally controlled conductive polymeric nanostructures has burgeoned over the past decades due to their appreciable electrical properties combined with a wide range of applications in drug-delivery systems, energy conversion systems, sensors, and as photocatalysts. In particular, the superior physical and chemical properties of nanosized polypyrrole (PPY), such as their high stability in environmental applications, biocompatibility and substantial electrical conductivity, have led to the emergence of various commercial applications [12].

In addition, being able to regulate the orientation of polymeric nanomaterials during polymerization is a significantly important consideration. In general, there are a variety of methods for the preparation of oriented PPY based nanorods and nanofibers, such as template-based synthesis, interfacial polymerization, and seed or oligomer assisted synthesis [13]. However, the preparation of template-free PPY nanomaterials has attracted enormous attention in the field of functional polymer science. The electropolymerization methods in the presence of non-acidic and weak-acidic anions are the main methods followed for template-free synthesis of polymeric materials [14]. However, electropolymerization methods have the disadvantages of being time-consuming, and difficulty controlling the size of the nanomaterial [15]. However, cyclodextrin (CD) shield polyconjugated monomers can be used to create novel functional compounds with CDs as molecular building blocks but this has posed great challenges in the field of supramolecular chemistry [16]. CDs have been used extensively for supramolecular assemblies and are able to provide channel structures, which can be applied as templates for the production of rod-like assemblies [17,18].

Herein, we report on the fabrication and electrochemical sensing behavior of dimensionally controlled PPY-IC nanorods facilitated by the formation of polyrotaxane. PPY-IC was fabricated by the formation of inclusion complexes between the  $\beta$ -CD complex and PPY through the simple self-assembly method and using  $\text{FeCl}_3$  as the initiator. The self-assembly behavior and structures of PPY-IC were characterized by spectroscopic techniques, powder X-ray diffraction studies and field emission scanning electron microscopy. The obtained results show that the resulting complexes of  $\beta$ -CD with guest molecules is a key step for preparing self-assembled conjugated polypseudorotaxane hexagonal assemblies. The PPY-IC displayed different self-assembly behavior with various concentrations of the monomer complex and its use as a dopamine sensor was demonstrated.

## 2. Experimental

### 2.1. Materials

The pyrrole (Py),  $\beta$ -cyclodextrin ( $\beta$ -CD), dopamine (DA), and ferric chloride ( $\text{FeCl}_3$ ) were purchased from Aldrich. All aqueous solutions were prepared with double-distilled water and the chemicals were used without further purification.

### 2.2. Synthetic procedure of self-assembled PPY-IC

First, the water-soluble pyrrole- $\beta$ -cyclodextrin (PY/ $\beta$ -CD) inclusion complex was prepared by mixing equal molar ratios of PY and  $\beta$ -CD. The mixture was then stirred for 4 h at room temperature before being stored in a refrigerator overnight at  $0 \pm 5^\circ\text{C}$ . The PY/ $\beta$ -CD inclusion complex was collected as a precipitate after being filtered and washed with cold water then dried at room temperature. Then, an aqueous solution of  $\text{FeCl}_3$  was quickly added to the calculated quantity of monomer complex aqueous solution at  $25^\circ\text{C}$  and polymerization was carried out for 10 min. The resulting

solution was kept at room temperature for 5 days without stirring, and a blackish-green product was formed gradually. The PPY-IC precipitate was collected after immersion in methanol and acetone to remove the monomer complex and initiators, respectively. It was then washed with cold water and subsequently vacuum dried for 24 h.

### 2.3. Measurements

A Nicolet 8700 (Thermo scientific) FT-IR spectrometer was used for the FT-IR measurements. The morphology of the PPY-IC nanomaterials was studied on a Hitachi H-7000 JEOL JSM-6500F field emission scanning electron microscope (FESEM). Wide-angle and small-angle X-ray diffraction (WAXD and SAXS) measurement of the PPY-IC was carried out using the BL17A (powder X-ray scattering end station) X-ray diffractometer of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. The incident beam was focused on a toroidal mirror and monochromated ( $\lambda = 1.333621 \text{ \AA}$  for BL17A) by a Ge double crystal monochromator. Cyclic voltammetry (CV) experiments were carried out using a CHI-1205 electrochemical workstation (CH Inc., USA) with a conventional three-electrode cell and a glassy carbon electrode used as the working electrode. The auxiliary electrode consisted of a platinum wire, and Ag/AgCl was used as the reference electrode.

## 3. Results and discussion

### 3.1. Morphology evaluation

The dynamic response characteristics of the host-guest matrix which may be expected to be controlled by the density of the inclusion complex network density, were effectively taken advantage of for biosensor construction. In particular, the incorporation of the electroactive PPY component within the cavities of the  $\beta$ -CD may alter the diffusion properties of the analyte. To investigate this, we evaluated a series of PPY-ICs with their unique hexagonally shaped morphology which were prepared using different PY/ $\beta$ -CD monomer complex ratios and then utilized for DA sensing. Hexagonal-shaped PPY-IC was prepared by the simple oxidation polymerization of the PY/ $\beta$ -CD monomer complex, followed by the crystal growth step of PPY-IC. Fig. 1 shows an SEM image of the as prepared PPY-IC, which is mainly comprised of the unique rectangular cross-sectioned hexagonal-shaped plate-like morphology with a smooth surface, and sequential arrangement. The average length and thickness of the PPY-IC hexagonal particles are about ca.  $1 \mu\text{m}$  and  $0.25 \mu\text{m}$ , respectively. Fig. 1b shows a single hexagonal-shaped plate, with a thickness of about 50 nm. The microstructure was also observed by TEM as presented in Fig. 1c.

In order to investigate the formation mechanism of the oriented hexagonal-shaped PPY-IC plate-like morphology, the polymerization of samples with different ratios of PY/ $\beta$ -CD monomer complex to initiator was studied at room temperature. Fig. 2a shows random disordered hexagonal-shaped PPY-IC particles with a thickness of 30–50 nm and length of  $1 \mu\text{m}$  observed when the molar ratio of the PY/ $\beta$ -CD monomer complex to  $\text{FeCl}_3$  was 0.5:1. When the ratio of the PY/ $\beta$ -CD monomer complex to  $\text{FeCl}_3$  was increased to 1:1, hexagonal-shaped particles began to aggregate which were then gradually connected together (Fig. 2b). The proportion of fused particles increased, and more complete closely packed hexagonal-shaped PPY-IC microcrystals appeared when the molar ratio of the PY/ $\beta$ -CD monomer complex to  $\text{FeCl}_3$  was increased to 1.5:1 (Fig. 2c). After increasing the PY/ $\beta$ -CD monomer complex to 2:1, the rod-like morphology became dominant (Fig. 2d), with the diameter of the rods being obtained being about 60–70 nm. A regular rod-like arrangement could be observed. With an increase in the amount of PY/ $\beta$ -CD monomer complex, there was an increase in the

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