

Tailoring the gold–polypyrrole nanostructures at water–toluene interphase

Chepuri R.K. Rao, D.C. Trivedi*

*Center for Studies in Conducting Polymers, Electrochemical Materials Science Division,
Central Electrochemical Research Institute, Karaikudi 630006, India*

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Abstract

A method is described to obtain gold–polypyrrole nanostructures by reacting gold chloride with pyrrole at toluene–water interphase. By adjusting the concentration of the stabilizer, namely, pyridine-3-sulphonate, the shape of the nanostructures formed at the interphase can be tailored. This novel method facilitates the fabrication of Au–Ppy composite material that gives wider scope for biosensing applications.

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1. Introduction

In recent times nanomaterials have received tremendous attention due to their potential applications in important areas such as biology, medicine [1] and are now limelight for many scientists research programmes. Gold nanoparticles are biocompatible, nontoxic, bind readily to large range of biomolecules such as aminoacids, proteins/enzymes and DNA [2]. On the other hand, conducting polymers (CPs), better known as advanced materials, are now foci of materials science and many applications are in vogue such as electrochromic displays [3], corrosion protection [4], electrostatic discharge/EMI shielding [5], batteries [6,7], sensors and electrocatalysis [8,9]. Polypyrrole (Ppy), an important CP, has excellent film forming property with good conductivity and is known for its unique biosensing/drug delivery [10] due to its biocompatibility. The drawback of this polymer is that the adsorption of desired biomolecules sometimes is difficult and not stable. The aim of the present work is to fabricate a nanocomposite, Au(0)–PPY, by incorporating a biologically active metal, gold, into biocompatible conducting polymer polypyrrole and thereby enhancing the utility for biosensing.

In our efforts to synthesize such metal–CP composite materials, we recently demonstrated method to incorporate palladium particles into Ppy matrix [11a] and modified Ppy surface with silver nanoparticles [11b]. Synthesis of conducting polymers such as polypyrrole and polyaniline using auric acid as oxidizing agent is known in literature [12–14]. Selvam et al. first synthesized gold–polypyrrole composite in a diblock copolymer micellar solution with HAuCl_4 as an oxidizing agent [12]. Liu et al. investigated [13] the pathways of auto-polymerization using complexes that contain chloride and gold. Report [14] on synthesis of polyaniline using tetrachloroaurate showed that gold colloids and short chained polyaniline are rapidly formed. The short chained polyaniline slowly transformed into long chain polyaniline.

In the present communication, for the first time, we describe an effective and novel method to incorporate gold nanoparticles into conducting polypyrrole matrix, at an interphase. We used AuCl_3 as an oxidizing agent which oxidatively polymerizes pyrrole and concomitantly gets into the formed polymer as a nanosized metal particles at the toluene–water interphase. The morphology of Au–Ppy composite can be tailored to nanorods/colloids by adjusting the concentration of the stabilizer, namely, sodium pyridine-3-sulfonate (SPS). In the absence of the stabilizer, a copper colored powdery Au–Ppy material composed of nanosized particles is obtained. The results are presented and discussed.

* Corresponding author. Fax: +91 4565 227713.

E-mail address: rkkousik@rediffmail.com (D.C. Trivedi).

2. Experimental

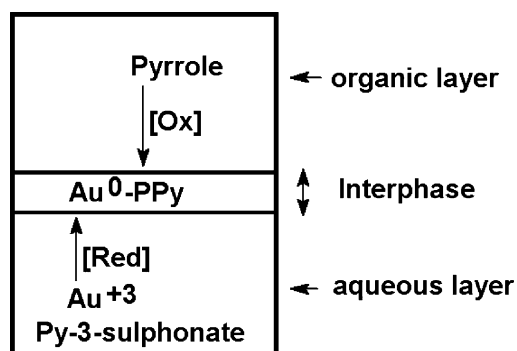
All chemicals are A.R quality and were obtained from Aldrich chemicals. Solvent toluene and methanol were purchased from C.D.H. (India) Chemicals. The SEM measurements were performed on a Hitachi-3000H microscope. TEM experiments were performed on a JEOL JEM-200FXII electron microscope with an acceleration voltage of 200 kV. X-ray diffraction patterns (XRD) were obtained with PANalytical MPD diffractometer using Cu K α radiation. FTIR Spectra of KBr powder-pressed pellets were recorded on a model no. Paragon-500 from Perkin-Elmer Spectrometer. Cyclic voltammetry was performed on Solartron SI1287 electrochemical system using three electrode assembly consisting of a platinum (0.25 cm²) working electrode, a platinum wire auxiliary electrode and a saturated calomel electrode. Conductivity of the samples were measured by four-probe method using KEITHLEY nanovoltmeter after pressing the samples into 1 cm dia, 1.5 mm thick pellets under 3 tonnes pressure.

2.1. Synthesis of Au–Ppy rods, colloids and powder

On to the aqueous solution of gold chloride and sodium salt of pyridine-3-sulphonic acid (SPS) [0.1 M, 10 ml each] in a long cylindrical jar (aprox. 3.2 cm dia), was carefully placed pyrrole (0.1 ml) in 40 ml of toluene. The two phases were allowed to react for 12–18 h at room temperature. The formed Au–Ppy composite in the form of rods at the interphase was filtered and washed with distilled water and methanol. To obtain Au–Ppy colloids, the concentration of SPS was increased to 0.4 M and heated with gold chloride (0.1 M) to form a light yellow SPS–gold complex solution. The cooled SPS–gold complex was reacted with pyrrole (0.1 M) at the interphase. The formed Au–Ppy colloids were collected by centrifuge and washed with minimum amounts of water. Au–Ppy powder was obtained when 0.1 M concentrations of gold chloride and pyrrole were reacted in the above fashion without addition of SPS.

3. Results and discussion

Au–Ppy nanorods are formed at toluene–water interphase (as explained in Scheme 1) when gold chloride and pyrrole (1:1 M)



Scheme 1. Schematic representation for gold–polypyrrole composite synthesis at water–toluene interphase.

monomers are reacted in presence of low concentration of SPS over a period of 18–24 h. As suggested by Diaz et al. [15] electrochemical oxidation process of pyrrole to polypyrrole consumes a current equal to 2 F. However, invariably all the times, this number is found to be lie between 2.2 and 2.4 F, the extra (0.2–0.4 F) being accounted for the formation of macro cation. Similar situation is observed here also. Extra gold(III) chloride is essential (0.33 mol extra, based on the fact that each mole of pyrrole need 0.67 mol gold chloride) to get the nanorods. Fig. 1a and b shows the SEM image of a bundle of gold incorporated polypyrrole nanorods which are 300–500 nm long with diameters of 50–180 nm. XRD (Fig. 2) profile for this Au–Ppy nanocomposite exhibited peaks at $2\theta = 38.62, 44.83, 64.98, 77.94$ and 82.08 due to the Bragg reflections corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) sets of lattice planes which may be indexed based on the fcc structure of gold. Further, a broad absorption between $2\theta = 10\text{--}30^\circ$, is also seen due to host matrix amorphous polypyrrole. The FT-IR spectrum of the composite showed charge carriers, bipolaron bands at 930 and 1200 cm⁻¹ indicating the Ppy formed is in oxidized state [16]. The peaks between 1636, 1540 and 1456 cm⁻¹ are assigned to fundamental vibrations of pyrrole rings [17]. The peak at 3400 cm⁻¹ is assigned to N–H stretching vibration from pyrrole. The Raman spectrum for this compound exhibited bands as follows: The C=C stretching is found at 1605 cm⁻¹. The C–N-antisymmetrical stretching observed at 1380 cm⁻¹ in pure polypyrrole [18] is shifted to 1400 cm⁻¹ in the present case due to the possible –N...Au interaction in the composite. The other bands found are due to symmetrical C–H in-plane bending associated with dication at 1080 cm⁻¹, ring deformation associated with dication at 950 cm⁻¹. The structure of the nanorods are susceptible for breakage while dispersing in toluene by sonication for TEM analysis. Most of the nanorods were broken to smaller size (<50 nm) platelets. The survived nanorods are typically 300 nm long with a diameter of 180 nm as suggested by TEM images (Fig. 1c).

Colloidal Au–Ppy solutions are obtained when higher concentrations (>0.4 M) of SPS are used. The colloid particles are dispersible in water. TEM analysis of the system showed the presence of circular platelets of 12–20 nm size. The size of the incorporated gold nanoparticles is around 10 nm as observed in TEM images (Fig. 1d) and XRD analysis (Fig. 2). The UV–vis spectrum (Fig. 3) of the colloidal solution exhibited broad and intense absorption above 600 (upto ≈ 900 nm), similar to reported values [19] which arises from polarons suggesting that the colloids system is in its conducting form. The routine surface plasmon band of Au(0) nanoparticles, which is generally observed at about 550 nm, is obscured by high intense polaron band.

Au–Ppy powder composed of nanosized particles is obtained, at the interphase, when no SPS was used (Fig. 1e and f). As there is no large functional anion [i.e., SPS], present in the medium to promote the growth of nanorods or colloidal platelets, the product is obtained as powder containing nanosized particles of gold with globular structures of polypyrrole of approximately 20–30 nm as suggested by SEM. TEM analysis (Fig. 4a) of this sample showed distribution of gold particles in the Ppy matrix.

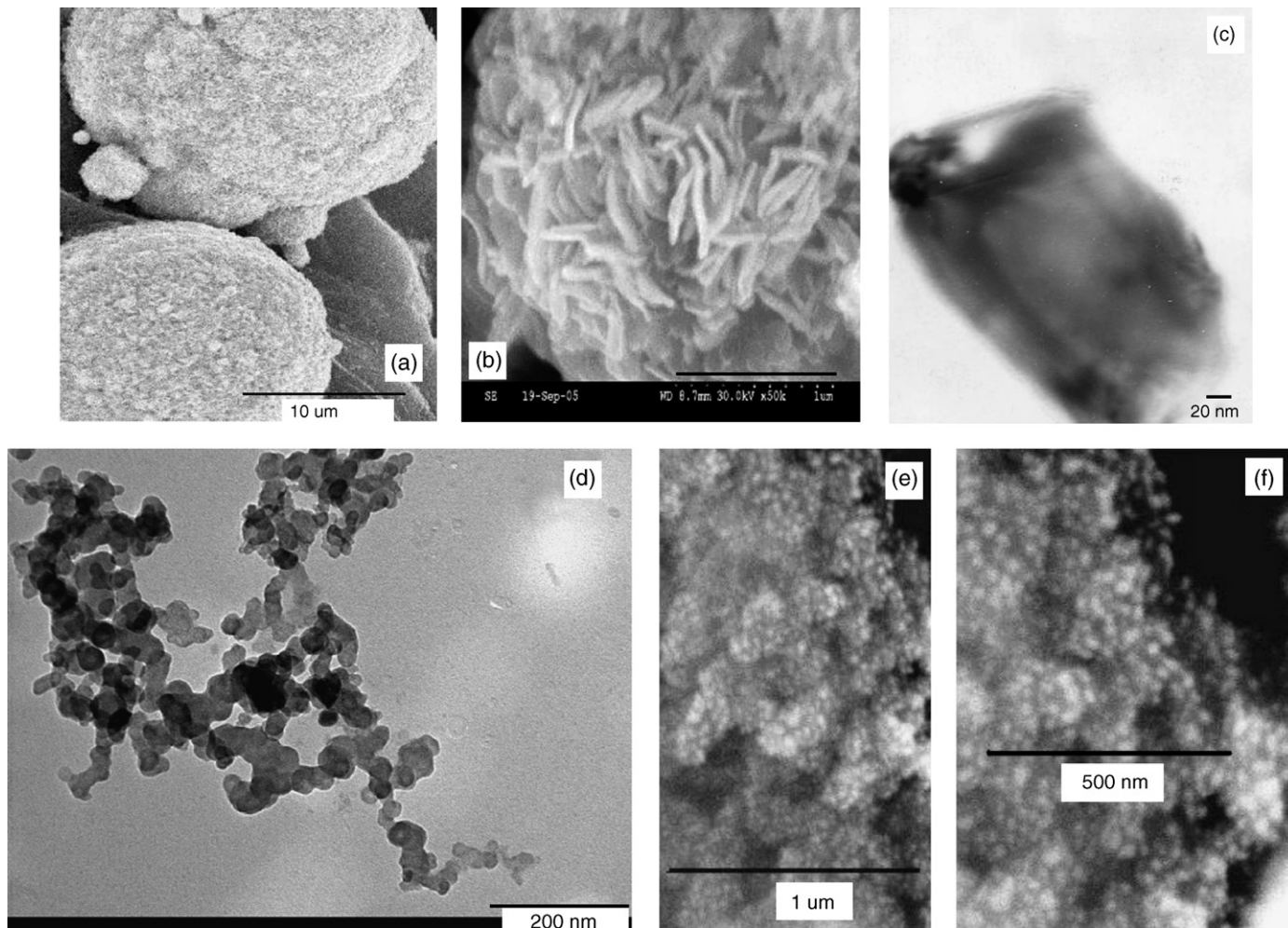


Fig. 1. (a and b) Scanning electron micrographs of Au-Ppy nanorods; (c) TEM image of a nanorod; (d) TEM image of colloid; (e and f) SEM of the nanopowder.

Fig. 4b shows the corresponding SAED pattern suggesting the crystalline nature of the gold particles.

The possible mechanism for formation of gold embedded polypyrrole structures is as follows: The potential of 1.5 V (ver-

sus NHE) for the half cell reaction $\text{Au}^{3+} \rightarrow \text{Au}^0$ is more than sufficient to oxidize the pyrrole (Py) monomer to form nanostructured polypyrrole (Ppy) at the interphase. Presence of low concentration of SPS and its mixing with gold chloride at room

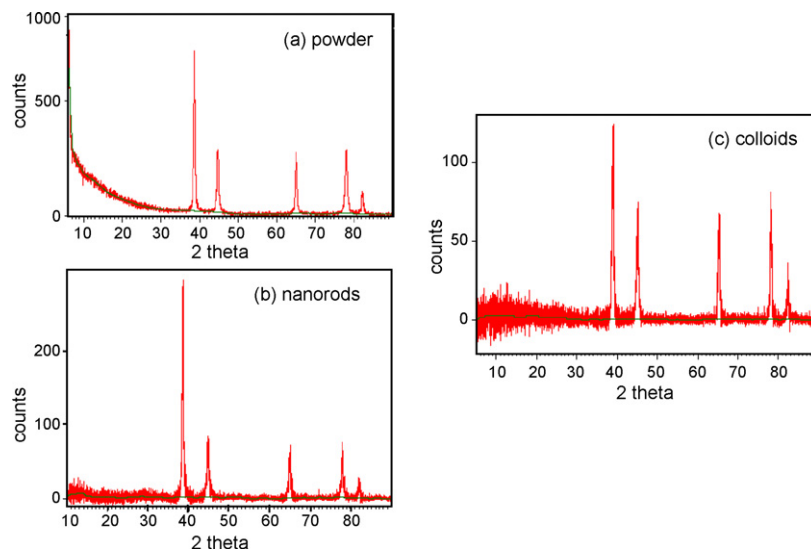


Fig. 2. XRD spectrum of the composites.

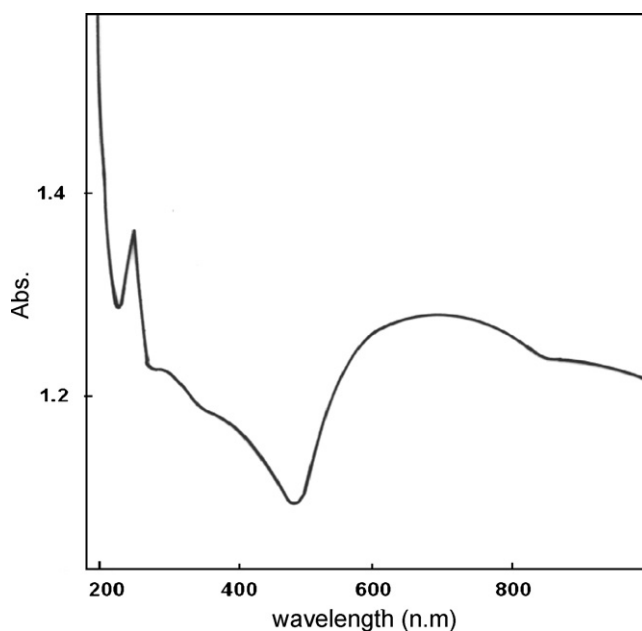


Fig. 3. UV-vis spectrum of Au-Ppy colloidal solution.

temperature did not alter the redox potential of Au(III)/Au(0) couple significantly and this condition promoted the growth of Ppy in the form of nanorods. The reduced gold particles are embedded/deposited on the polymer nanorods simultaneously resulting in homogenous Au-Ppy composite.

When high concentration (>0.4 M) of SPS is heated with gold(III) chloride, a light yellow pyridine \rightarrow Au(III) complex is formed. Complex formation lowered the redox potential of $\text{Au}^{3+} \rightarrow \text{Au}^0$ reaction. This makes Au(III) to act as weaker oxidizing agent. Here the reactions at the interphase were found to be slow and Au-polypyrrole colloids are obtained by 24 h. The formed gold nanoparticles are simultaneously capped by polypyrrole. When equimolar concentrations of AuCl_3 and pyrrole are reacted in absence of SPS, Au-Ppy powder composed of nanosized particles is obtained within 12–18 h. Thus the structures of the Au-Ppy composites can be tailored by adjusting the concentrations of SPS.

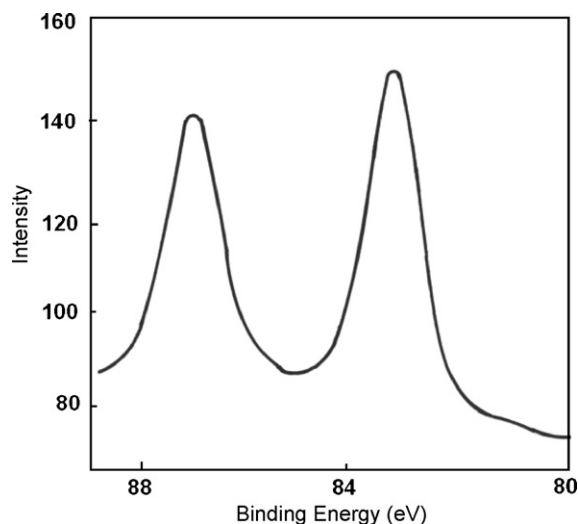


Fig. 5. Representative XPS spectrum of Au-Ppy nanorods.

The existence of zero valent gold particles in the polymer is confirmed by subjecting the composite to XPS analysis. The spectrum (Fig. 5) exhibited two doublet peaks at 87.5 and 83.8 eV originating from 4 f shell of Au(0) atoms. These values are comparable to literature values for gold in zero valent state [20]. Cyclic voltammetric (Fig. 6) investigation on the chemically grown Au-Ppy film in presence of SPS on platinum substrate showed that it undergoes oxidation at 1.0 V (versus SCE) and a corresponding reduction at 0.68 V. As known earlier [21], the anodic peak at 1.0 V is the result of oxidation of Au(0) to Au(III) state and this forms a possible coordination complex with PPy [21]. The coordinated Au(III) center gets reduced to Au(I) state at 0.68 V in the reverse scan [21]. The TGA analyses (Fig. 7) on Au-Ppy nanorods and powder showed that these composites are stable up to 270 °C and start decomposing after this temperature. They incurred a final weight loss of 25 and 29%, respectively at 600 °C. The nanorod composite film showed a surface conductivity of 0.7 S/cm. The pressed pellets of powder samples showed a conductivity of 1–20 S/cm. The higher conductivity of the powder is due to heavy gold deposits

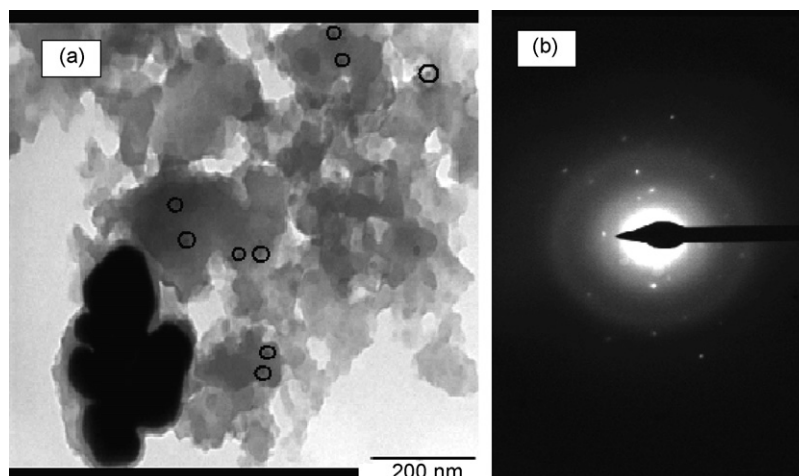


Fig. 4. (a) TEM image (b) SAED image of the Au-PPy nanopowder.

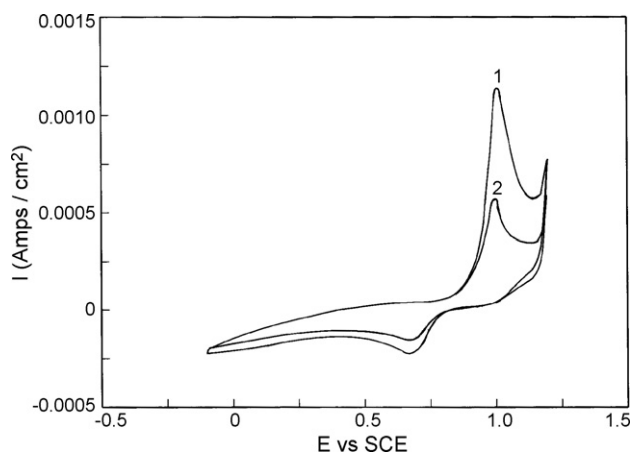


Fig. 6. Cyclic voltammogram exhibited by Au-Ppy composite. The scan rate is 50 mV/s.

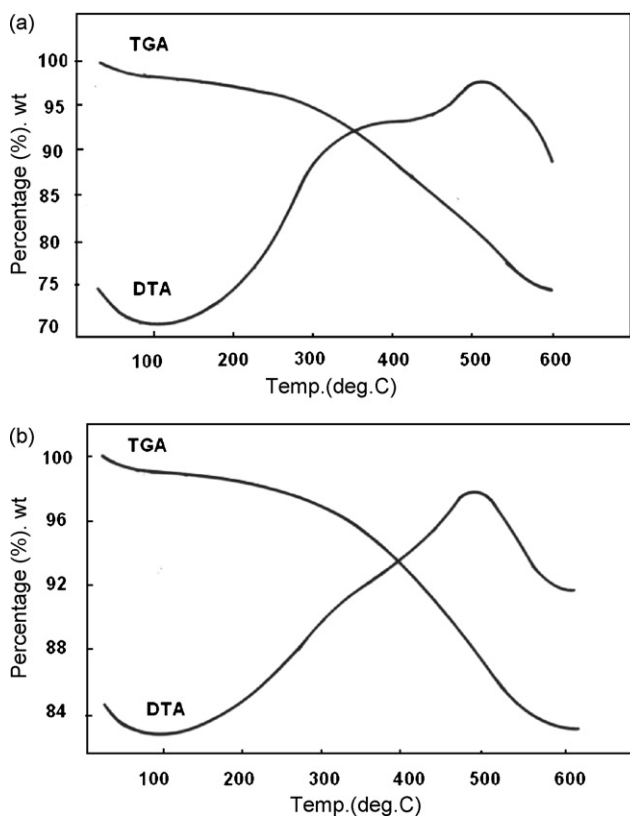


Fig. 7. TGA curves for (a) nanorods and (b) nanopowders.

on the surface of the polymer which are well connected after pelletization.

4. Conclusion

In conclusion, we have demonstrated a novel method to synthesize, Au-Ppy nanostructured composites with tunable shapes at toluene–water interphase, using gold trichloride as oxidizing agent. The preliminary investigations on the role of these composites in biosensing of certain biologically important molecules such as dopamine is encouraging and are in progress.

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