



Research paper

Studies on clay-gelatin nanocomposite as urea sensor

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ABSTRACT

Homogeneous gelatin organogel-based nanocomposite (GA-NC) was prepared by Lap as fillers. For customized thermal and viscoelastic properties, saturation binding of Lap to GA chain was probed in aqueous solution, and Lap = 0.03% (w/v), (glycerol) = 30% (v/v) and (GA) = 3% (w/v) was used for organogel nanocomposite. The Lap platelets were successfully exfoliated in the organogel matrix giving rise to a homogeneous phase. The interaction of GA-NC with urea was studied using electrochemical as well as optical technique. For electrochemical study, a thin film of this GA-NC was prepared onto indium tin oxide (ITO) coated glass plate via drop-casting. This GA-NC/ITO electrode was characterized by electrochemical, FTIR and SEM techniques. This GA-NC/ITO electrode exhibited electrochemical response specific for urea with sensitivity of 32.7 and 5.56 $\mu\text{A mM}^{-2} \text{cm}^{-2}$ in the two concentration range of 0.1 to 2 and 2 to 20 mM, respectively. The electrochemical profile of this electrode was sensitive towards urea which opens up the possibility for development of strip-based enzyme-free sensors for field applications. This GA-NC material in solution phase also shows optical response for urea with binding constant of 63.93 M^{-1} .

1. Introduction

Urea is a well-known bio-molecule that plays a variety of roles in the metabolic pathway of protein processing in the body, and it is also important as a fertilizer. The urea concentration in body fluid is inversely related to the rate of excretion of urea, depends on protein intake and nitrogen metabolism. An increase in urea level [normal range 8 to 20 mg dL^{-1} (2.5–7.5 mM)] in body fluid cause kidney relating diseases, dehydration, shock, and can result in gastrointestinal bleeding and reduced urea level may also cause hepatic failure, nephritic syndrome, and cachexia (Singh et al., 2008). On the other hand, urea detection in the environment, drinking water, and food samples is also important because it is easily washed out into the water bodies from the herbicides applied on crops, but polluting the surface and groundwater. The techniques currently used for the estimation of urea in tissue, and body fluids include ion chromatography, fluorimetric analysis and electrochemical biosensing (Shukla et al., 2014). However, electrochemical analysis has the inherent advantage of simplicity, high sensitivity, relatively low cost, and rapid response as compared to other sophisticated methods (Song et al., 2014). The electrochemical nanostructured based urea biosensors utilized enzymes i.e. urease/glutamate dehydrogenase (GLDH) to detect urea levels (Luo and Do, 2004; Massafra and Torresi, 2009; Massafra and Torresi, 2011; Rajesh et al., 2005; Solanki et al., 2008) have reported. Among these enzyme based

urea sensors, some reports are available on non-enzyme based electrochemical urea sensor too (Dutta et al., 2014). Mondal and Sangaranarayanan (2013) have reported the potentiodynamic polymerized pyrrole film made on platinum (Pt) electrode, and utilized it for development of non-enzymatic urea sensor which, worked in mildly acidic conditions with sensitivity obtained as 1.11 $\mu\text{A} \mu\text{M}^{-1} \text{cm}^{-1}$. Patzer et al. (1989) fabricated a Pt based urea sensor which works in the alkaline medium, and produce NH_4^+ ions with potentials ranging from 0.06 to 0.3 V. These Pt based electrode could affect real sample analysis, and are prone to toxicity upon continuous exposure to body fluids, are the major disadvantages of the previous reported urea sensor (Petrii and Vassina, 1993). Thus, there is urgent need to find a new material/platform, which works at neutral pH, is biocompatible, inexpensive, and with fast detection potential accurate for determination of content of urea in real samples.

Recently, organic and inorganic nanocomposite materials have attracted much attention because their synergetic combination offers enhanced properties at the nanoscale level (Herrera et al., 2005; Sigolaeva et al., 2014). Generally, nanocomposite (NC) materials comprise of three main constituents: the (bio)-polymer matrix, the nanomaterial (fillers), and the solvent (continuous phase). In most of the studies not much attention is paid to the role played by the interface. This interface region exchanges energy between the matrix and filler and is associated with properties different from that of the bulk

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because of its active coupling to the filler surface (Sudha et al., 2011). In most of the cases, the secondary forces between fillers, and the matrices, enhance interfacial adhesion, and improve their physical and electrochemical properties of NC materials. The exfoliated systems, being more homogeneous, produce enhanced physical, mechanical properties and stability which are most suitable for sensor application. The Lap, mono-dispersed layers consisting of numerous negative charge on the surface and residual positive charge at the edges (Fatnassi and Es-Souni, 2015). The Lap is easily modified with polymer to improve their properties, such as hydrophobicity and affinity for adsorbents, because the intercalated molecules can expand the layered structure in such a way that the exfoliation occurs (separation of the individual layers), and subsequently yielding functionalized leaflets with high surface area (Wagner and Vaia, 2004). However, Lap contains a relatively low amount of hydroxyls located at the edge of the individual particles, which can bind only to a small proportion of organics (Rausell-Colom and Serratos, 1987). To overcome the low reactivity of Lap surfaces towards organic molecules, several authors have used different strategies to enhance the reactivity. Herrera et al. (2005) reported Lap particles grafted with monofunctional *c*-methacryloxypropyl dimethyl methoxysilane (*c*-MPTDES), and trifunctional *c*-methacryloxy propyl trimethoxysilane (*c*-MPTMS) coupling agents. Few reports have reported using Lap in the form of NC coupled with different polymers/bio-polymers tailored for biomedical applications. A nanocomposite of Lap/chitosan was used to immobilize polyphenol oxidase on the surface of a glassy carbon electrode for phenol determination (Fan et al., 2007). The non-enzymatic electrode sensor comprising of Lap-ionic liquid was fabricated for oxalic acid detection using electrochemical techniques (Joshi et al., 2015). Recently, the change in photo-physical and biocidal properties of cationic *p*-phenyleneethynylene oligomers (OPEs) with Lap was studied (Hill et al., 2015). Thus, there is a wide scope to explore the Lap based biocompatible NC for non-enzymatic electrochemical sensor development.

In the present manuscript, gelatin (GA) obtained by partial degradation of collagen was used as matrix because the material has gained attention as edible films for its abundance, hydrophilicity, biodegradability, relatively low cost, good affinity, compatibility and excellent functional properties (Rivero et al., 2009). The physical properties of GA organogel have been exhaustively studied by Sanwlan et al. (2011). This type of NCs is useful due to their unexpected marketable potential for exploitation in electrochemical sensors, batteries, enzyme immunoassay etc. (Shukla et al., 2014). Further, it provides thermal stability, chemical inertia, well-defined layered structure, ion-exchange properties and low cost. Moreover, the permeability of this material provides electrostatic interactions due to the charge, and cationic-exchange properties of the clay minerals, which greatly affects the biosensor performance (Hu et al., 2002).

Keeping these points in view, a thin film of gelatin-organogel with Lap filler onto indium tin oxide (ITO) substrate by drop casting method was fabricated. Glycerol was added as a plasticizer to enhance the functional properties of films, and improved film flexibility. The results compared based on GA-NC are compared to different enzymatic and non-enzymatic urea biosensors reported in the literature.

2. Materials and methods

2.1. Materials

Gelatin-A (GA) (Extracted from Porcine skin and bloom number 300), having nominal molecular weight 50 kDa bought from Sigma-Aldrich, USA, was used for sample preparation. The Lap was purchased from Southern Clay Products, USA. For solution preparation de-ionized water was used, purchased from Organo Biotech Laboratories, India. Indium tin oxide (ITO) coated glass plates having a resistance of $25 \Omega \text{ sq}^{-1}$, the transmittance of 90% and thickness of 1.1 mm was procured from Blazers, UK. Urea and glycerol were

purchased from Sisco Research Laboratory Pvt. Ltd. India.

2.2. Sample preparation

To prepare solutions, GA powder (3% w/v) was dissolved in the required glycerol solutions (30% v/v) and mixed under continuous stirring for 1 h at 50 °C to homogenize. The Lap powder was dried at 120 °C for 4 h to remove the moisture (Pujala et al., 2011). The Lap concentration 0.03% (w/v) with GA powder (3% w/v) in glycerol solutions (30% v/v) was used for electrode fabrication and found film stable. Different concentrations of urea (Ur) were freshly prepared in deionized water from stock solution (20 mM), and stored in refrigerator (4 °C).

2.3. Preparation of GA/ITO and GA-NC/ITO electrodes

The dispersion of GA prepared with glycerol solution [30% (v/v)] and Lap [0.03% (w/v)] was used for GA-NC/ITO electrode fabrication. GA-NC/ITO electrode was prepared by drop-casting of 10 μL of the above dispersion onto an ITO electrode surface (0.25 cm^2), then dried at room temperature (20 °C) for about 24 h. Similarly, a thin film of GA in glycerol [30% (v/v)] solution without Lap, GA/ITO was also made. To remove any unbound particles from the GA/ITO and GA-NC/ITO electrodes, the electrodes were washed with deionized water and stored in refrigerator (4 °C) when not in use. Scheme 1 shows the different steps of GA-NC/ITO electrode fabrication.

2.4. Optical studies

The photometric response of GA-NC was monitored as a function of substrate concentration using UV-Vis spectrophotometer Sigma protocol with slight modification to ascertain the selectivity and sensitivity of the matrix (GA-NC) with Ur in the solution phase. UV-Vis titration measurements were conducted with the addition of different concentrations of Ur from 0 to 20 mM.

2.5. Characterization

GA, Lap and GA-NC were characterized using X-ray diffraction (XRD, PANalytical X'pert PRO 2200 diffractometer with $\text{CuK}\alpha$ radiation at $\lambda = 1.5406 \text{ \AA}$) with 2θ range from 3 to 33°, step size of 0.22 and scan rate of 1°/min with an accelerating voltage of 40 kV. The availability of functional group on GA, Lap, GA-NC and changes in GA-NC after interaction with Ur were recorded by Fourier transforms infrared spectroscopic (FTIR, 600 UMA Varian spectrometer) with in the range of 400–4000 cm^{-1} and number of scan 65. All the samples individually were prepared by drop-casting of 10 μL of each samples (GA, Lap, GA-NC) onto an ITO electrode surface (0.25 cm^2), then dried at room temperature (25 °C) for about 24 h. The surface morphology of GA-NC/ITO electrode before and after interaction with Ur was recorded using Scanning electron microscopy (SEM, Lvo 40 Zeiss instrument). During the SEM measurement, the GA-NC/ITO electrode was attached on double stick carbon tape and fixed on aluminum stubs. The photometric response studies of GA-NC nanocomposite as a function of Ur concentration were investigated by UV/Vis Spectrophotometer (PG Instruments T90 + Double Beam Scanning) at spectrum range of 200–800 nm. The electrochemical studies [cyclic voltammetry (CV) in the potential range of –0.1 to 0.4 V and impedance spectroscopy (FRA) in the frequency range 0.01–10⁵ Hz] were conducted on Autolab Potentiostat/Galvanostat Model PGSTAT302N (Eco Chemie, Netherlands) using three electrode cell system; where GA-NC/ITO was used as working electrode, platinum (Pt) wire was the auxiliary electrode and Ag/AgCl as reference electrode in phosphate buffer saline (PBS, pH 7.0, 0.9% KCl) containing 3.3 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$. All the experiments were repeated three times under the same experimental conditions to check the reliability and reproducibility of the results.

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