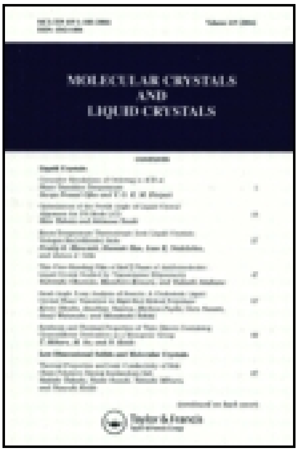

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Poly(3,4-Ethylenedioxythiophene)-Indium Tin Oxide Nanocomposites: Improved Electrochromic Response and Efficiency

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Poly(3,4-Ethylenedioxythiophene)-Indium Tin Oxide Nanocomposites: Improved Electrochromic Response and Efficiency

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Poly(3,4-ethylenedioxythiophene) (PEDOT)-indium tin oxide (ITO) nanocomposites were synthesized via a solution route. The electrochromic behavior of the devices was investigated in terms of particle sizes, dispersibility and electrical conductivity of the nanocomposites. The electrical conductivity of PEDOT-ITO composite thin films were in the range of 0.1∼15 S/cm with transparency changes from 25% to 85%. The electrochromic properties of the nanocomposite as an active material for the devices (ECDs) are discussed in terms of conductivity and transparency. The electrochromic behavior was confirmed with colored state and blanched state at +3.1 V∼−2.9 V which transparency difference about 50∼60% at 600 nm. The switching speeds of the ECD are closely correlated with the changes in the electrical conductivity and the morphology of the nanocomposite.

Keywords Indium Tin Oxide; conductive polymer; nanocomposite; electrochromism; nanoparticles; poly(3,4-ethylenedioxythiophene)

1. Introduction

Recently, electrochromic devices (ECDs) have received considerable attention primarily because of various applications such as electrochromic windows, displays, anti-glare mirrors, eye-glasses and solar-attenuated windows. ECDs utilize a reversible and repeatable change of optical properties by electrochemical oxidation and reduction states of the materials. 1,2 Advantages of ECD include low power consumption, low manufacturing cost, good contrast and scalability of manufacturing sizes. A few representative materials having electrochromic properties are mostly inorganic transition metal oxides of Vanadium (V), Molybdenum (Mo), Neodymium (Nb), and Titanium (Ti). Recently, conducting polymers have gained considerable attention due to their ease of synthesis, faster response times, and high optical contrasts and the ability to modify their structure to create multicolor electrochromes. Of the conjugated electrochromic polymers, the derivatives of

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polythiophene (PTh), polypyrrole (PPy), and polyaniline (PANI) are widely studied [6]. More recently, composite systems, where organic molecules are adsorbed on mesoporous nanoparticles of doped metal oxides, have shown improved electrochromic properties (thermal stability, electrochemical, catalytic, magnetic, mechanical, optical, dielectrical and electro-rhelogical properties etc) [7–11]. Also, the transition metal nanoparticles in conducting polymeric matrixes allow the development of materials in various applications in the field of electrocatalysis, sensors, microelectronics, and magnetism. The unique properties of such polymer-coated metal nanocomposite materials show strongly dependency on their particle size and shape [13]. Parvatikar et al. [12] synthesized WO_3–PANI composites that improved electrical conductivity than that of pure PANI. Ma et al. prepared PEDOT-TiO_2 nanocomposite electrode-based electrochromic devices with enhanced long-term stability [10].

We report here that poly (3,4-ethylenedioxythiophene) (PEDOT)-Indium Tin Oxide (ITO) nanocomposites were synthesized via a solution route. ITO is an n-type semiconductor with a band gap between 3.5 eV and 4.3 eV and a maximum charge carrier concentration in the order of 10^{21} cm^{-3} [16]. In addition to its highly conductivity, ITO is transparent to visible and near- infrared light.

Experimental

Synthesis of PEDOT-ITO Nanocomposite

For the synthesis of ITO nanoparticles, we closely followed the procedure by R.Nonninger et al.[17] The obtained ITO powders were treated at annealing temperature of 300°C with forming gas (8% H2, 92% N2). Since the hydrogen molecules in the forming gas lead to oxygen vacancies in the ITO lattice structure, the observed color changes from yellow-green to sky blue of the powders might explain the improved conductivity of the nanoparticles. The annealed ITO powders were use to prepare the aqueous solution of ITO with 3,6,9-trioxadecanoic acid (TODA) as surface-modifying components.

The PEDOT-ITO composite particles were synthesized through the oxidative polymerization of the 3,4-ethylenedioxythiophene (EDOT) on the ITO particles following a method modified from the literature [18]. For the PEDOT-ITO synthesis, aqueous solution of ITO colloid was added to solution (water:methanol = 9:1 vol%) of *p*-TSA solution containing ammonium peroxide sulfate (APS) at room temperature with rigorous stirring. The use of TSA led to a dramatic increase in the aqueous solubility of the EDOT monomer, which most likely protonated the conductive polymer by this strong acid. This led to faster rates of polymerization and hence higher yields of PEDOT. In addition, the TSA is presumably incorporated as a dopant anion in preference to the SO_4^{2-} or HSO_4^{-} anions derived from the APS oxidant, which would account for the higher conductivities obtained from the syntheses involving TSA [18].

The polymerization reaction was allowed to proceed for 20 h. The resulting reaction mixture was separated by centrifugation. The obtained dark blue sediment was washed with mixture solution (water : methanol = 1:1 vol%) in an ultrasonic bath.

Electrochromic Device Construction

Before coating, the ITO glass substrates were cleaned ultrasonically for 60 minutes in acetone, followed by ethanol rinse, and then blow-dried with a nitrogen gun. PEDOT-ITO composite solution was coated on the substrate using a spin-coating process for the electroactive layer of an ECD on the ITO glass. After the spin-casting, the films were dried in atmosphere in the range of 150°C for 15 min. For the device construction, the ITO glass substrate coated with electrochromic mixture were covered with another piece of ITO. Then electrolyte solution (0.7M $LiClO_4$ with propylene Carbonate, Aldrich Korea) was injected into the gap between the two substrates.

Characterizations

PEDOT-ITO composite particles size was measured by a Particle Size Analysis (Otsuka Electronics, PHOTAL ELSZ) according to the amount of ITO particles. And PEDOT-ITO films were measured thickness and electro conductivity used to Alpha-Step (KLA-Tencor, Alpha-step IQ) and 4-point probe (Mitsubishi Chemical Corporation, Loresta-GP (MCP-T600)). PEDOT-ITO composite solution was coated on the glass substrate using a spin-coating process. Then PEDOT-ITO thin film was dried at 150°C on Hot Plat. A scanning electron microscopy (SEM) was employed for the purpose of studying surface morphologies of PEDOT-ITO thin films on a JEOL, JSM-7401F. PEDOT-ITO composite particles the present work involves synthesis of PEDOT and ITO-incorporated PEDOT nanomaterials through surfactant chemistry and their characterization using X-ray Photoelectron Spectroscopy (XPS, Thermo Fisher Scientific, K-Alpha) techniques. The PEDOT-ITO coated surface was measured by a 3D Microscope (Keyence, VK-9700). Electrochromic properties were measured by the Optical Measurement System (Otsuka Electronics, LCD2000SR).

Results and Discussion

Analysis of PEDOT-ITO Composite

For bulk PEDOT and PEDOT-ITO composite samples synthesized, the room temperature conductivity varies from 10^{-1} to 101 S/cm. The Films were prepared by spin-coating process (1000 rpm/30 sec). The particle size and electro conductivity of bulk PEDOT film were 23 μm and 0.13 S/cm. but PEDOT-ITO composite film was observed 16 μm and 16.3 S/cm. PEDOT-ITO composite film were higher electro conductivity then bulk PEDOT film and do not changed widely with particle size with added ITO particles. The ITO particles of high charge carrier (oxygen vacancies) with forming gas can be understood by considering the insertion of PEDOT in ITO particle as a composite system in which two different type of low-dimensional electronic conductors coexist.

Figure 1 shows the SEM and TEM images of the PEDOT and the PEDOT-ITO composite. In general, the morphology of the bulk PEDOT shows that the PEDOT nanoparticles formed are uniform in size (Fig. 1 (a)). The image of the PEDOT-ITO composite shows discrete areas with high contrast, suggesting the presence of ITO (Fig. 1 (b)). The PEDOT-ITO composite particles shows that it comprises of many particles, thus joined to form an aggregate. Using HRTEM, we confirmed the morphology and size of the PEDOT-ITO composite particles. Figure 1 (c) and (d) shows the TEM images of the PEDOT-ITO composite where the black spots correspond to ITO nanoparticles embedded in the polymer matrix, and light part of image correspond to the PEDOT matrix. The matrix of polymer is amorphous and the black spots are crystalline. The ITO particles are dispersed uniformly on the polymer matrix. The formation of indium was also confirmed by EDS measurements.

X-ray Photoelectron Spectroscopy (XPS) of PEDOT-ITO composite is shown in Fig. 2. Photoelectron peaks corresponding to In, Sn, O, S and C were recorded for the composite film in the binding energy range from 0 to 1300 eV (Fig. 2 (a)). The binding energy of the

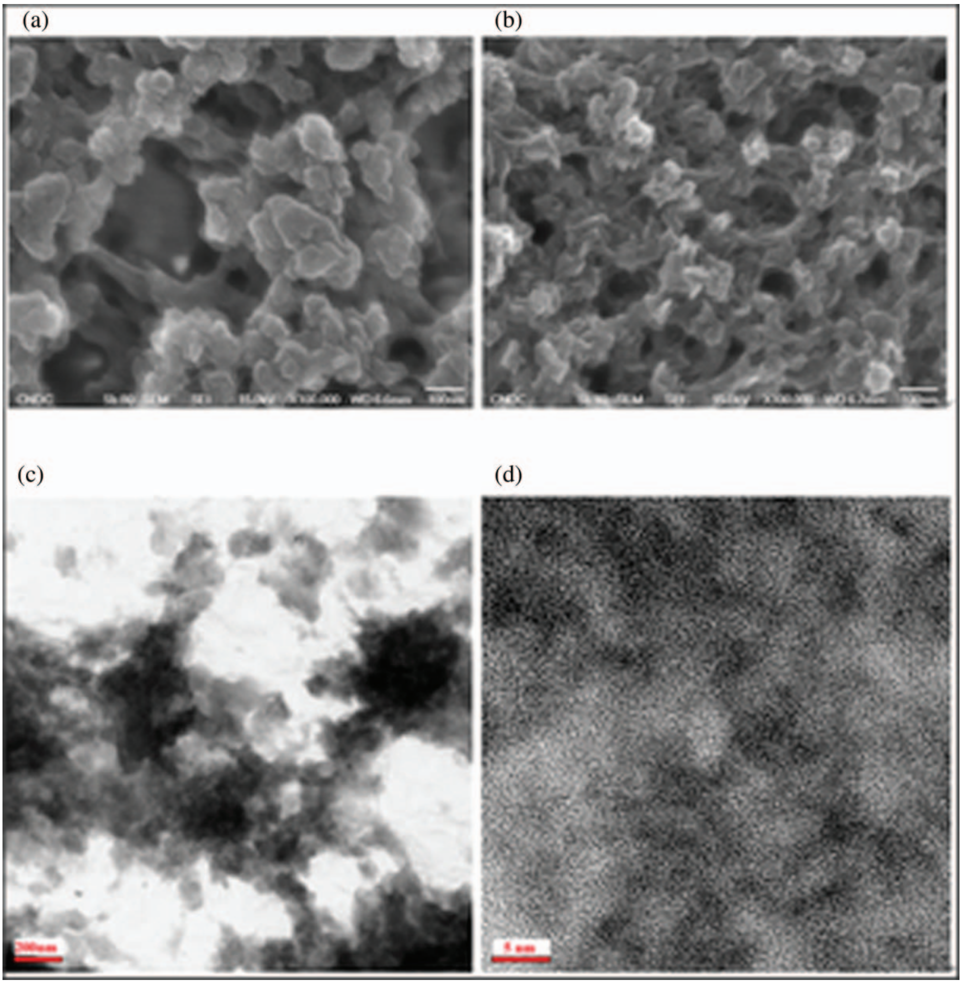

Figure 1. SEM and TEM images of PEDOT-ITO composite films. SEM image of (a) Bulk PEDOT, (b) PEDOT-ITO composite, and TEM image of (c)(d) PEDOT-ITO composite at different magnification.

O 1s and C 1s photoelectron peaks is at 534 eV and 284 eV, respectively. The In 3d and Sn 3d peaks at a binding energy from ITO is also observed at 445 eV and 487 eV on the surface of the film. The binding energy of the S 1p from PEDOT is observed at 165 eV. The XPS spectra of ITO film and PEDOT-ITO composite film for In 3d and S 2p peaks are shown in Fig. 2 (b) and (c). The binding energy of In 3d 5/2 at 445.1 eV measured from ITO film and composite film can be attributed to the In3+ bonding state from In_2O_3 [19–21]. The main peak of S 2p has been fitted with three components: neutral S (164–165.2 eV) and cationic S^+ (165.8–167.2 eV) associated with the PEDOT backbone and highly oxidized SO^{3-} (167.8–169.4 eV) due to the dopant anion [22,23].

Electrochromic Properties

The Cyclic voltammetric(CV) curves of PEDOT and PEDOT-ITO in 1.0M $LiClO_4$/ Propylene carbonate solution at the scan rate 100 mV/s are shown in Fig. 3. the

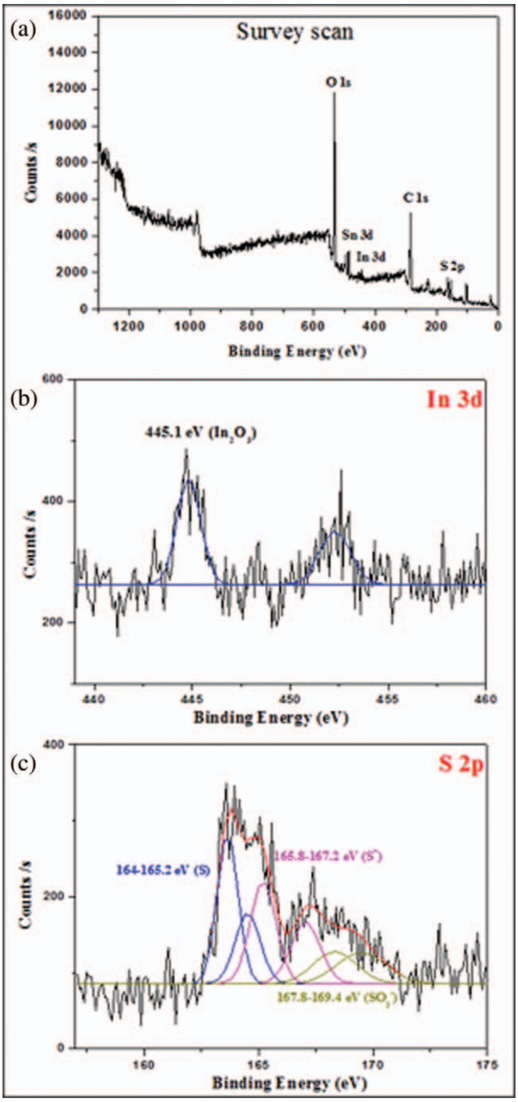

Figure 2. XPS scan spectra of PEDOT-ITO composite film deposited on glass. (a) The wide scan of PEDOT-ITO composite, XPS narrow scan (c) In 3d scan and (d) S 2p scan of PEDOT-ITO composite

oxidation and reduction peaks of PEDOT appear at −1.4234, 1.877 and −1.0765, −1.9767 V, respectively. Similarly, the oxidation and reduction peaks of PEDOT-ITO composite appear at almost same potentials, which confirm that PEDOT-ITO possesses the same electrochemical property with that of bulk PEDOT.

Figure 4 presents the electrochromic results of PEDOT-ITO ECDs in conjunction with optical images of the device in the colored and bleached state. The transmittance spectra of the PEDOT device were obtained at 300 mV increments between −3.2 V and +2.9 V. The absorption is converts from transmittance. The absorption clearly reflects the changes in the major absorption bands as a consequence of the redox state of the PEDOT. The absorption band at 560 nm is characteristic of the bleached form of PEDOT, corresponding to the p–p*

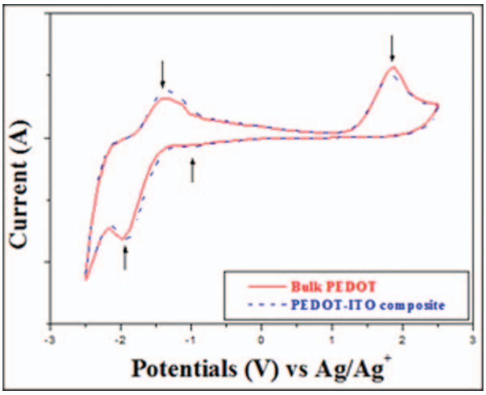

Figure 3. Cycle voltammetric curve of PEDOT and PEDOT-ITO composite in 1.0M LiClO4/PC solution scanned between −2.5 and 2.5 V (versus Ag/Ag+) at the scan rate of 100 mV/s.

transition and the absorption band at approximately 800 nm represents the colored state of PEDOT, originated from polaronic absorption. As the electrode potential is raised from −3.2 V to +2.9 V, the absorption band at 780 nm increases, with a simultaneous decrease in the absorption band intensity at 560 nm resulting from the progressive oxidation of PEDOT from its bleached state to its colored state [24,25].

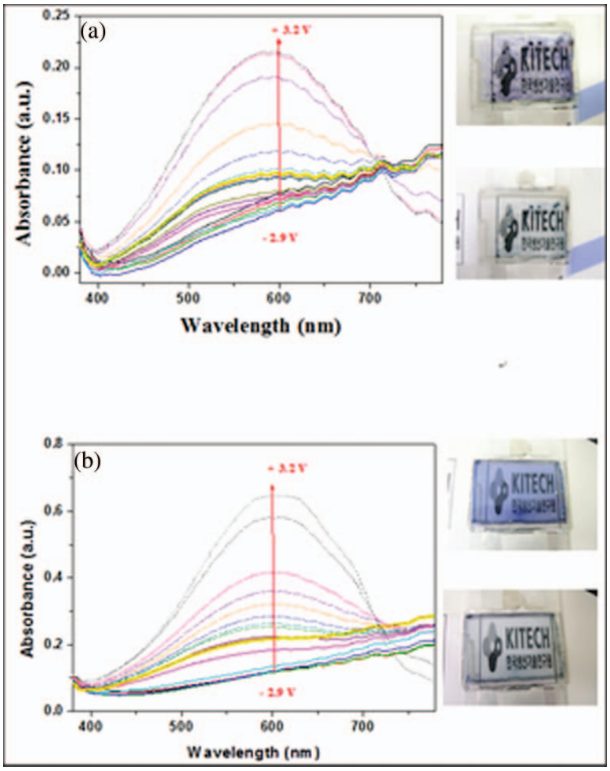

Figure 4. Electrochromic properties of (a) bulk PEDOT and (b) PEDOT-ITO composite.

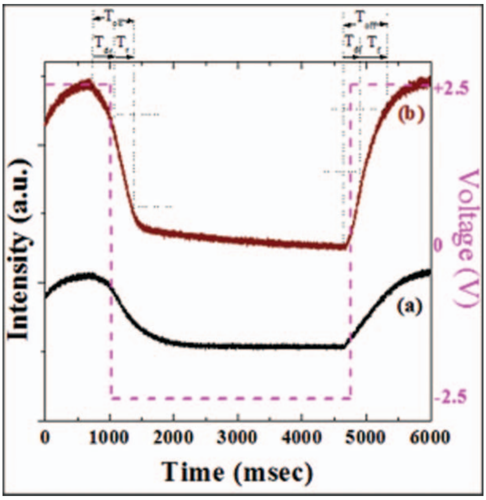

Figure 5. Switching speed of PEDOT-ITO composites ECDs. (a) Bulk PEDOT, and (b) PEDOT-ITO composite.

The wavelength dependence of coloration efficiency (CE), which is defined as the change in the optical density (ΔOD) for the charge (q) consumed per unit electrode area (A), is also shown in Fig. 4.

$$CE(\lambda) = \Delta OD(\lambda)/(q/A) = \log(Tb/Tc)\lambda/(q/A) = \Delta A\lambda/(q/A)$$

Tb and Tc are the transmittances of the device in the bleached and colored states, respectively [26]. The optical density (ΔOD), variation(of absorption value (ΔAλ), was increased with the added ITO particles. ΔA600nm of bulk PEDOT, PEDOT-ITO composite ratio 1:1 was 0.137 and 0.525 from −3.1 V to +2.9 V, respectively. PEDOT is the only species which oxidizes and reduces in the PEDOT device. The switching characteristics of the PEDOT-ITO composite film were analyzed by monitoring the change in reflectance. The studies were performed by three stepping the voltages between −2.5 and +2.5 V with a 1, 4, 1 sec, respectively. (In this case, the switching time was defined as the time required for a system to reach 90% of its full response). The reflectance dynamic response and resultant current-time response are shown in Fig. 5. The response time of PEDOT and PEDOT-ITO composite for bleaching and coloration (Ton) is found to be about 1260

Table 1. Switching speed of PEDOT-ITO ECDs[a]

Sample	Bulk PEDOT	PEDOT-ITO composite
Ton[msec]	1260	1030
Toff[msec]	907	800
Tr[msec]	790	605
Tf[msec]	690	537

[a] The time required for a system to reach 90% of its full reflection (Rise high) from ON state (Ton) and OFF state (Toff). The time required for a system to reach 10% after starting of OFF state (Decay high; Tdf) and ON state(Rise low; Tdr). Tr : Rise high—Rise low, Tf : Decay high—Decay low.

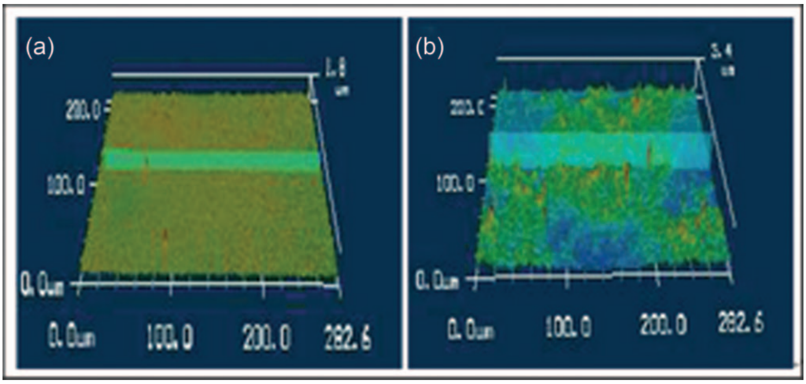

Figure 6. 3D Microscope images of PEDOT-ITO composite films. (a) Bulk PEDOT, and (b) PEDOT-ITO composite.

and 1030 ms, respectively (Table 1). The switching speed of PEDOT-ITO composite films is lower than those obtained in bulk PEDOT film. It is known that the switching speed of electrochromic device is dependent on several factors (ionic conductivity of the electrolyte, accessibility of the ions to the electroactive sites (ion diffusion in thin films), magnitude of the applied potential, film thickness, and morphology of the thin film).[27] The faster response time, i.e. relatively short switching speed of PEDOT-ITO mixed device, means the improved efficiency of the device in terms of energy utilization to be able to accomplish the same level of opaqueness in the lower voltage. Fig. 6 shows the surface of PEDOT-ITO composite film used to 3D-microscope. The roughness is increased with the adding ITO particles. The fast switching speed is mainly due to the highly electro conductivity and roughness surface of films, which benefits electrolyte penetration and provides larger surface area for charge-transfer reactions. The highly electro conductivity allows the easy diffusion of electron among them and lead to fast switching speed.

Conclusions

Indium tin oxide, high electrical conductive and transmittance material, and poly(3,4-ethylenedioxythiophene), electrochoromic material, was prepared to form nanocomposite particles with good electric properties for ECDs. SEM-EDS and XPS analysis has indicating the well formation of PEDOT-ITO composite. The optical density (ΔOD) was increased with the composite particles then PEDOT. ΔA600nm of bulk PEDOT and PEDOT-ITO composite was 0.137 and 0.525 from -3.1 V to $+2.9$ V, respectively. The switching speed of PEDOT-ITO composite film is faster than those obtained with bulk PEDOT only film due to the higher electric conductivity and better surface morphology of the films.

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