

Screen printed Sri Lankan vein graphite/polyaniline composite counter electrode for dye sensitized solar cells

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Abstract: Dye sensitized solar cells (DSSCs), described as one of the most prominent third generation solar cells, stand out in the photovoltaic category. In general, DSSCs consist of a large band gap n-type semiconductor electrode (photoanode), a sensitizer (dye), a redox electrolyte, and a counter electrode (CE). A platinized glass substrate is commonly used as the CE which acts as a catalyst for the redox reaction taking place in the cell. Further, it collects electrons from the external load and sends them to the electrolyte. Although Pt has several advantages characteristics, Pt free CE materials have drawn the attention of researchers because Pt is an extremely expensive and diminishing noble metal. According to various researches, carbonaceous materials are promising alternatives for the Pt CE. In this study we report the use of Sri Lankan vein graphite/polyaniline (SLVG/PANI) composite as the counter electrode material for DSSCs. Sri Lankan vein graphite (SLVG) is highly crystalline and is a potential low cost alternative to expensive Pt. Polyaniline was prepared by oxidative polymerization of aniline with potassium peroxydisulfate. SLVG/PANI composites were screen printed on fluorine doped tin oxide (FTO) glass substrate using carboxymethyl cellulose (CMC) as the binder. The performance of the new counter electrode was studied by analyzing the I-V characteristics of the DSSCs and the highest efficiency of 5.0% was recorded. DSSCs with new counter electrodes were further characterized using powder X-ray diffraction and Fourier Transform Infrared studies.

Keywords: Polyaniline, Sri Lankan vein graphite, Composites, Counter electrode, Dye-sensitized solar cells.

INTRODUCTION

The energy demand with the development of the quality of human life is projected to be increased by 48% from 2012 - 2040 for a period of 28 years (Cases, 2019). With the depletion of the available fossil fuels and the increment of amount of harmful greenhouse gases emitted into the atmosphere by the combustion of such fossil fuels has led scientists on focusing research upon harvesting energy from renewable energy sources such as wind, tide, geothermal and solar energy (World-nuclear.org., 2019; Anon, 2019).

In comparison with other renewable energy sources, solar energy is the most abundant, constant and least polluting energy source which can be harvested (Panwar, 2011). The amount of energy falling on the surface of the

earth from the sun is about 3×10^{24} J year⁻¹ or 10^4 times the consumption of the world. By covering 0.1% of earth's area using 10% efficient solar cells (SCs) would be adequate to meet up the global energy demand (Grätzel, 2005).

Silicon based SCs are the most popular SCs in the market which give efficiencies up to 15-17% (Lee *et al.*, 2014). Major problem with these SCs are their high manufacturing cost. To use silicon in a SC it must be purified up to 99.9999% thus making the SC expensive (Braga *et al.*, 2008). Promising solution for the latter problem was given by Grätzel (Grätzel, 2003) with the breakthrough on DSSC challenging Perovskite SCs in higher flexibility, higher transparency and less environmental pollution in addition to being low-cost (O'Regan and Grätzel, 1991, Grätzel, 2003, Deepak *et al.*, 2014). Basic components of DSSCs are, working electrode [n-type TiO₂ nanoparticle film deposited on a transparent conducting substance adsorbed with sensitizer (dye)], redox electrolyte usually I^{3-/I} (Boschloo and Hagfeldt, 2009) and counter electrode (CE) which acts as the cathode. CE of DSSC is one of the main components which catalyzes the redox reaction taking place in the cell and it collects electrons from the external load and sends them to the electrolyte. Traditionally Platinum (Pt) is widely used as counter electrode material as it gives high efficiencies. However, since Pt is extremely expensive, diminishing noble metal and decrease in catalytic activity (in long term application) when exposed to corrosive I^{3-/I} redox electrolyte encourage researchers to find alternatives for Pt electrodes (Theerthagiri *et al.*, 2015). Carbonaceous materials such as graphite, graphene, carbon nanotubes, carbon black etc. have grasped attention due to their good electrical conductivity, corrosion resistivity and low-cost (Kouhnavard *et al.*, 2015).

This study reports the use of SLVG/PANI composite as the CE material for DSSCs. Sri Lankan vein graphite is highly crystalline and is a good low-cost material with a good electrical conductivity. Conjugated polymers such as polyaniline (PANI) have been used in organic solar cells due to their excellent electrochemical, optical properties and environmental stability (Han *et al.*, 2014). Unlike all other conducting polymers, the conductivity

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of PANI can be tuned by varying the degree of oxidation (Morsi, Ebrahim and Soliman, 2012).

Emeraldine Base (EB) of PANI is composed of two benzoid units and one quinoid unit alternatively positioned in the polymer chain. Doped EB form of PANI shows electrical conductivity through delocalization of polarons formed on the conjugated polymer chain (de Albuquerque *et al.*, 2004). In this study protonated Emeraldine Base (EB) form of PANI has been used for the fabrication of electrodes, which is the highest conductive form of PANI (Bhadraet *al.*, 2009). Incorporation of additives such as graphite to PANI, has been recorded to enhance its electrical conductivity in literature (Wang *et al.*, 2011). Therefore, the SLVG/PANI composite reported in this study would be a promising alternative counter electrode material for DSSCs with enhanced conductivity, reduced cost and easy fabrication process compared to the conventional Pt counter electrode.

Many methods such as screen printing, doctor blade, thermal decomposition, electrochemical deposition etc. have been reported to fabricate different counter electrodes for DSSCs (Kumar, 2019, Gomes, 2015, Hao, 2014, Tsai, 2018). Among them, screen printing method was used for the fabrication of composite electrodes along with a binder, since the method results in uniform layer of SLVG/PANI composite on the surface of FTO glass substrates easily. Desired thickness of the active film can be obtained by repeating the printing process several times.

MATERIALS AND METHODS

Preparation of TiO₂ colloidal solution

Titanium tetraisopropoxide (TIP) (20.00 mL), acetic acid (2.50 mL) and ethanol (25.00 mL) were mixed and steam was passed through the solution. Rapid hydrolysis of TIP and the expulsion of ethanol by steam produced a

transparent TiO₂ colloids. Above TiO₂ colloids were ground with 5.00 mL of water in a mortar and autoclaved at 150 °C for three hours.

Preparation of TiO₂ spray solution

Autoclaved solution (20.00 mL), acetic acid (5.50 mL), ethanol (20.00 mL) and 5 drops of Triton X-100 were mixed and sonicated for 10 minutes.

Fabrication of TiO₂ on FTO plate

TiO₂ spray solution was sprayed to heated FTO glass plate (Temperature 160 °C) with KM-150 spray pyrolysis machine until the film thickness reached about 12 μm. This plate was sintered at 450 °C for 30 minutes in air and allowed to cool gradually. The plate was soaked in dye solution [Ruthenium-719 in acetonitrile:tert-butyl alcohol solution (1:1)] at room temperature for 12 hours.

Fabrication of the counter electrode

Preparation of polyaniline

Distilled aniline (10.00 mL) and 1 mol dm⁻³ HCl (300.0 mL) were mixed (1:30 v/v %) and then mixed with 3.00 g of K₂S₂O₈ which was dissolved in 1 mol dm⁻³ HCl (100 mL). The solution was stirred for 6 hours using a stirrer and the resultant polyaniline precipitate was filtered. Polyaniline precipitate was washed using three 100 mL portions of 0.5 mol dm⁻³ HCl followed by acetone and dried in a desiccator for 12 hours.

Preparation of SLVG/PANI composite slurry for screen printing

Different mass ratios of Sri Lankan vein graphite and polyaniline (w/w %) were mixed thoroughly in a mortar using a pestle. 10% (w/w %) carboxymethyl cellulose (CMC) was added which was dissolved in minimum

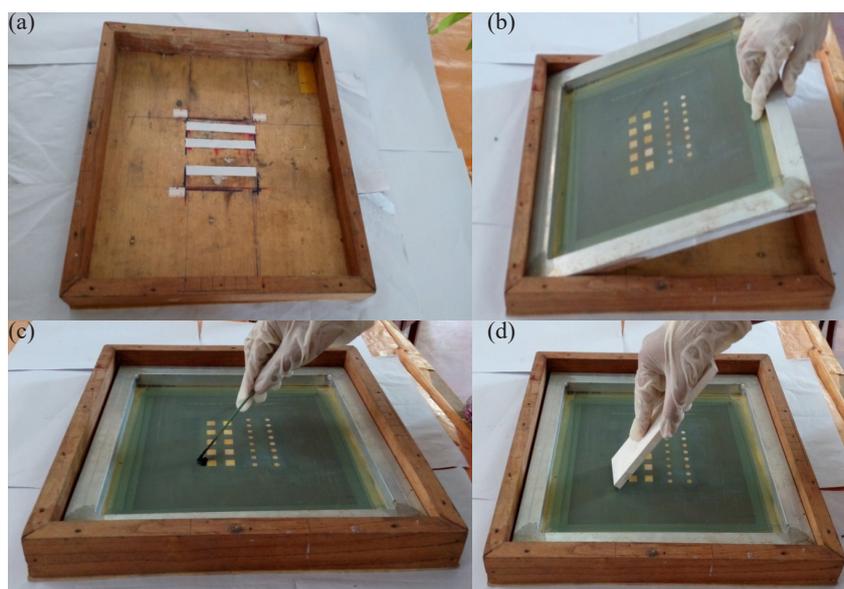


Figure 1: Steps followed in screen printing method; (a) mount FTO glass was inside the frame, (b) place the screen, (c,d) place the slurry on the screen.

amount of distilled water along with 1 drop of Triton X-100, and mixed thoroughly in the mortar, next the mixture was heated to 60 °C until a slurry was obtained.

Screen printing of SLVG/PANI composite

Screen printing was done on cleaned FTO glasses using the above prepared slurry. Screen printing process was done several times till the desired thickness of the electrode was achieved. First the FTO glass was mounted inside the frame using double sided glue tape [Figure 1(a)]. Then the screen was carefully placed on top of the FTO glass as shown in the Figure 1 (b). Next the prepared slurry was placed on the screen as shown in Figure 1 (c). The slurry was printed on FTO glass substrate as a uniform layer in the screen using a squeegee as shown in the Figure 1 (d). This process was done repeatedly until the desired thickness is obtained on the FTO glass.

Fabrication of DSSC

Few drops of electrolyte was sandwiched in between fabricated working electrode and the counter electrode using clippers and the photo voltaic measurements were taken by connecting those electrodes to the solar simulator.

Characterization of SLVG/PANI composite

Synthesized PANI and SLVG/PANI composites were characterized using Powder X-ray Diffraction (PXRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FITR).

RESULTS AND DISCUSSION

EB form of PANI, the structure is consisted of equal proportions of amines ($-NH-$) and imine ($=N-$) sites. Protonic acids used during the synthesis are capable of protonating the imine sites creating a bipolaron (Stafström *et al.*, 1987). The resultant bipolaron then undergoes further rearrangements to form the delocalized polaron lattice enabling the conductivity of PANI. The resulting emeraldine salt (ES) has conductivity on a semiconductor level of the order of 100 S cm^{-1} (Bhadra *et al.*, 2009). A suitable binder for the screen printing process was selected using the trial and error method. The binders tested for the screen printing process were carboxymethylcellulose (CMC) and poly(ethylene glycol) (PEG). PEG did not show promising characteristics as a binder since the

counter electrode materials including PANI, SLVG and PANI/SLVG composites were tend to peel off with PEG upon introducing the liquid electrolyte. This could have been overcome by employing high temperature, however, sintering was not done during the fabrication, since there is a possibility of polymer degradation at high temperatures. On the other hand, CMC showed promising binding capabilities between the developed counter electrode materials and FTO glass substrate even at room temperature. The film was stable upon introducing the liquid electrolyte. CMC could increase the binding capability by acting as an intermediate between PANI/SLVG and FTO substrate. The strong binding between CMC and both the counter electrode material (PANI/SLVG) and FTO glass substrate can be expected through hydrogen bonding because of the presence of many hydroxyl groups on CMC, N-H groups on PANI and oxygen atoms on FTO coating (SnO_2). It has been reported in literature that the oxygen atoms in hydroxyl groups in CMC can strongly interact with amine groups in polyaniline forcing its molecules to align along (Jayanty *et al.*, 2015). In addition to the strong binding capability, due to aligning of the PANI molecules, it is stated that CMC leads to a more ordered chain which results in better conductivity, since these arrangement of molecules flatten the structure of molecule in the region of delocalization occurs. However, upon increasing the CMC amount, the conductivity of the counter electrode exponentially decreased due to insulating properties of the binder CMC.

Characterization of SLVG/PANI composite by PXRD analysis

When considering the diffraction pattern of pure SLVG which is shown in Figure 2 (b), two distinguishable peaks at $2\theta = 26.52^\circ$ and $2\theta = 54.61^\circ$ are corresponding to $(0\ 0\ 2)$ and $(1\ 1\ 0)$ planes of graphite respectively. Since PANI has an amorphous character, distinguishable peaks are not observed in the diffraction pattern which is shown in Figure 2 (a), only a broad peak centered around 30° was observed. The peaks of $2\theta = 26.52^\circ$ and $2\theta = 54.61^\circ$ of graphite are clearly visible in the diffraction pattern of SLVG/PANI composite which is shown in Figure 3.2 (c). Although the relative intensities of peaks of graphite in the SLVG/PANI composite are low compared with that of the neat graphite upon composite formation, the presence of the peaks

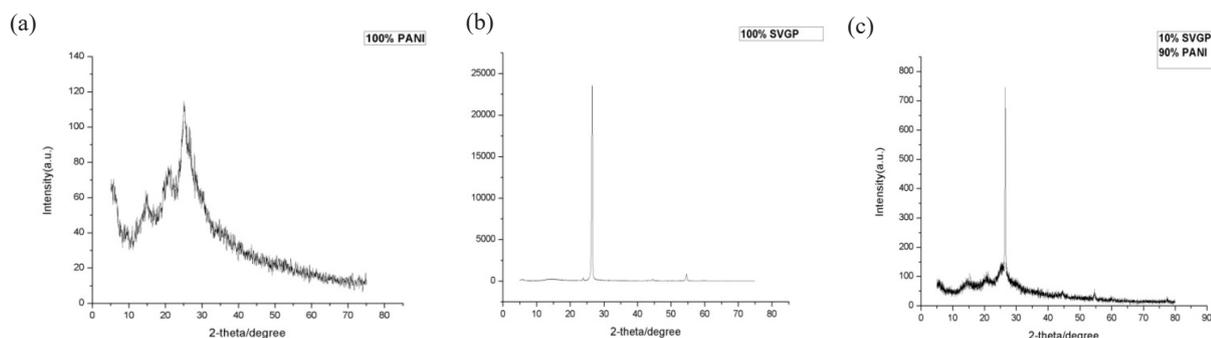


Figure 2: PXRD patterns of (a) 100% PANI (b) 100% SLVG (c) 10%/90% SLVG/PANI composite

of SLVG confirms that SLVG has retained its structure even though it is dispersed in PANI. Further, broad peaks observed in pure PANI were also observed in SLVG/PANI composite indicating the formation of composite.

Characterization of SLVG/PANI composite by SEM Analysis

SEM analysis was carried out on pure PANI, pure SLVG and SLVG/PANI (10%/90%) composite which were screen printed on FTO glasses using CMC in order to study the variation of the morphology of the counter electrode surface. The composition 10%/90% SLVG/PANI was selected as this composition gave the best efficiency of 5.0% in DSSCs fabricated (Table 1). According to the above SEM images the plate like surface morphology of graphite [Figure 3 (b)] has been transformed into a porous structure as in the pure PANI [Figure 3 (a)] upon the composite [Figure 3 (c)] formation by indicating the distribution of SLVG in PANI during the composite preparation. Furthermore, catalytic activity of the counter electrode can be explained by the high surface area of the composite which is due to the porous structure given by the composite. According to SEM images, the average particle size of SLVG and PANI are 2.05 μm and 1.58 μm respectively, while the particle size has been reduced to 0.95 μm upon the preparation of the PANI/SLVG composite. This reflects that the reduction in particle size also enables a high surface area for the adsorption of the liquid electrolyte in the counter electrode surface.

FT-IR Analysis of SLVG/PANI composites

FT-IR analysis was carried out for different ratios of

SLVG/PANI composites in order to find the functional groups present in the composites and the spectra are shown in Figure 4. Further, FT-IR analysis on pure PANI was used to confirm the formation of the PANI by chemical polymerization method. When considering FT-IR spectrum of the 100% PANI it clearly indicates two characteristic peaks of PANI around at 3400 cm^{-1} and 1200 cm^{-1} . Peak around 3400 cm^{-1} is due to the N-H stretching of -NH-functional group while peak around 1195 cm^{-1} may refer to C-N stretching of secondary amine. The peaks at 1512 cm^{-1} and 1624 cm^{-1} correspond to the benzenoid and quinoid vibrations of PANI (Nikzad *et al.*, 2009). From the FT-IR spectrum of 100% PANI, it can be predicted that PANI has been formed. Those characteristic peaks discussed above are depleted in intensity upon increasing the graphite ratio, indicating that the composition of the composites has been varied as intended.

Photo current-voltage characteristics (I-V curves)

I-V curves were plotted for each measurement taken for the fabricated solar cells with I^-/I_3^- redox mediator and their performances were investigated. Pt electrode was used as the standard counter electrode for the comparison with the fabricated SLVG/PANI counter electrode as a substitute for the Pt electrode.

The current-voltage (I-V) characteristics of the cells at AM 1.5 (100 mW cm^{-2}) simulated sunlight irradiation with an active area of 1.0 cm^2 were recorded with a calibrated solar-cell evaluation system (PECCELL PEC-L01) solar simulator.

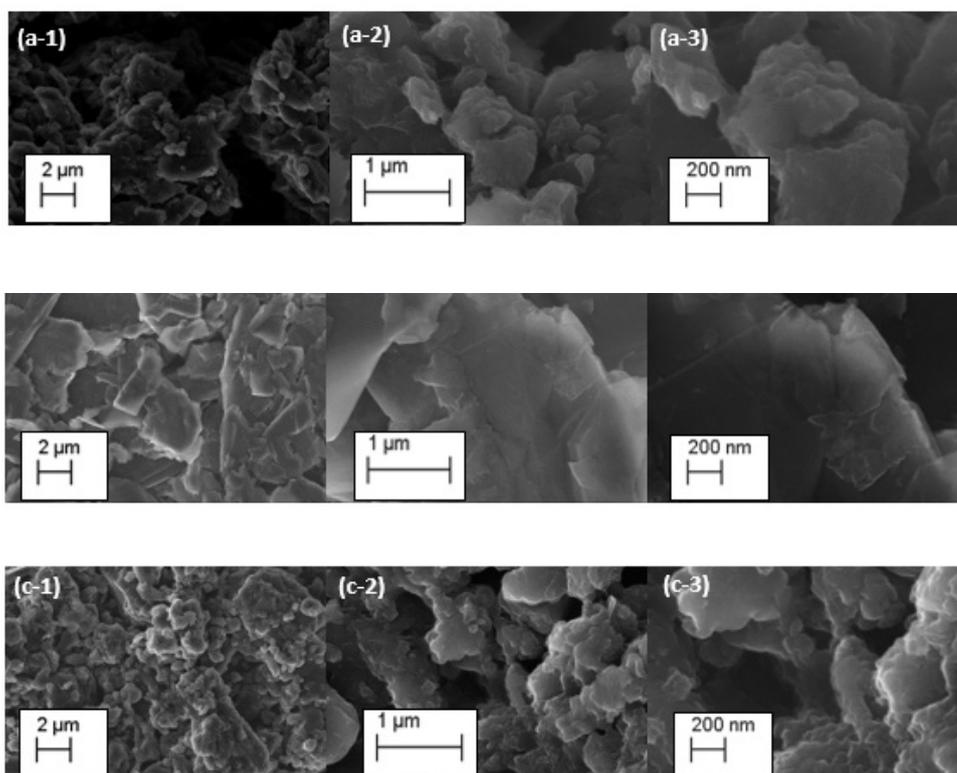


Figure 3: SEM images of (a) 100% PANI (b) 100% SLVG (c) 10%/90% SLVG/PANI composite.

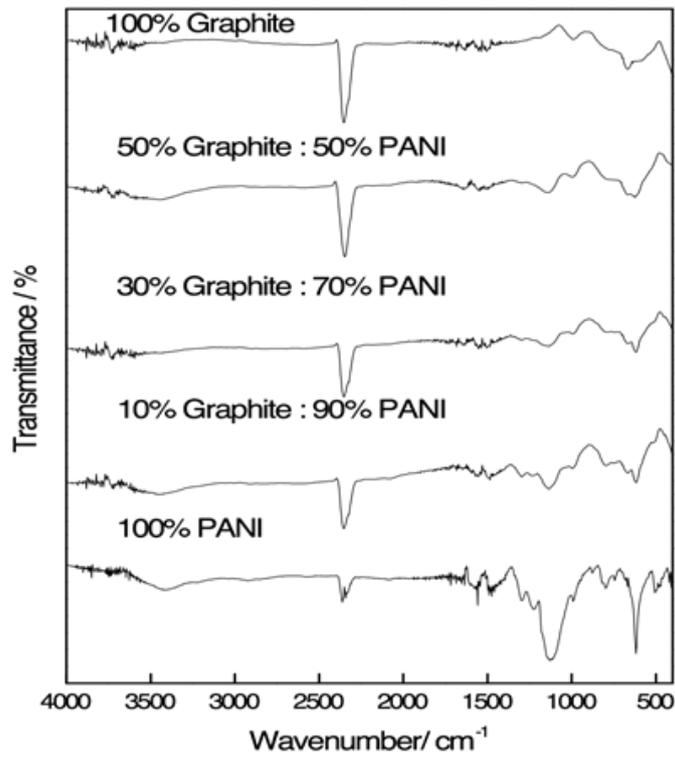


Figure 4: FT-IR spectra of different ratios of SLVG/PANI composites.

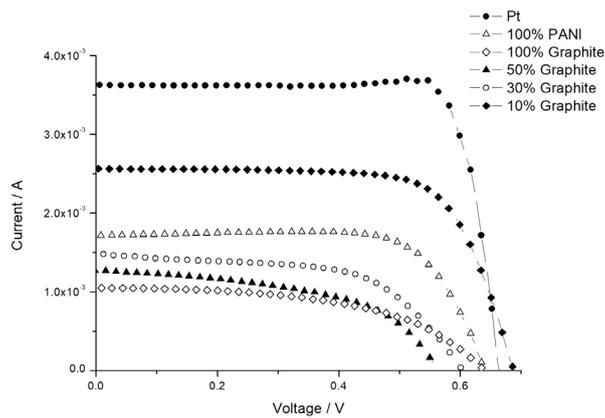


Figure 5: Photocurrent-voltage characteristics with different Graphite/PANI ratios and standard Pt electrode.

Table 1: Photocurrent-voltage characteristics with different Graphite:PANI ratios compared to Pt counter.

Counter Electrode	V_{oc} mV	J_{sc} mA cm ⁻²	FF/ %	η / %
Pt	663	14.5	84.0	8.1
0:100 (SLVG:PANI)	641	6.8	74.0	3.2
10:90 (SLVG:PANI)	688	10.2	72.0	5.0
30:70 (SLVG:PANI)	605	5.9	58.0	2.1
50:50 (SLVG:PANI)	563	5.1	52.0	1.5
100:0 (SLVG:PANI)	638	4.2	53.0	1.4

* The maximum values are reported out of five cells tested from each type

As can be seen from Figure 5 and Table 1, the maximum efficiency was observed with the counter electrode with SLVG/PANI 10:90 (w/w %) composite. Efficiency of the DSSC with 10:90 composite increases compared to the DSSC with pure PANI because of the high electrochemical activity of SLVG. According to previous research done on graphite/polyaniline composites, the conductivity of the composite increases upon increasing the amount of graphite in the composite (Wang *et al.*, 2011). However, the results of this study indicate that the efficiency of the DSSC decreases when the graphite content is increased. This may be because of the disordered transmission pathways of electrons as the SLVG content increases beyond the optimum value.

CONCLUSIONS

In conclusion, SLVG/PANI composite can be considered as a promising material to be used as a counter electrode in DSSC. The composite can be successfully prepared by blending SLVG and PANI synthesized by chemical oxidative polymerization. The counter electrode fabricated on FTO glass substrate by screen printing method with 1:9 (w/w) ratio of SLVG:PANI showed a maximum efficiency of 5.0% with 688 mV open circuit voltage, 10.2 mA cm⁻² current density and 72.0 fill factor.

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