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TAILORED Mn-DOPED CuS NANOPARTICLES: SYNTHESIS, STRUCTURAL, OPTICAL AND THERMAL CHARACTERIZATION

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Abstract: Pure and Manganese(Mn) doped Covellite (CuS) nanoparticles were synthesized by chemical precipitation method.The XRD analysis confirmed the formation of hexagonal phase for both pure and Mn doped CuS nanoparticles with average crystallite sizes 3.8 nm and 5.7 nm respectively .The Energy Dispersive Spectra(EDS) Analysis confirmed the elemental composition for pure and Mn doped CuS.Surface Morphology Analysis by Field Emission Scanning Electron Microscopy (FE-SEM) showed the formation of irregular nano flakes.The optical properties were studied by UV-visible Diffuse Reflectance Spectroscopy.Thermal behaviour of pure and doped covellite nanoparticles were analyzed through TGA-DSC measurements.

***Key Words* – XRD, Covellite, nanoparticles, FE-SEM, EDS.**

1.**Introduction**

Copper sulfide (Cu_xS_y) is an important class of binary inorganic compound consisting of copper and sulfur, known for exhibiting a variety of stoichiometric phases such as chalcocite (Cu_2S), djurleite ($Cu_{1.95}S$), digenite ($Cu_{1.8}S$), anilite ($Cu_{1.75}S$), and covellite (CuS) [1]. Among these, covellite (CuS) stands out due to its unique structural and electronic characteristics, placing it at the forefront of nanomaterials research. As a prominent member of the metal chalcogenide family, copper sulfide has gained substantial attention for its remarkable physical and chemical properties, including its metallic conductivity, tunable bandgap, and intriguing superconducting behavior, particularly its ability to become superconducting below 1.6 K [2-5].

At the nanoscale, CuS exhibits enhanced and distinct properties compared to its bulk counterpart, owing to quantum confinement effects, high surface-to-volume ratio, and morphological diversity. These nanoscale materials demonstrate promising performance in various applications such as photocatalysis, energy storage, optoelectronics, and chemical sensing[4-7]. In particular, covellite (CuS), a naturally p-type semiconductor, has been actively explored for solar energy conversion, photocatalytic degradation of pollutants, biosensing, and use in optoelectronic devices. Furthermore, CuS has also been studied as a cathode material in lithium-ion batteries due to its layered structure and good electrochemical stability [7-9].

The physical and chemical properties of copper sulfide nanostructures are greatly influenced by their size, shape, and morphology. Different morphologies, such as nanowires, nanoplates, nanorods, hollow spheres, nanotubes, nanobelts, flower-like structures, and hierarchical micro/nanoarchitectures, have been synthesized through various chemical and physical routes [3-6]]. For instance, nanowires have been prepared via surfactant-assisted methods, microemulsion techniques, and hydrothermal synthesis, while flower-like nanostructures were obtained through solvothermal processes. Hollow nanospheres were synthesized using hydrothermal, sonochemical, and solvothermal approaches. Additionally, template-assisted and wet chemical routes have been used to obtain nanorods and nanotubes, respectively, while complex hierarchical morphologies have been developed using modified solvothermal or chemical vapor deposition methods [10-12].

In the present study, we focus on the synthesis and characterization of undoped and manganese (Mn)-doped covellite (CuS) nanoparticles. Manganese, a transition metal with multiple oxidation states, is known to modulate the electronic and structural properties of host lattices, potentially enhancing the functionality of CuS nanoparticles. Here, a simple chemical precipitation method was employed for the synthesis, owing to its low cost, ease of processing, and scalability[13]. The as-prepared nanoparticles were subjected to extensive physicochemical characterizations to understand the impact of Mn doping on their structural, optical, morphological, elemental, and thermal properties.

The characterization techniques employed include Powder X-Ray Diffraction (XRD) for crystallographic analysis, UV-Visible Diffuse Reflectance Spectroscopy (UV-DRS) for optical band gap estimation, Energy Dispersive Spectroscopy (EDS) coupled with Field Emission Scanning Electron Microscopy (FE-SEM) for compositional and morphological analysis, and Thermogravimetric-Differential Scanning Calorimetry (TGA-DSC) for evaluating thermal stability and phase transition behavior. This comprehensive investigation provides insight into the dopant-induced modifications and their implications on the performance of CuS nanoparticles in advanced applications.

2. MATERIALS AND METHODS:

Copper chloride dihydrate ($CuCl_2 2H_2O$), thiourea,Manganese Chloride tetrahydrate ($MnCl_2$ $4H_2O$)and sodium hydroxide (NaOH) pellets were used for sample preparation. All chemicals were analytical grade and purchased from Merck, India. Deionized water was used throughout the synthesis.

For pure CuS nanoparticles, 0.2 M copper chloride solution was added to 0.4 M thiourea solution under vigorous stirring.To the white precipitate formed, 0.4 M NaOH solution was added drop wise until the pH attains 9, which was verified using pH indicator strips. After continuing stirring for 10-15 minutes, the mixture was allowed to stand for 2-3 hours in air atmosphere. The mixture slowly turned to greenish black copper sulfide nanoparticles. Then the product was washed with de-ionized water and absolute ethanol for several times using centrifuge and then dried in vacuum oven and ground well for further characterizations. For Mn doped covellite nanoparticles, 2 wt% Manganese Chloride is solution is mixed with $CuCl_2$ solution and the above procedure is repeated.

Synthesis procedure at a glance:

Prepare 0.2 M $CuCl_2$ solution

↓

Stirred it well for 5 minutes using a
magnetic stirrer to have uniform concentration
throughout the solution.

↓

Add 0.4 M thiourea solution taken in a burette
drop wise to this under vigorous stirring.

↓

Immediate white precipitate is formed and
stirring can continue for another 5 minutes.

↓

After this 0.4 M NaOH solution is added drop wise to this
drop mixture until the pH of the solution attains 9,
this was verified using pH indication strips.

↓

The mixture is allowed to stand for 2-3 hrs in
the air atmosphere. It slowly turned to brown and
then black CuS nanoparticles.

↓

The product is washed with de-ionized water and ethanol several times using a centrifuge machine at 4000 rpm

↓

Dried it in a vacuum oven at 100°C for 1 hr.
Grind it well using a mortar and pestle to get fine particles.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

The XRD pattern of pure and Mn doped CuS nanostructures is shown in Figure 1. All the observed peaks can be indexed to hexagonal CuS structure as compared to the ICDD data file(PDF-00-006-0464)[14]. The diffraction peaks appear at 29.29^0, 31.44º, 32.70º, 47.92º, 52.71^0,and 58.38º and can be indexed to the lattice planes(102), (103), (006), (110),(108)and (116) which confirms the formation of CuS nanoparticles. No signifying peak related to Mn doping is observed,but the peaks are slightly shifted compared to pure one.Both samples exhibit broadened peaks revealing the nanocrystalline nature.

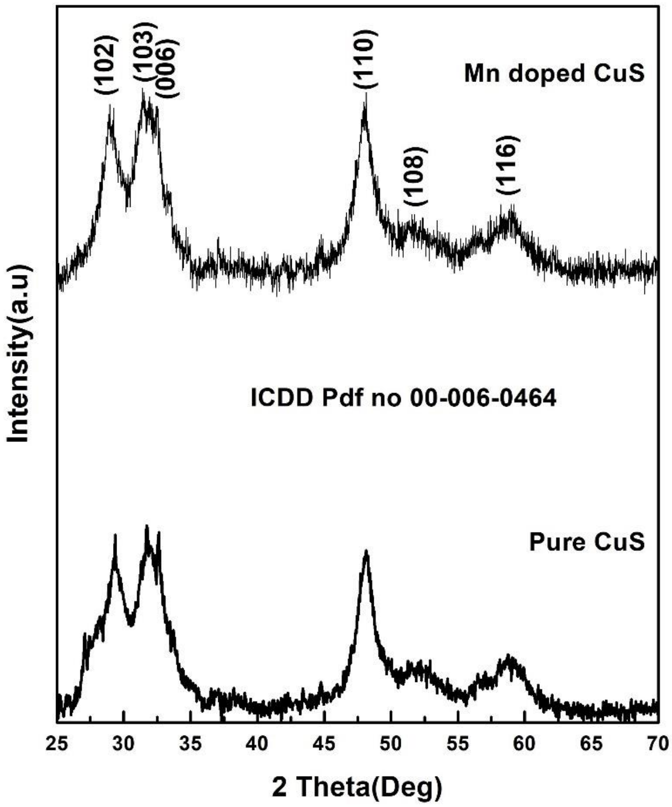

Fig1: XRD spectrum of pure and Mn doped CuS nanoparticles

The average crystallite size of pure and doped CuS nanoparticles was computed from the XRD pattern through the Debye - Scherrer equation[15],

$$D = \frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

Where D is the crystallite size ,λ is the wavelength of X ray source (λ=1.54 A^{o}) θ is the diffraction angle and β is the full width at half maximum (FWHM)in radian. The average crystallite sizes from the XRD analysis using Scherrer formula is found to be 3.80 nm and 5.7 nm for pure and doped Covellite nanoparticles respectively.

3.2 UV-VIS DRS Analysis

To characterize the optical properties of the CuS nanoparticles, UV-VIS spectrum analysis was performed in the diffuse reflectance mode. Figure 2 shows the UV-VIS absorption spectrum of pure and Mn doped CuS samples. From the absorption spectra, it is clear that the both CuS nanoparticles showed 2 broad absorptions, one in the UV-VIS region and other extending in the near IR region with a broad shoulder around 620 nm[16]. The obtained UV-VIS spectrum is slightly blue shifted due to quantum confinement effect as compared to bulk. The broad band extending in the near IR region is a characteristics of covellite (CuS)[17-19].

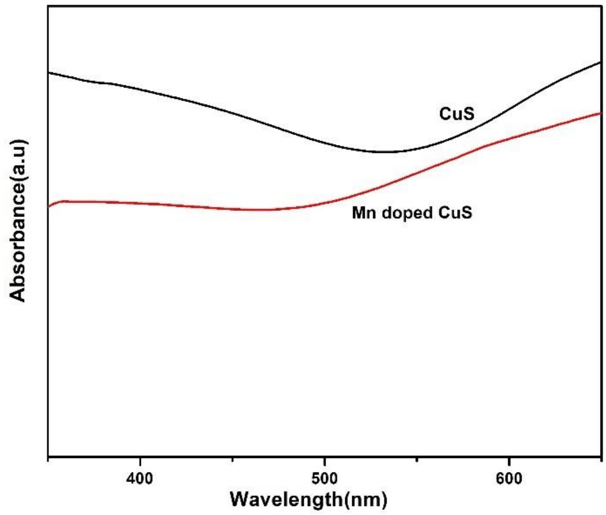

Fig 2: UV-VIS absorption spectrum of pure and Mn doped CuS

The reflectance spectrum was analyzed by Kubelka –Munk formalism [20-23] to obtain equivalent absorption coefficient (F(R)) using the relation :

$$F(R) = \frac{K}{S} \quad (2)$$

$$F(R) = \frac{(1-R)^2}{2R} \quad (3)$$

where K is the molar absorption coefficient,$K = (1-R)^2$ (4)

S is the scattering factor,

S=2R, (5)

where R is the reflectance of the sample.

The optical band gap of CuS was calculated from F(R) using the following equation associated with the direct transition:

$$F(R)h\nu = A(h\nu - Eg)^{1/2} \quad (6)$$

where hν is the photon energy A is a constant E_g is the band gap, $F(R)$is the Kubelka-Munk function.

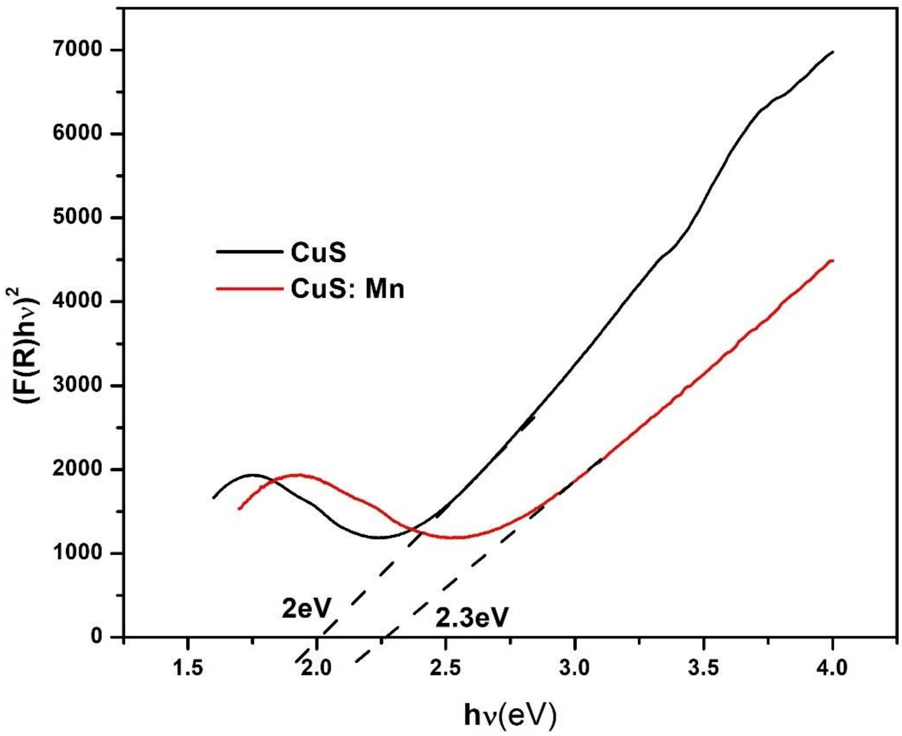

Fig 3: K-M plots for pure and Mn doped CuS

A plot of$(F(R)h\nu)^2$ versus hν is shown in figure 3.The extrapolated linear portion of the plot to photon energy axis gives the Eg value of pure CuS and Mn doped CuS as 2.1 eV and 2.3 eV respectively which are relatively larger than the reported band gap value of bulk CuS (1.85eV), indicating small size effect. [24].

3.3 Elemental Study

The elemental examination of bare and Mn doped CuS samples was carried out through EDS.Figure 4(a) and (b) depicts the EDS spectra of pure and 2 wt% Mn doped CuS samples respectively.The obtained spectra predict that solely anticipated elements Cu,Mn and S are present in the CuS/Mn doped samples.

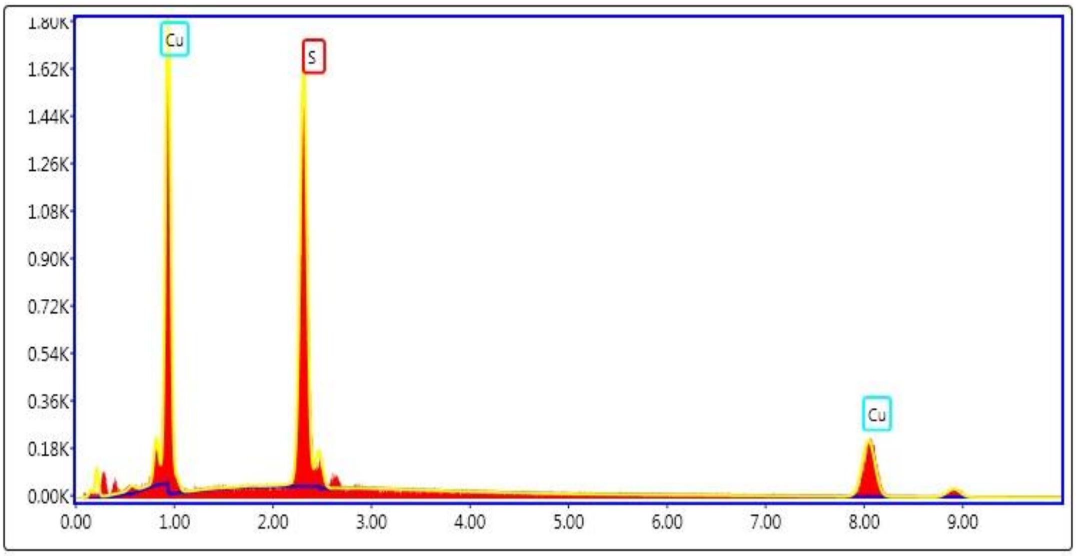

Fig 4(a): EDS spectrum of pure CuS

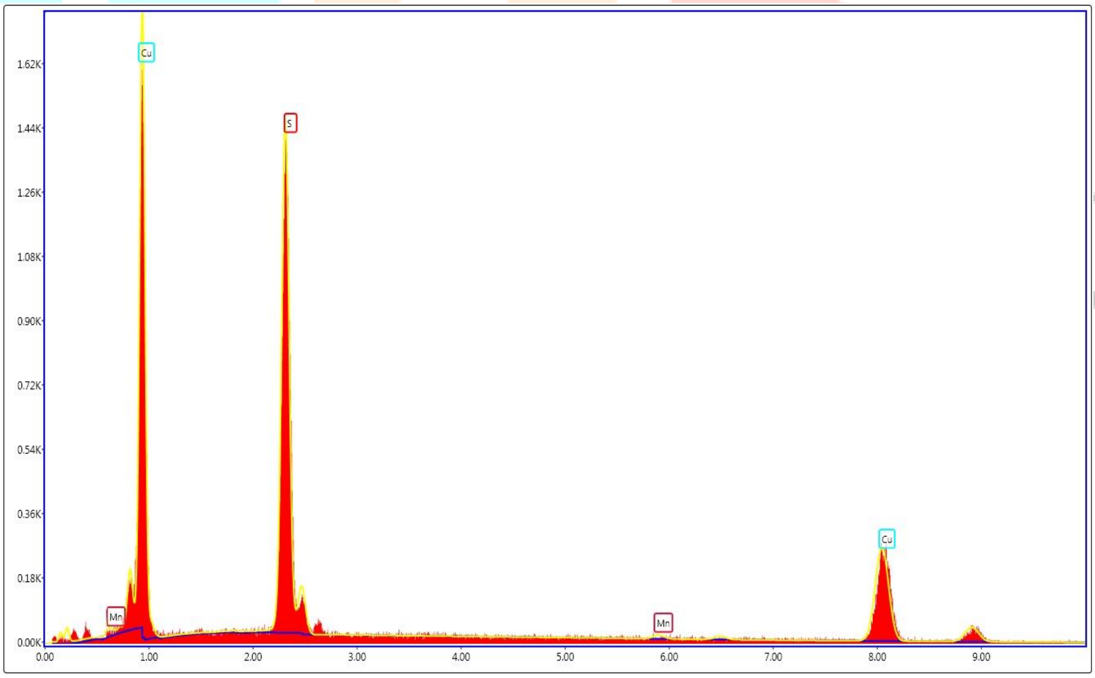

Fig 4(b): EDS spectra of Mn doped CuS

3.4 Morphological Analysis by FE-SEM

The surface morphology and homogeneity of undoped and Mn doped CuS nano powder studied through FE-SEM. Fig 5(a) shows that the undoped CuS nanoparticles are flake-like in shape and are distributed uniformly. Fig 5(b) shows that the Mn doped CuS nanoparticles also have flake like morphology[25], but agglomeration is happened. The change in the morphology is due to Mn ions replacing Cu ions in CuS nanoparticles. Presence of Mn impurity increase the nucleation and growth rate of CuS nanoflakes.Thus, doping affects the morphology of nanoparticles[26].

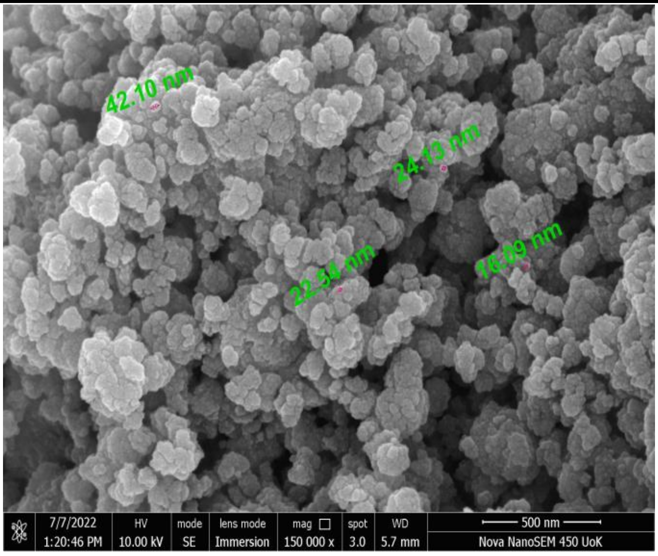

Fig 5(a): FE-SEM image of pure CuS

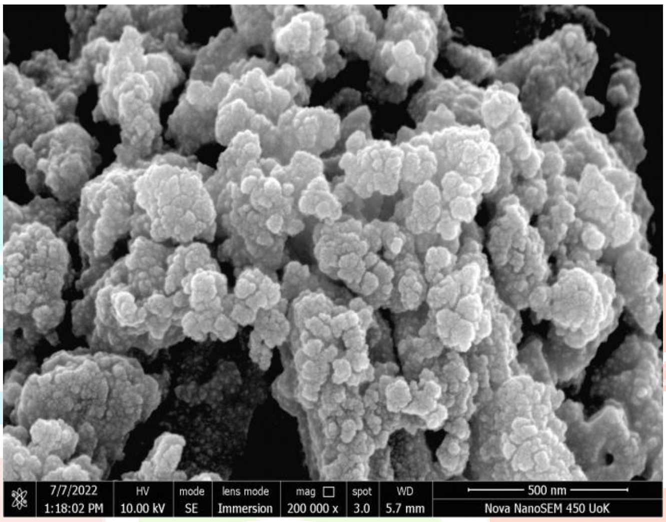

Fig 5(b): FE-SEM image of Mn doped CuS

3.5 Thermal Analysis

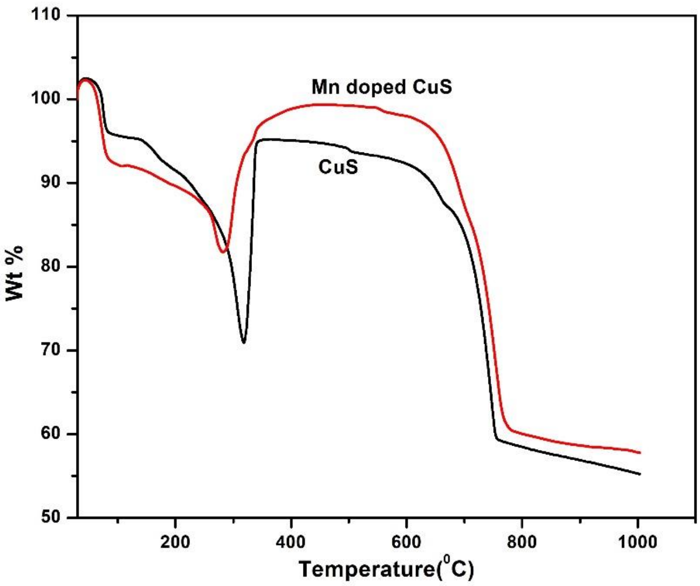

Fig 6:TGA analysis of pure and Mn doped CuS

Thermal analysis of CuS nanospheres indicates a multistage decomposition pathway extending up to 1008 °C. An initial, slight weight reduction is observed between 61–82 °C, attributed to the evaporation of ethanol. The next notable mass loss between 144–179 °C is likely due to the breakdown of residual thiourea. A further decline in mass from 179–319 °C corresponds to the partial transformation of covellite (CuS) into digenite (Cu_9S_5). At around 319 °C, a sharp increase in mass is recorded, suggesting the formation of the $CuSO_4$ (chalcanthite) phase. Following this, a significant mass loss beyond 500 °C is associated with the thermal decomposition of $CuSO_4$ into CuO (copper oxide)[27,28]. Compared to pure CuS, the Mn-doped CuS samples show lower overall weight loss, reflecting enhanced thermal stability.

4. Conclusion

Pure and Mn doped CuS nanoparticles were synthesized by chemical precipitation method.The samples were characterized by XRD,UV-DRS,EDS, FE-SEM and TGA. Average crystallite size is found to increase as a result of doping with Mn. Increase in band gap values with Mn doping was observed from UV-DRS studies. Nano flake like morphology and elemental compositions were obtained from FE-SEM and EDS spectra respectively.Mn doping results slight agglomeration for the nanoparticles.TGA analysis revealed that pure and doped samples followed a multistep decomposition of CuS to CuO through compounds digenite and chalcanthite.The thermal decomposition of Mn doped CuS nanoparticles is found to be less compared to undoped CuS.

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