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Synthesis and Characterization of Blue Light Emitting Glassy Cadmium Selenite Nanoparticles

[1]S. Nima Jessieba Daniel, [2]N. Joseph John

1Department of Physics, Govt. Arts College, Udhagamandalam, Tamilnadu, India.

2Department of Physics, Kamarajar Govt. Arts College, Surandai, Tamilnadu, India.

Abstract: White transparent cadmium selenite nanoparticles for optoelectronic devices were prepared from aqueous solution of cadmium acetate dihydrate and sodium selenite by facile microwave assisted hydrothermal method. The average size of the prepared $CdSeO_3$ nanocrystallite is found to be 20nm. XRD, EDX and FTIR studies confirm the structure and composition of $CdSeO_3$ nanoparticles. The optical band gap energy of the material was estimated to be 4.8eV. Uniform transmittance is observed throughout ultra violet and visible region. PL spectrum of $CdSeO_3$ exhibits a sharp blue emission peak at 439nm. TGA shows that the prepared $CdSeO_3$ nanoparticles are very stable up to 655^{0}C.

Index Terms - cadmium selenite, luminophores, microwave, monoclinic, nanoparticles, semiconductor, transparent.

I. INTRODUCTION

Nanoparticles are small-sized particles exhibit unique size and shape-dependent optical properties due to the quantum confinement effects because of its large surface to volume ratio and thus find a wide range of applications in optoelectronic devices, photo catalysis, solar energy conversion and biological imaging and labeling[1,2,3]. These nanoparticles having structural arrangements similar to bulk materials and very different electronic, optical, magnetic and thermal properties[4] are usually composed of combination of elements from groups II–VI, III–V, or IV–VI of the periodic table[5]. Among the family of II–VI semiconductors, ZnSe, ZnS, CdS, ZnO, CdSe are the most extensively studied candidates because of their electronic and optical properties for optoelectronic applications[6, 7,8]. In particular, CdSe quantum dot (QD) is an important II–VI semiconductor having a wide optical band gap[9]showing unique and fascinating optical properties are excellent emitters which can be tuned in the visible spectral region[10], making it a very attractive material for optical applications such as photovoltaic devices, light emitting diodes, laser diodes, biological imaging and bio diagnostics. Compared with the conventional dyes, CdSe-based colloidal nanoparticles have very good photo stability, narrow emission without cross coupling of signals and numerous colors excited by a single source allowing for multiplex detection[9]. Cadmium selenite is an oxide of compound semiconductor cadmium selenide. Oxy chalcogenides optically transparent in the visible light region, although simple chalcogenides are transparent only in the IR region[11]. Transparent conducting oxides are electrically conductive materials with comparably low absorption of light[12] which are useful in optoelectronic devices. Most selenites are used as pigments in ceramics and glass industries, as luminophore,[13, 14].

Cadmium forms several selenites, like other transition metals. Cadmium selenite exists in two polymorphic forms, orthorhombic $CdSeO_3$ (oP20) and monoclinic $CdSeO_3$ (mP40). In the orthorhombic form, the coordination polyhedron around cadmium is an octahedron and the CdO_6 octahedra share only corners. In the monoclinic form, the coordination polyhedron around cadmium is a trigonal prism, and CdO_6 trigonal prisms and SeO_3 tetrahedra share common edges[15]. $CdSeO_3$ melts at 943 K[14]. Cadmium selenite nanoparticles are transparent fluorescent n-type material having wide direct bandgap and high photosensitivity. Materials which are transparent to visible light are useful to develop transparent electronics, UV optoelectronics, and integrated sensors[16]. In this paper, we present the systematic study of synthesis, structural, optical and thermal characterization of transparent monoclinic $CdSeO_3$ nanoparticles for optoelectronic devices.

In recent times, a variety of techniques have been developed to synthesize nanoparticles. Methods we use nowadays to prepare nanoparticles are complicated, require specific equipment and produce small amounts of nanomaterials. The objective of this work is to combine both advantages of the tedious solvothermal synthesis and the rapid and efficient microwave heating for the fast preparation of nanomaterials. High-frequency electromagnetic radiation (2.45 GHz) that interacts with the dipole moment of the molecules produces necessary heat. Water has a very high dipole moment that makes it one of the best solvents for microwave-assisted reactions [17]. In this work transparent, luminescent $CdSeO_3$ nanoparticles were synthesized by microwave-assisted hydrothermal methods.

2 EXPERIMENTAL

2.1 Synthesis of $CdSeO_3$

Cadmium selenite nanoparticles (NP) were fabricated from an aqueous solution of cadmium acetate dihydrate and sodium selenite. Cadmium acetate dihydrate and sodium selenite in the molar ratio 2:1 were mixed with distilled water under fast stirring using a magnetic stirrer. All the chemicals were analytical grade and used without any further purification. Then the prepared solution is irradiated with microwave till the water gets evaporated in a microwave oven operating at a power of 800 W and frequency 2450 MHz. The obtained colloidal precipitate is washed several times with distilled water and acetone and then filtered. Then the obtained nanoparticles were collected and dried. The prepared nanoparticles are annealed for one hour at 100^0C to improve ordering[3],[18]. The total product mass was measured to find the yield percentage.

2.2 Characterization

The powder XRD pattern for the as prepared sample was done using Bruker AXS D8 Advance diffractometer with Copper target and Cu-Kα (λ=1.5406 Å) radiation. Energy Dispersive X-ray EDX analysis was done using Oxford XMX N EDX analyser. A scanning electron microscope (SEM) was employed for morphological study using Hitachi S-3400 N operated at 3kV. FTIR spectrum in the range of 400-4000 cm-1 was recorded by means of a Thermo Nicolet, model 6700 Fourier transform infrared spectrometer. The UV-Vis absorption spectral studies were carried out using VARIAN 5000 UV-Vis-NIR Spectrophotometer in the spectral region of 200 and 800 nm. The photoluminescence spectra of the samples were recorded with a VARIAN ECLIPSE Fluorescence Spectrophotometer. Thermogravimetric (TG) and Differential thermogravimetric analysis (DTG) for the air-dried sample was performed on a Q600 SDT Thermal analyser at a heating rate of 20 °C min^{-1}

3 Results and Discussion

3.1 Powder X-Ray Diffraction (XRD) Analysis

Fig.1 shows the XRD diffractogram of the as prepared $CdSeO_3$ nanoparticles. The sharp and narrow peaks observed in the XRD pattern reveals that the nanoparticles are highly crystalline. The peak positions and intensities were matching well with the standard data for monoclinic crystals of $CdSeO_3$ (PDF 01-082-1208), with the space group P21/c(14) having unit cell parameters a= 5.70840Aº, b=12.82830 Aº, c=8.58600 Aº, β=101.21º, Z=8, mol weight =239.37, volume[CD]= 616.75$(Aº)^3$, Dx= 5.15 [15]. The diffracted peaks corresponding to monoclinic structure of $CdSeO_3$ can be indexed to the planes (011), (021), (012)(-121), (031), (022), (130),(131), (040), (102), (-141),(041)(032), (-113), (042), (-222), (151)(-232), (240)(043), (-124)(-242), (232), (250)(134), (-162)(104), (124)(242), (311)(-331) (063)(134) located at 2Ɵ angles 12.5, 17.3, 22.1, 23.3, 25.2, 26.2, 27.0, 27.7, 28.8, 29.7, 32.8, 33.5, 35.1, 37.6, 41.0, 42.7, 45.2, 47.3, 48.1, 49.1, 51.2, 52.7,and 53.8. The average crystallite size calculated by Debye-Scherer formula[19],[20],[21],[22],[23],[24] is 26 nm. The size of the particles ranges from 9 nm to 40 nm.

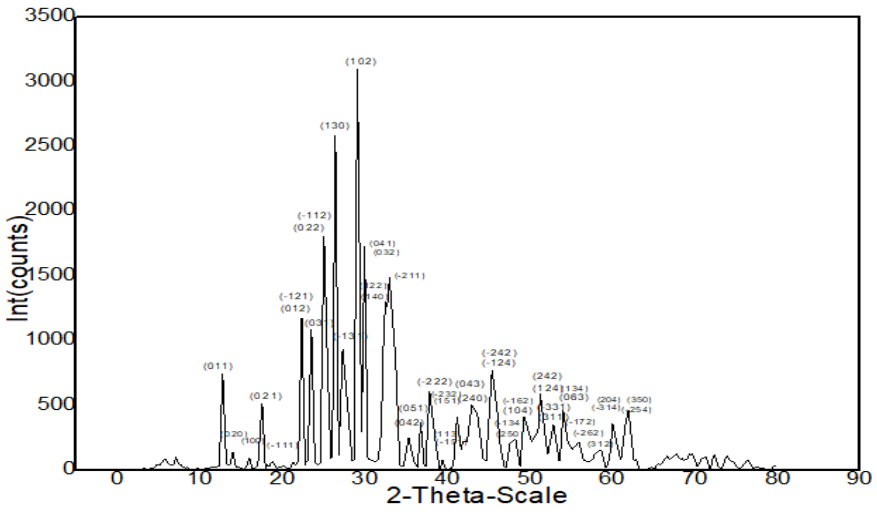

Fig. 1. XRD pattern of as prepared $CdSeO_3$ nanoparticles

3.2. Energy Dispersive X-Ray Spectroscopy (EDX) Analysis

EDX is an important technique to analyze the composition of elements quantitatively and to find the chemical identity of the elements. Fig.2 shows the EDX spectrum of as prepared $CdSeO_3$ nanoparticles. The EDX studies on the as prepared nanoparticles confirm the presence of Cd, Se and O. No trace of other elements was observed. From the EDX analysis, it is clear that the obtained products are pure cadmium selenite nanoparticles.

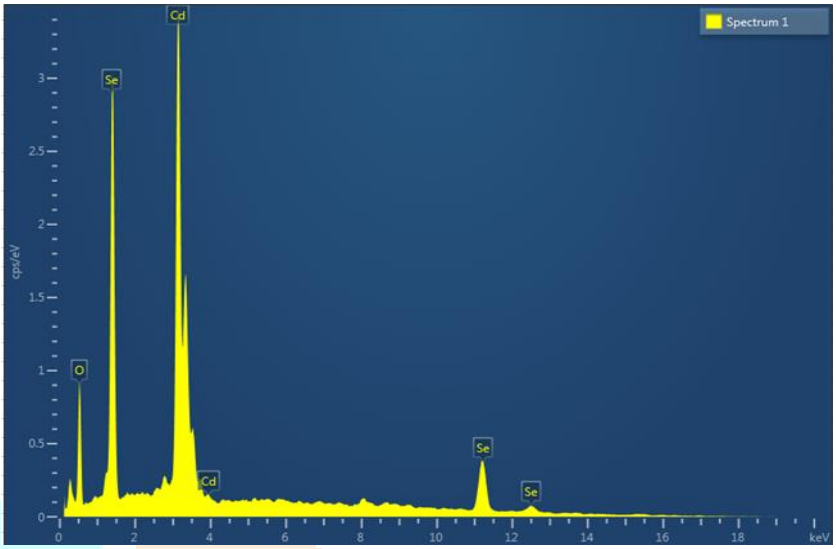

Fig. 2. EDX spectrum of as prepared $CdSeO_3$ nanoparticles

3.3 Scanning Electron Microscope (SEM) Analysis

Scanning electron microscopy (SEM) was carried out to analyze the morphology and the growth features of the as-prepared nanoparticles. SEM images of as-prepared cadmium selenite nanoparticles at various magnification are shown in fig.3. The pictures clearly indicate the formation of sawtooth shaped nanoclusters. The grains have aggregated to form clusters. High magnification image fig, 3(d) confirms the formation of spherical luminous cadmium selenite nanoparticles.

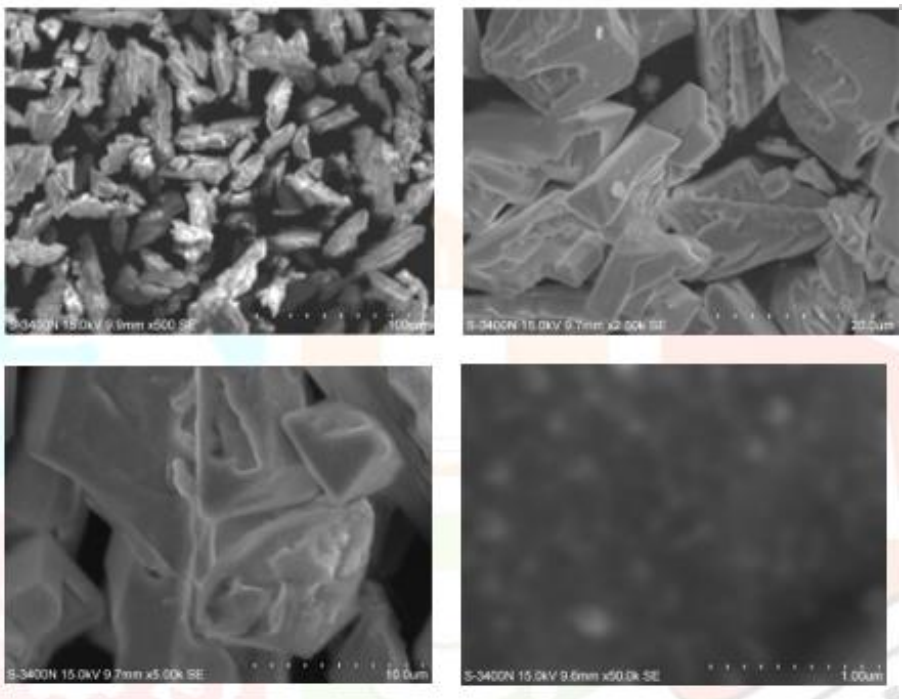

Fig. 3. SEM micrograph of as prepared $CdSeO_3$ nanoparticles

3.4 FTIR Spectroscopy Analysis

FTIR studies were carried out to determine the presence of functional groups and chemical bonding, as well as to study the surface changes in the nanostructures. The infrared molecular spectrum of as-prepared $CdSeO_3$ nanoparticles is shown in the fig.4. The presence of selenite (SeO_3) functional group is confirmed by its characteristic vibrational deformation peaks at 441.9 cm^{-1}, 470.3 cm^{-1}, and 504.9 cm^{-1}, the corresponding asymmetric stretching at 725.9 $cm^{-1}$and symmetric stretching at 815.6cm^{-1} [25,26,27, 28]. Considerable splitting in the band confirms the crystallinity of the material. The weak peak at 1417 cm^{-1} is assigned to CO_3^{2-}traces. The weak peak at 1542 cm^{-1} is assigned to δ (H_2O) due to moisture absorbed on the surface of $CdSeO_3$[27].

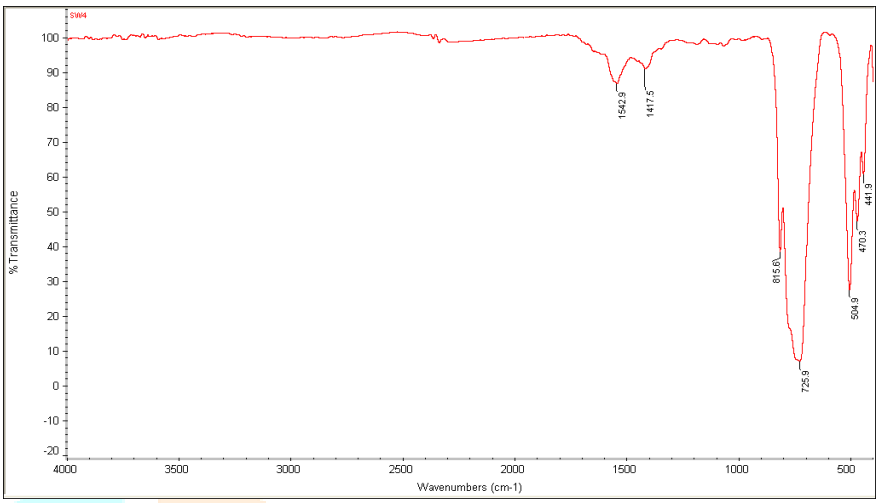

Fig. 4. The FTIR spectrum of as prepared $CdSeO_3$ nanoparticles

3.5. UV-Vis absorption spectroscopy Analysis

Ultraviolet-visible (UV-Vis) spectroscopy involves the absorption of photons in the ultraviolet and visible regions. Fig.5(a) shows the absorption spectrum of the as-prepared cadmium selenite nanoparticles in the wavelength range of 200-800 nm. An absorption edge at 260 nm is observed in the absorption spectrum. It can be seen from the spectrum that there is comparably low absorption in the ultraviolet and visible regions. This reveals that this material is transparent in UV and visible region and can be used as a window material.

The UV-Vis absorption spectrum is very useful in estimating the optical band gap (Eg). From the relationship of near-edge optical absorption of semiconductors [29]:

$$(h\nu)\ A = k\ (h\nu - Eg)^{n/2} \qquad (2)$$

where k represents constant, Eg is the optical energy band gap and n is 1 for direct bandgap semiconductors.

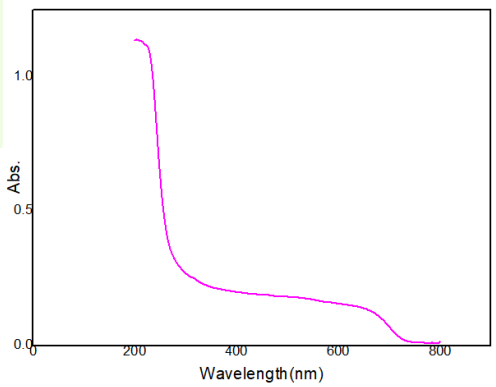

Fig. 5. a) UV-VIS-IR absorption spectrum of as prepared $CdSeO_3$ nanoparticles

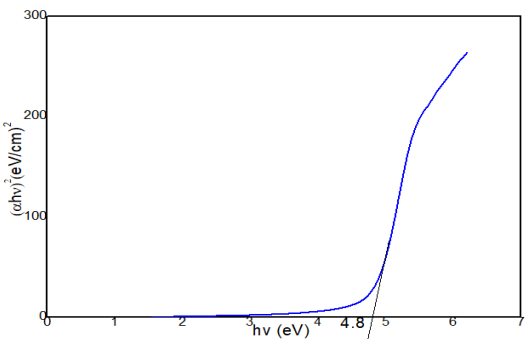

Fig. 5(b). Tauc plot of as prepared $CdSeO_3$nanoparticles

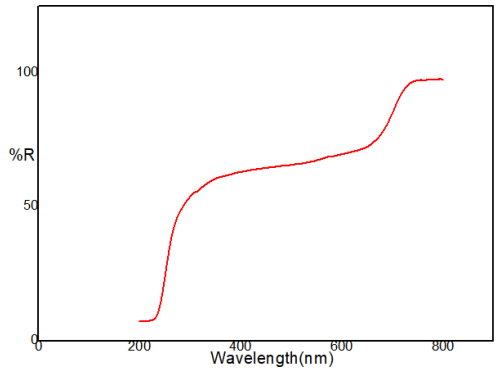

Fig. 5(c) Diffused reflectance spectrum of as prepared $CdSeO_3$ nanoparticles.

The plot of $(\alpha h\nu)^2$ vs. hν is shown in Fig.5(b). Extrapolating the linear fit of this plot for zero absorption coefficient gives the direct bandgap of nanoparticles which is shown in Fig. 5(b). The optical bandgap of the nanoparticles thus calculated from the Taucplot was 4.8 eV which is in good agreement with the bandgap calculated from the absorption edge.

The calculated band gap may be originated from the magnitude of Cd 4d orbital participation as well as the distortion resulting from SeO_3 groups in conduction bands. In fact, the observed larger bandgap for $CdSeO_3$ nanoparticles compared to other reported materials should be attributed to the stabilization of the relative energy arising from the distortions of SeO_3, which is consistent with the dipole moments calculations [30]. Fig.5(c) shows the diffused reflectance spectrum of as prepared $CdSeO_3$ nanoparticles. This spectrum shows that the material is transparent to ultraviolet and visible rays.

3.6 Photoluminescence (PL) Analysis

Photoluminescence is the measure of photoabsorption and emission of light indirect bandgap material. The photoluminescence spectrum of as-prepared CdSeO3 nanoparticles had been recorded in the range of 400 - 900 nm is shown in fig.6. Strong blue luminescence is observed in the spectrum centered at 439 nm from vibrational relaxation. Vibrational relaxation is a decay process in the form of photons that occurs after the electrons of a molecule move from a high vibrational energy level to the lowest vibrational energy level. This process is exhibited by direct bandgap material. Owing to its luminescence and transparency this could be a potential material for light-emitting diode, laser diodes, biological imaging and labeling.

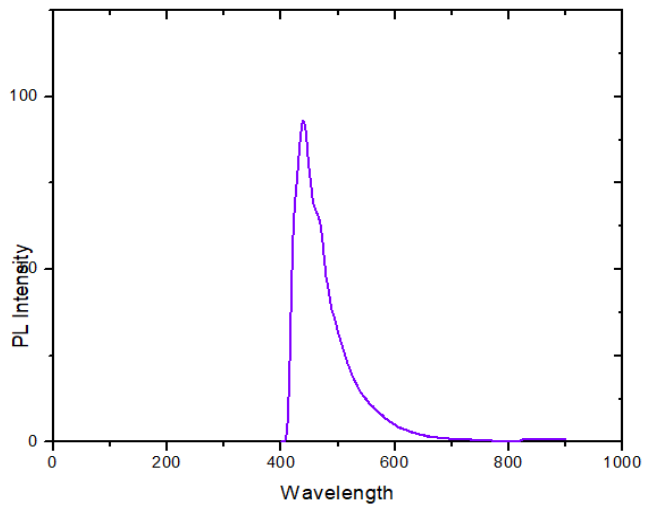

Fig. 6. Photoluminescence spectrum of as prepared $CdSeO_3$ nanoparticles

3.7 Thermal Analysis

Thermogravimetric (TG) and Differential thermogravimetric analysis (DTA) for the air-dried sample was performed on a Q600 SDT thermal analyzer at a heating rate of 20 °C /min. Fig.7 shows the TG/DTA curve of as prepared CdSeO3 nanoparticles. The thermogravimetric curve of as prepared cadmium selenite nanoparticles shows one major weight loss. It is observed from the thermogram that the material is stable up to 650°C. From 650°C to 750°C a huge mass loss of 48% is observed and in the DTA curve due to the endothermic peak at 670°C, could be due to the decomposition of $CdSeO_3$ to CdO upon sublimation of SeO_3 at high temperature [30,31, 32].

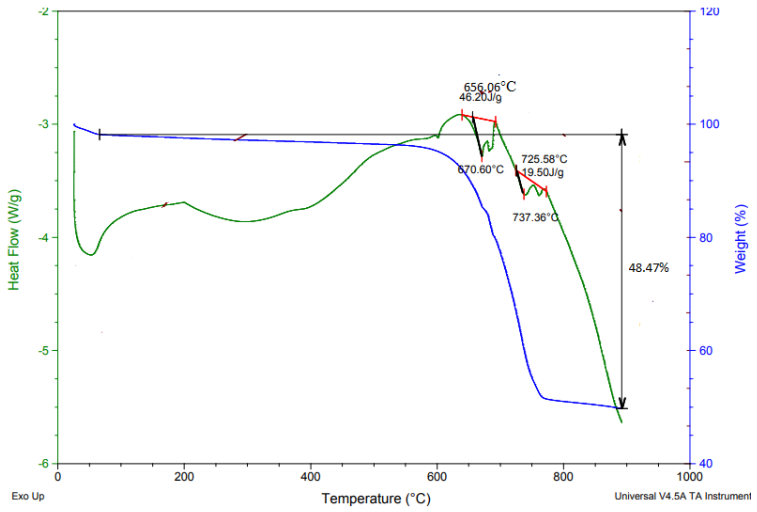

Fig. 7. TG/DTA curve of as prepared $CdSeO_3$ nanoparticles.

4 CONCLUSION

The nanostructured monoclinic cadmium selenite nanoparticles were successfully prepared by a simple microwave assisted hydrothermal method. From the structural analysis carried out, it is confirmed that the material is $CdSeO_3$ nanoparticle. UV-Visible absorption spectrum reveals that the material is transparent with a wide band gap. EDX analysis confirms the presence of Cd, Se and O in the prepared sample. The FTIR studies confirm the presence of functional group SeO_3. PL spectrum of the sample exhibits a sharp, intense peak shows that it is a blue luminophore. Material is stable up to 650 ^oC. Owing to its various interesting properties such as wide bandgap, transparency in UV and visible region, luminescence, large surface to volume ratio and thermal stability, cadmium selenite luminophores could be promising material for potential applications in optoelectronic devices, photocatalysis, solar energy conversion and biological imaging and labeling.

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