Research Article

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Morphological Controlled $BaSO_4$ Nanostructures by Solvents and Molar Concentrations

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ABSTRACT

The aim of the present work is to synthesize environmentally friendly nanomaterials, which are viable and better alternative method for distinct applications. The co-precipitation method is used for the preparation of $BaSO_4$ nanostructures with the influence of Azedarach indica leaf extracts as organic stabilizing agents. For synthesizing nanostructures, two different solvents (Ethanol and deionized water) were taken along with distinct molar concentration (0.05 and 1.0 M) are investigated by various characterization techniques. Initially, the XRD pattern revealing the orthorhombic phase structure was well-matched with JCPDS file. Next, FTIR transmission spectrum confirmed the presence of Ba and SO_4 stretching vibration molecules. The morphological studies of SEM evidenced at 1 and 2 µm scale level the successful preparation of rice grain (or nanorods) like nanostructures with the average diameter of ~73.5 nm (ethanol) and 222 nm (DI water). Also, the prepared sample elements were evidenced by the EDX spectra. This employed experimental study revealed that the DI water solvent with higher molar concentrations plays a crucial role in the morphology and size of $BaSO_4$ nanostructures. In the future, these nanocrystalline materials could be find applications in antimicrobial activities.

Keywords: Green synthesis; *Azadirachta indica*; $BaSO_4$; Antimicrobial; Nanostructures.

1. INTRODUCTION

Nowadays, science and technology have been garnering great attention at nanoscale level. Also, the production and control of nanostructure size and shape have become remarkable research subjects for various applications. It is a known fact that materials could have various unique structural, electronic, optical, magnetic, physical, and chemical properties because of their size changes from bulk materials at the nanoscale level. The preparation of organic or inorganic powders ($BaSO_4$) by controlling size and morphologies is attracting and increasing interest. It has more advantages, for example, whiteness, inertness, and high specific gravity. This $BaSO_4$ nanostructure is useful for packing and additives in painting, thin film coating, plastics, and medicines, as reported by various researchers (Wu *et al*. 2007; Shen *et al*. 2007; Kucher *et al*. 2008). Many researchers have been reported for the synthesis and preparation of $BaSO_4$ nanostructures with the addition of different additives and methods, such as the co-precipitation method, sol-gel, microemulsion, membrane separation, microchannel reactor, etc. (Jones *et al*. 2004; Wang *et al*. 2005; Adityawarman *et al*. 2005; Nagaraja *et al*. 2007; Wang *et al*. 2009). Currently, the researchers are focused on green-synthesis-based $BaSO_4$ nanoparticles. Omid (Amiri *et al*. 2022) presented the enhanced piezocatalytic activity of $BaSO_4$ by coupling different materials ($BaTiO_3$, Cu: $BaTiO_3$, Fe: $BaTiO_3$, S: $BaTiO_3$). By doping $BaTiO_3$ with $BaSO_4$, they achieved a achieved a highly improved efficiency of 89.2% and decontamination.

Jha *et al*. (2019) demonstrated the green synthesized barium sulfate nanoparticles with the influence of Azadirachta indica leaf extract by the sonochemical method. The prepared nanoparticles underwent structural, morphological, functional, and elemental studies. These results strongly confirm the thermally stable and highly crystalline $BaSO_4$ nanoparticles. Emel Akyol and Murat Alper (2016) experimentally investigated the size and morphology of barium sulfate nanostructures by using various crystal growth modifiers such as polyacrylic acid, polyvinyl sulfonic acid, and ethylenediaminetetraacetic acid. They reported that additive concentration and pH play a pivotal role in the effect of morphology and size on $BaSO_4$ nanostructures. Furthermore, the organic and inorganic materials that incorporated $BaSO_4$ were reported by various researchers (Yu *et al*. 2005; Bala *et al*. 2006; Wang *et al*. 2006; Shen *et al*. 2007; Zhao *et al*. 2007; Jones *et al*. 2007; Gupta *et al*. 2010; Nandakumar and Kurian 2012). Mochahari (2024) proposed the influence of molar concentrations and studied their structural, morphological, optical and luminescence of polyvinyl alcohol-capped nanostructures ZnS films.

Koao *et al*. (2018) investigated the effect of octadecylammine molar concentration (0.3 to 15%) on the structural, morphological and optical properties of

ZnO nanostructures which was prepared by precipitation method. Finally, 10 molar concentrations generated the optimized results. Similar work carried out by (Chand *et al*. 2015) explored the morphology, optical and ferroelectric properties of CuO nanostructures by influence of NaOH concentrations (3, 5 and 6). With the effect of these molar concentrations, the optical band gap reduced from 3.55 to 2.95 eV due to increment of molar concentration 3, 5 and 6. Despite all these literature reviews, we are still finding suitable $BaSO_4$ nanostructure preparation using green leaf extract, which is eco-friendly and economical. It is exposed and compared with respect to the distinct solvents (ethanol and deionized water) and molarity by using various optical, structural, morphological, functional, and elemental characterization techniques. The selection of the solvents plays a crucial role for the preparation of nanostructures. There are several advantages and disadvantages like good solvency, low toxicity with environmental impact and volatility are more concerns. This report may be remarkable for biomineralization research and green synthesized inorganic nanomaterials.

2. EXPERIMENTAL SECTION

2.1 Materials

Initially, Azadirachta indica fresh leaves, barium chloride ($BaCl_2.2H_2O$), and anhydrous sodium sulphate (Na_2SO_4) were procured. Also, the ethanol (C_2H_6O) and distilled water (H_2O) were used as solvent in this throughout the process. They were used without any purification. Azadirachta leaves collected from Sri YN College campus, Narsapur, West Godavari (District), Andhra Pradesh. Glassware was cleaned with distilled water and acetone.

2.2 Preparation Method

Fig. 1 indicates the procedural steps for the preparation of $BaSO_4$ nanostructures. The nanostructures were obtained with the green leaves extracted. Initially, *Azadirachta indica* (A. Indica) leaves were collected from Y.N. College campus in Narsapur, West Godavari (AP). These leaves were washed with distilled water several times to move the unwanted dirt. Next, 30 grams of leaves were boiled in 80 ml of ethanol (C_2H_6O) and distilled water (H_2O) for two hours individually. Barium chloride ($BaCl_2.2H_2O$) and sodium sulphate (Na_2SO_4) are the source materials for the preparation of $BaSO_4$ nanostructures with 0.05 and 0.1M. Next, the A. Indica leaf extract was added to the solution. Using a magnetic stirrer, the solution mixed well and noticed white precipitate. Afterwards, the solution was kept in a hot-air oven at 100°C for 2 hours. The dried $BaSO_4$ powders were collected and named Sample B (0.05M) and Sample C (0.1M).

2.3. Characterization Techniques

The samples were characterized for their structural, functional, morphological and elemental properties by using X-ray diffraction (XRD, Rigaku Mini flex, Japan), Fourier transform infrared (FTIR, JASCO FT/IR 6600, Japan) spectroscopy, scanning electron microscopy (SEM, TESCAN VEGA3, Czech Republic) and energy dispersive X-ray (EDX, Genesis, US) spectroscopy.

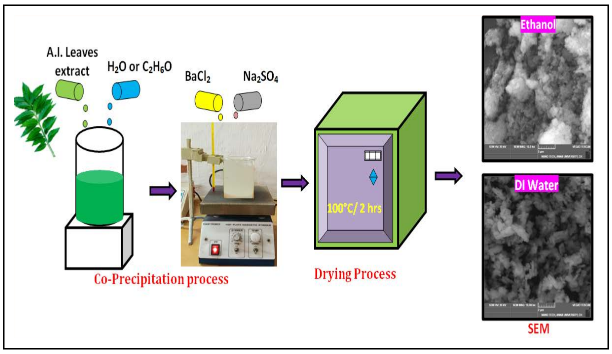

Fig. 1. The synthesis process of $BaSO_4$ nanostructures

3. RESULTS AND DISCUSSION

The XRD patterns of $BaSO_4$ nanostructure samples are shown in Fig. 2 (a)-(b). The indexed XRD pattern of $BaSO_4$ synthesized using de-ionized water and ethanol solvents along with various molar concentrations (0.05 and 0.1M). As compared to DI water, later one showed the strong and narrow diffraction peaks are notable as 24.39 (021), 28.9 (121), 32.2 (002), 46.7 (212). However, these peaks of both synthesized nanoparticles are well matched with JCPDS (2017) and 0020-024 (Kipp *et al*. 1996) JCPDS 1997 (Meagher *et al*. 2013). Also, XRD pattern exhibited the orthorhombic phase and nanoparticles are pure, with all the intense peaks according to the JCPDS file. These results are suitably aligning with the reported work.

It's indicated that the prepared good purity and a well crystalline structure. Also noticed (Fig. 5) some of the impurity elements (C, Na, S, Cl) appeared from the calcination (muffle furnace) process (or) testing atmosphere. The $BaSO_4$ nanostructures are characterized by the FTIR technique to determine the functional groups of the samples (organic and inorganic) which are synthesized by distinct solvents such as ethanol and deionized water. Fig. 3(a)-(b) shows the FTIR transmittance spectrum of green synthesized $BaSO_4$ nanostructures. The characteristic peaks of the sample located around 1224-1208 cm^{-1} are assigned to the plane bending vibrations of sulphate (SO_4^{2-}) (Manteghian and Sameni, 2019). The shoulder around ~1011 cm^{-1} is the vibration of sulphate groups. The absorption peaks at

~3400 and 1500 cm^{-1} are confirmed the water molecule (Chen *et al*. 2016; Saravanan *et al*. 2024).

The sample B (ethanol) shows the broader absorption curve as compared to sample C (DI water) due to the influence of solvents. The selection of the solvent, such as distilled water, ethanol can influence the growth of $BaSO_4$ nanoparticles in several ways. For that, solvents affect kinetic reactions, particle size and crystal morphology. Here, deionized water is a polar solvent which might Favor certain crystal facets. Also, while ethanol being less polar could be influencing the different patterns.

Additionally, solvent properties can impact the solubility of reactions, and the nucleation processes can also affect nanostructure size distributions. However, the selection of solvents should align with the desired properties of $BaSO_4$ nanoparticles. SEM morphological studies are shown in Fig. 4 (a)-(d). Using ethanol solvent, the micro image of the sample depicts (Fig. 4(a)) a rod- or rice-like structure (at 2µm), and the corresponding size calculated the diameter (at 1µm scale) as around 73 nm with some agglomeration (Fig. 4(b)).

Next, the morphological images of deionized (DI) solvent- based $BaSO_4$ structure as shown in Figure 4(c). The effect of increasing the size and morphological structures was noticed by changing the solvent of DI water. It depends on the solvent, specific reaction, and materials involved. Generally, increasing molar concentration ratio can lead to increased particle nucleation growth, potentially yielding larger or more numerous nanostructures. It's crucial to consider the reaction kinetics, solubility and other factors that can influence the sample's properties and nature. Also, adjusting the concentration ratio should be done cautiously, as it might also impact the stability and uniformity of the prepared nanostructures. However, in the morphological images at 1 µm, the diameter of nanorods around 222 nm which is very clear, as shown in Fig. 4(d). These selections of the solvents play key role in nano and microstructures. With respect the solvents nanomaterials size and shape could be controlled as reported by various scientific communities (Gholami *et al*. 2024). They experimentally demonstrated that the ethanol solvent endorsing the faster diffusion along with that smaller nanomaterials and DI water (solvent) generates the stronger attraction in between the particles and larger aggregates forming (Abdulkareem *et al*. 2023).

Fig. 5 (a)-(b) shows the EDX spectra of $BaSO_4$ nanoparticles. These elemental spectra confirm the presence of Ba, O and S in both samples. The impure elements are presented in between the calcination processes. But the peak intensity enhanced considerably due to increment of weight percentage (wt%) and atomic (at%). This EDX study shows the DI-based sample revealed an intense peak of Ba, S and O elements. Overall, DI water solvents is playing key role for the preparation of $BaSO_4$ with free standing nanostructures, which can be useful for various medical applications.

Overall, these optical, structural, functional, elemental studies are evidencing that the later (DI) solvents with highest molar concentrations showed the better results for antimicrobial activity. Furthermore, the green synthesized $BaSO_4$ nanostructures are widely useful in X-ray photography, gamma ray absorbers, white pigments etc. The merit is non-harmful to humans. Further useful in plastics, rubber, pharmaceutical and paint applications.

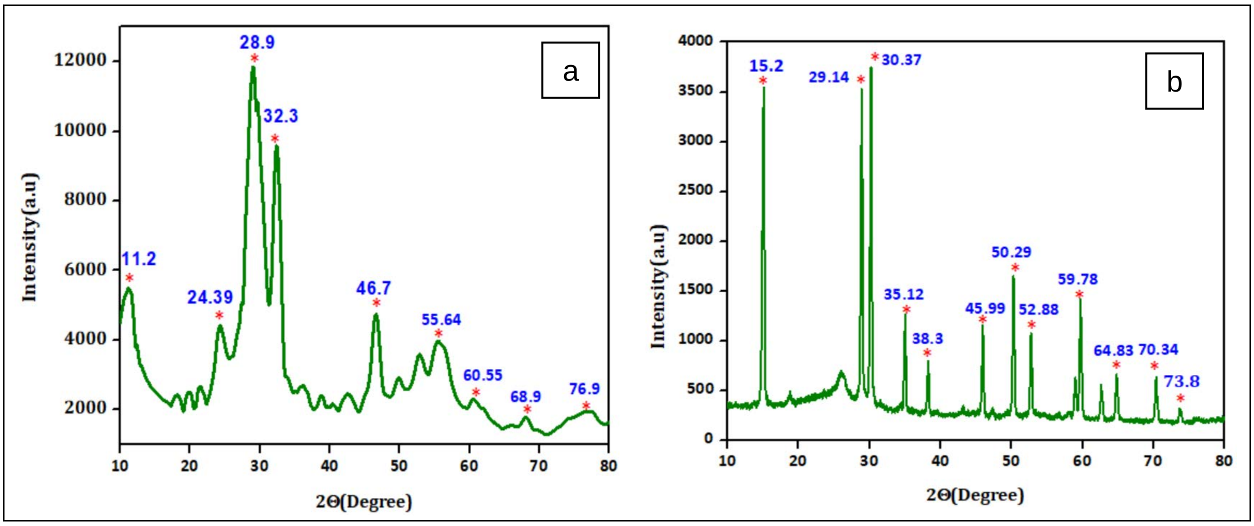

Fig. 2: XRD diffraction pattern of $BaSO_4$ nanostructures

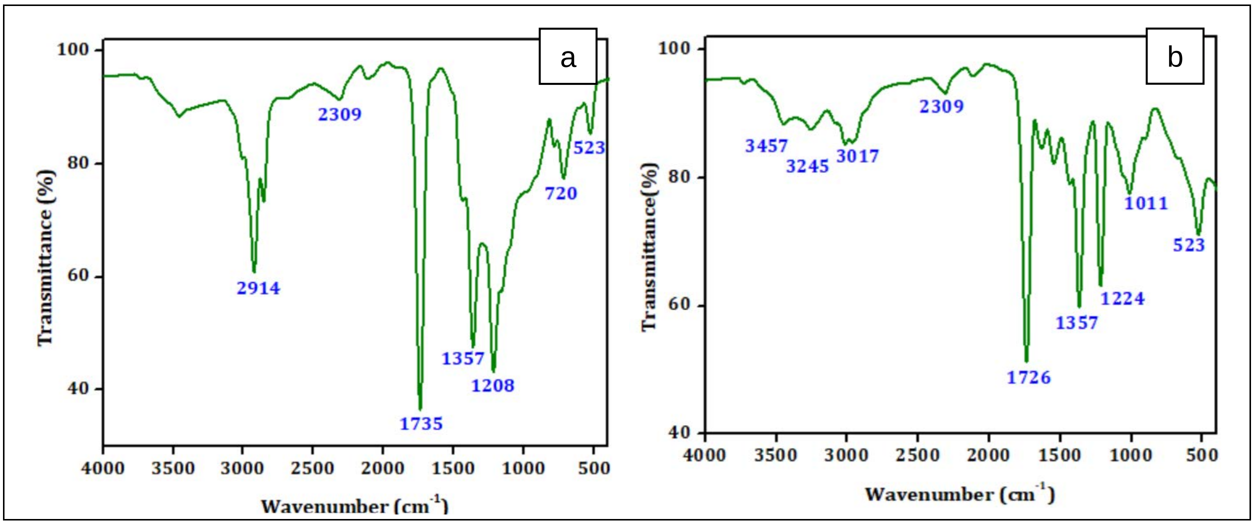

Fig. 3: FTIR transmittance spectra of $BaSO_4$ with ethanol (a) and Deionized water (b)

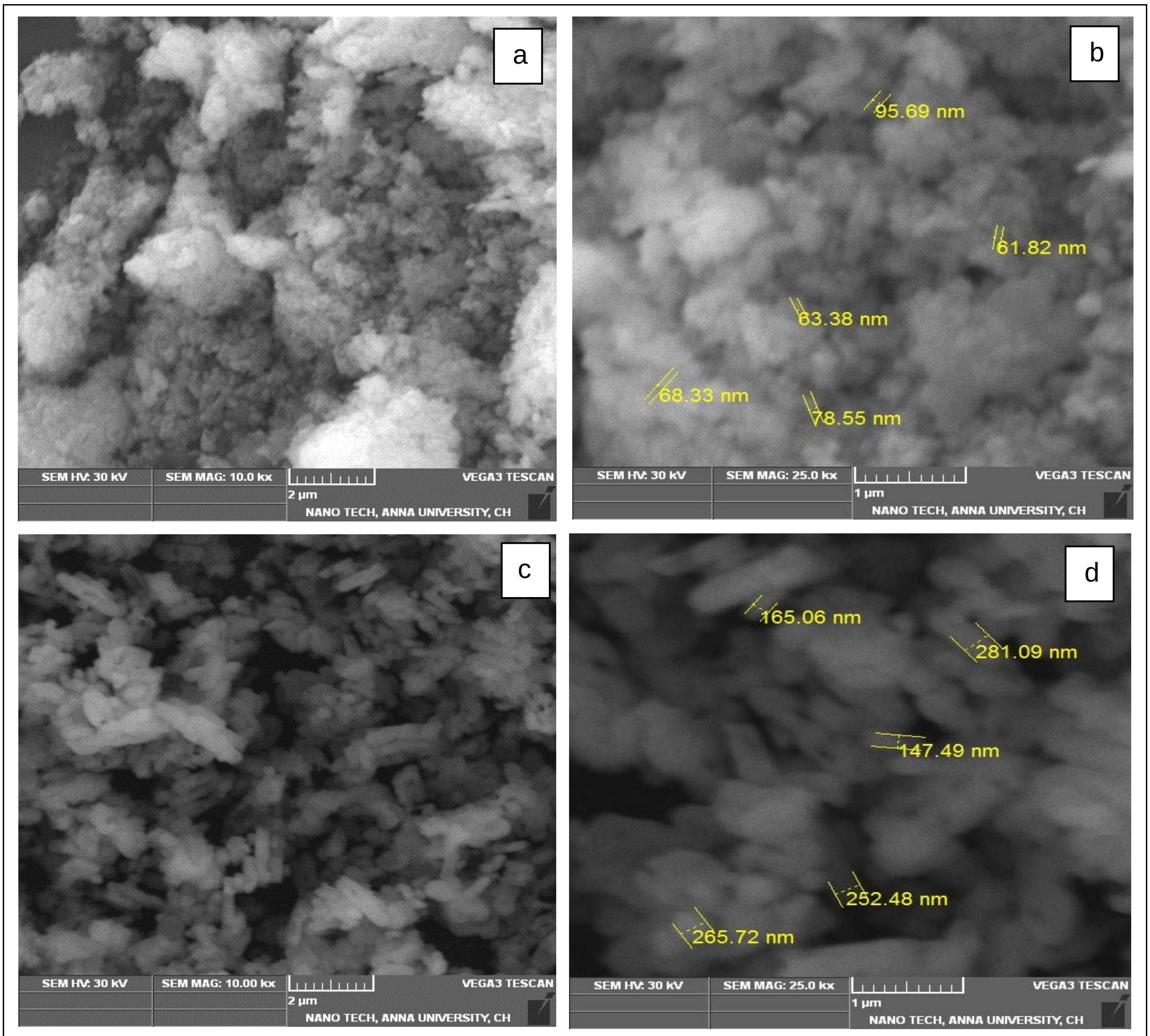

Fig. 4: SEM morphological images of $BaSO_4$ nano and microstructures, ethanol (a)-(b), Deionized water (c) -(d) solvent

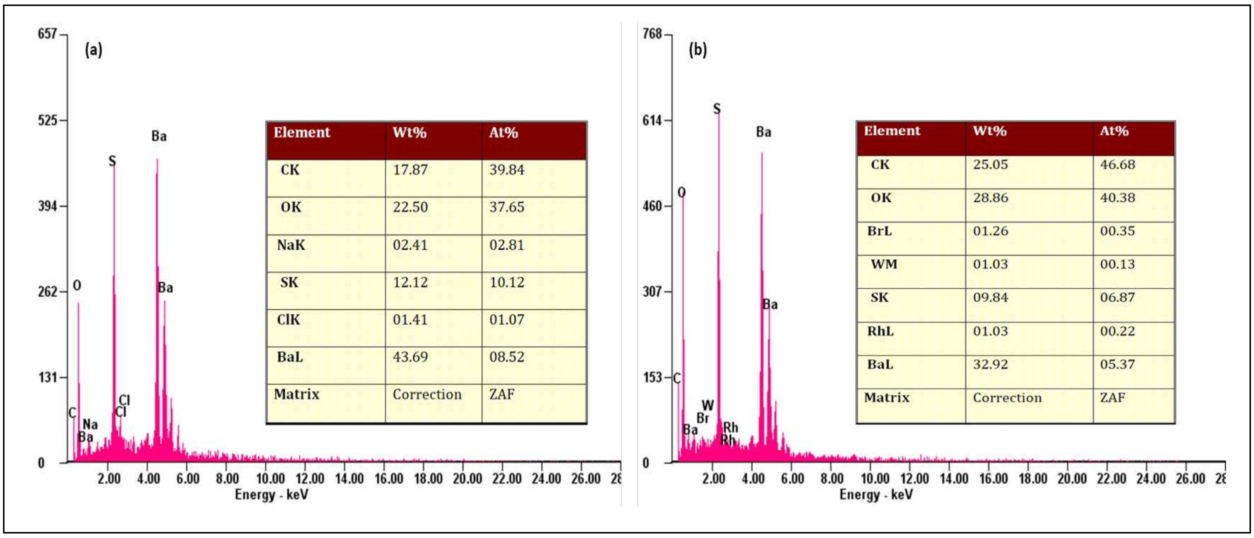

Fig. 5: EDX elemental images of $BaSO_4$ nanostructures based on ethanol (a) and deionized water (b)

4. CONCLUSIONS

In this work, we have successfully synthesized $BaSO_4$ nanorods by using different molar (0.05 & 0.1M) concentrations and solvents (Ethanol and DI water). The co-precipitation method has been employed for the preparation of samples with the addition of *Azadirachta indica* leaf extracts as organic stabilizing agent. The XRD was revealing the orthorhombic phase structure. FTIR transmittance spectra confirms the presence of Ba and SO_4 stretching vibration molecules. At microscale level, the SEM results showed that the micro image of $BaSO_4$ nanostructures was synthesized, and morphology was also effectively controlled under the experimental condition. This successful preparation is helping on nucleation studies of nanostructures with better resolution (0.1M) noticed as compared to 0.05M. Further, the prepared samples elements were evidenced by EDX spectra. Future, the molar concentration and solvents could be optimized with well-defined crystalline nanostructures for antimicrobial applications.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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