Antibacterial And Photocatalytic Properties Of Wet Chemically Fabricated Cus/Graphenenanocomposite

Ashish Kumar Sahoo, Eeshwar Chandra Tripathy

Abstract: In the present work a simple wet chemical method has been adopted for synthesis CuS and CuS-Graphene composite in low temperature range of 50-90 0C. The specified materials were characterized by X-ray diffraction and scanning electron microscopic (SEM) studies. XRD analysis shows cubic phase of thus prepared sample and morphology analysis by SEM indicates mono dispersed particle morphology. The corresponding graphene composite has been investigated as an efficient adsorbant as well as photocatalyst in the decomposition of methyl orange (MO) dye in the presence of sun-light with 80% degradation efficiency for an exposure time of 100 min. In addition, the composites also exhibit enhanced antibacterial activity towards E.Coli.

Keywords;Nanoparticle, Semiconductor, Graphene, Copper sulphide, Photocatalytic properties, Antibacterial Properties.

1. INTRODUCTION

In recent years, use of antibiotics have been the preferred mode of treatment method for bacterial infections owing to their powerful outcomes. Reagarding this, many researches has been focussed on the search for new antibacterial agents to combat the gradual developing resistance against potent antibiotics [1]. However studies have indicated that widespread use of antibiotics has led to emergence of bacterial resistance to multiple drugs. Such abuse of antibacterial drugs are known to be the cause of development of superbacteria which are reportedly resistant to nearly all antibiotics owing to presence of gene NDM-1 [2]. In addition, reckless use of antibiotics has led to various health hazards to public health such as superbugs that do not respond to any existing drugs [3]. Therefore, this necessitates a search for effective antibacterial materials. Regarding this, different nanoparticles have been used as alternative to antibiotics, which is because of the fact that nanoparticles are capable of preventing microbial drug resistance in certain cases [4-6]. In past few decades, semiconduting materials are gaining lots of attention because of their high chemical stability, processability and surface performances which are among the most attractive properties of these materials [7]. Added to these, many advantages of semiconducting materials such as less electron mobility, comprehensive band gap, which makes them effective in the operation of power devices at high as well as low temperatures [8, 9].The discovery of new semiconductor materials and the improvement of existing materials is an important area of study in materials science. Crystalline inorganic solids are mostly used as a semiconductor material. These materials have been classified according to the periodic table groups by means of their constituent atoms. During the past years, material scientists have shown considerable interest and made great efforts towards the developement and implementation oftransition-metal Chalcogenides.CuS is one of such materials which is a P-type compound semiconductors with a narrow band gap of 2.5 eV for bulk hexagonal wurtzite structure while the average refractive index laying in between 2.07 and 2.26 [10]. It draws its importance in superionic materials, cathode materials, catalysts, solar controllers, optical filter etc. [13]. Among various morphology of CuS reported [14] such as nanoparticles, nanorods, nanotubes, nanoplates, hollow spheres, nanoflakes, etc., the nanoparticle morphology has reportedly been found to be immensely useful due to its potential application in both conditional optical devices and new generation of nano-electronics and nano-optoelectronics because of special structure-related chemical and physical properties. Now-a-days composite materials, having conducting polymer and graphene as matrix, are gaining immense due to some enhancement of properties which are exclusive to the fillers. Further, it is known that, combination of semiconducting nanomaterials with such matrix do improve some of its useful properties such as thermal, mechanical, electro chemical and physicochemical qualities because of synergistic effects [16-25]. In this regard, graphene nanocomposites at very low semiconducting powder loading show appreciable enhancements in their functional aspects, compared to conventional materials as well as composites [26]. The remarkable properties of graphene are able to improve the physicochemical qualities of the host matrix upon distribution [27]. This helps in strengthening and increasing the interfacial bonds between the layers of graphene and the host matrix. It is this bonding that dictates the emergence of the cumulative properties of graphene in reinforced nanocomposites [19,20]. Among the different synthesis methods, the ‘wet chemical method’ which is a common name for a group of methods used for producing nano- and ultra-dispersed inorganic powders from aqueous and non-aqueous solutions [21,22]. The term "wet chemical methods" emerged in contrast to conventional and solid-state synthesis methods of compounds and materials. Now-a-days the term referes to liquid phase sol-gel process, hydrothermal synthesis, spray drying, aerosol spray pyrolysis etc., using liquid phase. Moreover, the wet chemical method is widely used for its cost effectiveness, capability of low temperature synthesis, use of different type

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of solvent by preference of viscosity, use of templating agent and polarity [12]. Thus from above discussions, we aimed at preparation of CuS nanoparticle morphology with different sizes, by altering the experimental conditions. Further these particles are to be used to study their efficiency towards photocatalytic degradation of harmful organic dye as well as study antibacterial activity towards E-coli. Further, graphene composites of the said nanoparticles also has to be studies so as to detect further enhancement of these properties.

2. EXPERIMENTAL

Materials and methods

All the Chemical reagents were of analytical grade without further purification. Graphite powder, hydrogen peroxide, zinc nitrate, cupric nitrate, sodium sulfide, methyl orange powder, sodium nitrate, potassium permanganate, were purchased from Nice chemical private limited, Sulphuric acid, disodium salt of ethylene diaminetetraacetic acid (EDTA) and sodium dodecyl sulphate (SDS) were procured from CDH chemicals private limited, while Sodium borohydrade and Ethylene diamine (EN) were procurred from Spectrochem private limited. The bacterial strain Escherichia coli (HO25), Nutrient agar, Nutrient broth, Mueller-Hinton agar was provided by the Department of paramedics, Centurion University of Technology and Management, Bhubaneswar, Odisha.

Preparation of CuS

Copper Sulfide was synthesised from Cupric Nitrate which by wet chemical method. In a typical procedure 0.73 g of cupric nitrate and 5 g of EDTA/ 5mL of ethylene diamine was added into 50 mL of water at 50oC under stirring for half an hour. After that 5.9g of SDS (5 times of CMC) was added followed by 0.6g of Sodium sulfide and temperature was increased up to 90 oC at reflux condition for 2hours. Then it was filtered and washed for several times to remove excesses amount of soluble impurities. Then resulting mixture was allowed to dry in vacuum oven at 60 ^{0}C.

Preparation of CuS-Graphenenano composite

CuS-Graphenenano composite was synthesised by wet chemical method. Here 0.5g of graphene oxide, 0.73 g of Cupric nitrate and 5 g of EDTA/ 5mL of Ethylene diamine was added into 50mL of water at 50 ^{0}C under stirring for half an hour. After that 5.9 g of SDS (5times of CMC) was added followed by 0.6g of Sodium sulfide and temperature was increased up to 90 ^{0}C at reflux condition for 2 hours. Subsequently 0.07g of sodium borohydrade was added into it, after 30min it was filtered and washed for several times to remove excesses amount of soluble impurities. Then resulting mixture was allowed to dry in vacuum oven at 60 ^{0}C.

Study of Photocatalytic activity

The photocatalytic degradation of methyl orange (MO) was carried out in order to evaluate the photocatalytic activity of the as prepared nanoparticles and nanocomposites. 10 mg of prepared samples was dispersed in 50 mL of an aqueous solution of MO with an initial concentration of 10 mg/L. The above mixture was first stirred for 30 min in the dark to ensure that the adsorption-desorption equilibrium was reach. Then, the photocatalyticdegradation reaction was carried out under the irradiation of sun light. At every 10 min interval during sun light irradiation, 3 mL of the suspension was collected and subsequently centrifuged. The degraded solution supernatants was measured using a colorimeter by using blue-green filter.

Antibacterial Study

The bacterial identification was verified by chromogenic medium (chromagar) and the antibiotic sensitivity profile was determined by using Mueller-Hinton agar (MHA*); the pH of the medium was adjusted to 7.0 and sterilized all media and glass wares at 25 lbs. pressure and 120 oC temperature in an autoclave. Subsequently 20ml of agar medium was poured into either 100mm or 150mm petri dishes and let's dry in a laminar air flow to solidify, which takes up to 20min. Using an aseptic technique, a sterile swab was placed into the broth culture of E.Coli and gently removed the excess liquid by pressing or rotating the swab against the inside of the tube and streaked the Mueller-Hinton agar plate to form a bacterial lawn. To obtain uniform growth the plates was streaked with the swab in one direction and again three times streaked the plate by rotating 90o in its direction. After that plates are allowed to dry for 5 minutes. Then by the help of a cork borer plates are pricked on its centre where the relevant samples are placed. After all plates are incubated overnight at an incubation temperature of 37 ^{0}C.

Characterization

Powder x-ray diffraction (XRD) of CuS, and rGO-based nanocomposites were conducted by a Siemens D5000 XRD Diffractometer. The diffraction patterns were collected using a fixed wavelength of CuKα radiation (λ = 1.54056 Å) over the range of 5^0 to 80^0 in 0.1^0 or 0.05^0 intervals. The surface morphology Mil-100 (Fe) in this study was analysed using SEM-Carl Zeiss Gambh, Ceminicolumn with 0.1-30 K eV with a resolution of 1.1nm.

3. RESULTS AND DISCUSSION

The XRD pattern of as-synthesized CuS nanoparticles with different temperature and different templating agent are shown in Figure 1 and Figure 2.

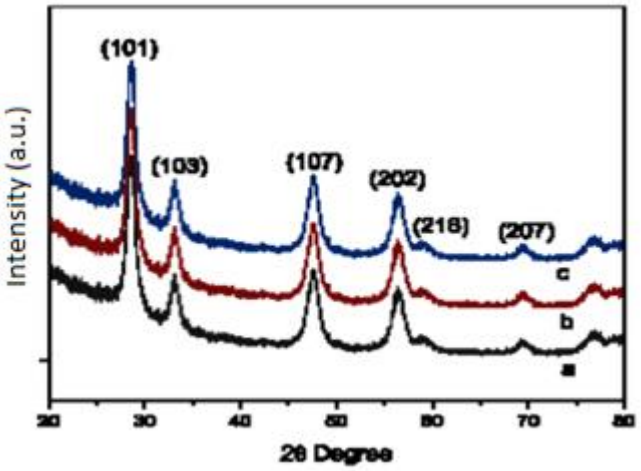

Figure 1. *XRD pattern of synthesized CuS particle prepared with EDTA at (a) 90 ^{0}C, (b) 70 ^{0}C and (c) 50 ^{0}C.*

The lattice parameters indicate hexagonal structure [JCPDS file No. 04-0464] having lattice parameters, a = 3.79 Á and c =16.34 Á. all XRD patterns show peaks at 2□= 28.519^0, 33.6^0, 47.358^0, 56.397, 59.9^0, 69.406^0, and corresponds to planes (101), (103), (107), (202), (116) and (207) respectively.

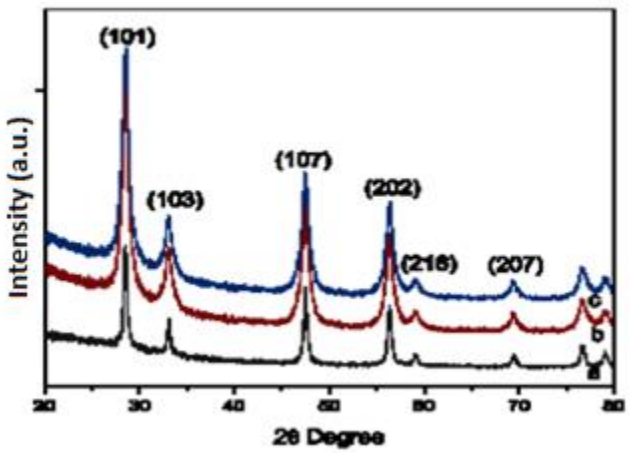

Figure 2. *XRD patterns of synthesized CuS particle prepared with ethylene diamine at (a) 90 ^{0}C, (b) 70 ^{0}C and (c) 50 ^{0}C.*

The prominent peaks were seen to be broadened indicating the nanocrystallinity of all the samples. The analysis of XRD pattern stated that CuS nanoparticles possess the average crystallite size determined using Debye Scherrer's equation,

D=K□□□□□cos□□□

WhereK, □□□□□□and□□are Scherrer constant, wavelength of X-ray radiation target used, maximum peak width in half height and angle of diffraction respectively.

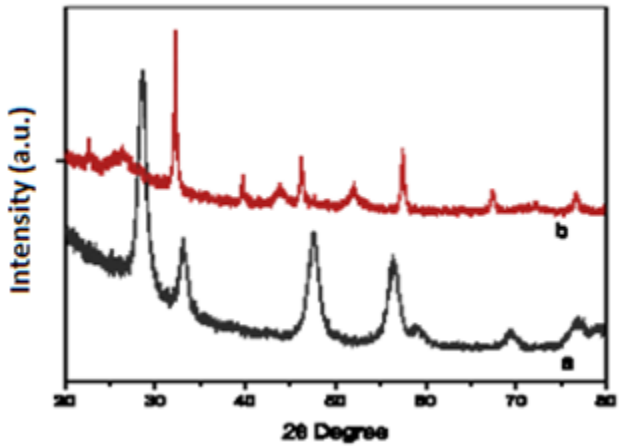

Figure 3*. XRD patterns of synthesized (a) CuS nanoparticle and (b) CuS-Graphenenanocomposite in presence of EDTA at a 90 ^{0}C*

The presented data shows the samples synthesized with EDTA at 90 ^{0}C, 70 ^{0}C, 50 ^{0}C have crystallite size 76, 55 and 44 nm respectively. Similarly samples prepared with ethylenediamine at 90 ^{0}C, 70 ^{0}C and 50 ^{0}C have crystallite size 82, 79 and 58 nm respectively. In addition, the improved intensity with sharper peaks indicates a higher crystallinity of the prepared material in when ethylene diamine is used as a templating agent. Such observations are not uncommon as ethylene diamine reportedly binds Cu^{2+} ions in a reversible step, whereby controlling the nucleating and growth step.

Figure 3 shows XRD patterns of CuS and CuS- graphene composite prepared with EDTA as templating agent. Which are indicated as (a) and (b) in both figure. The XRD patterns of CuS-Graphene show peaks at 2□= 22.72^0, 32.336^0, 39.785^0, 46.303^0, 52.15^0, 57.505^0, 67.46^0 and 76.76^0. The presented data shows the composite synthesized at 90 ^{0}C with EDTA, and at 90 ^{0}C with EN, have crystallite size 89 nm and 97 nm respectively. The improved intensity with well-defined sharper peaks indicates a higher crystallinity of the prepared material.

Morphology Analysis

Scanning Electron Microscope (SEM)

The surface morphology of the as synthesized CuS nanoparticles prepared at different temperatures was studied with the help of SEM and has been shown in Figure 4.

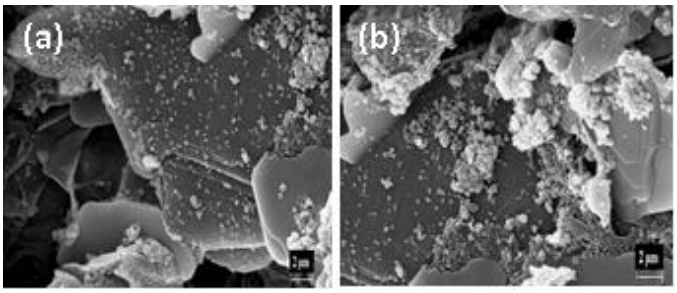

Figure 4. *SEM images of CuS at differen temperature as (a) 50 ^{0}C, (b) 70 ^{0}C, (c) 90 ^{0}C*

From the SEM images it is clearly revealed that the CuS has particle type morphology with uniform size distribution in the range of 500-700 nm. In addition it has also been observed that the particle size increases with rise in temperature from 50 to 90 ^{0}C. In addition, CuS powders synthesized using ethylene diamine have similar morphology patterns with slight increase in particle size in comparison to that synthesized with EDTA as templating agent. Figure 5 shows the SEM image of thus prepared CuS-graphene composite. It can be observed thatthat distinct CuS nanoparticles are uniformly deposited on the graphene sheets.

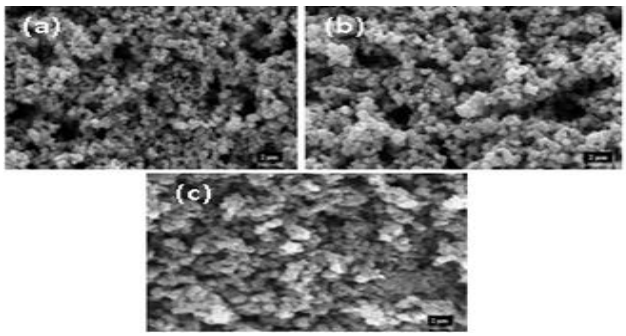

***Figure 5**. SEM images of CuSgraphenenanocomposite with EDTA*

Photocatalytic Studies

The photocatalytic activity of the synthesized nanomaterials was studied by using these nanomaterials as a catalyst for photodegradation of organic dye methyl orange in aqueous solution under visible light irradiation. Figure 6 shows the degradation of MO with naked eyes in several time intervals, in presence of CuS-graphene.

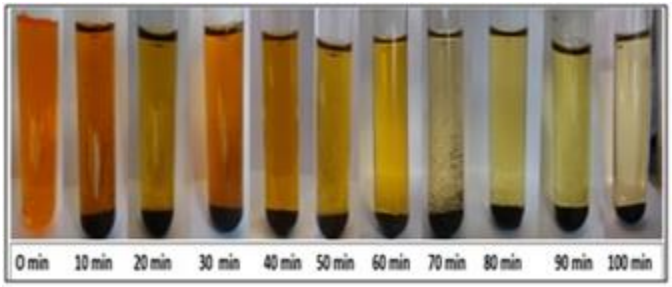

***Figure 6**. Degradation of MO with several time fraction in presence of CuS-Graphene*

The spectroscopic date has been shown in Figure 7 according to which the relative change in the concentration of MO in the presence and absence of different photocatalysts (CuS, CuS/Graphene and Graphene) as a function of time under visible light irradiation. The percentage decolorization of the dye follows the order; Graphene (10.5%) <CuS (68.4%) <CuS/Graphene (80 %). On the other hand, in the absence of photocatalyst, no observable decrease in the dye concentration was seen. The Figure 7 revealed that the nanocomposite of CuS was more photocatalytically active than naked CuS nanoparticles.

Antibacterial activity

The antimicrobial activity was studied using Escherichia coli bacteria. The inhibition zone was measured in millimetres around the 'well' having CuSnanopowdersynthesised at different experimental conditions along with CuS-Graphene composite and has been represented in Figures 9 and 10 and corresponding inhibition zones observed are represented in Table 1. The inhibition zone was for CuS which was prepared with EN at a temperature of 90 ^{0}C, was found to be 32 mm against E. coli and that in case of CuS-graphene composite was found to be 20 mm.

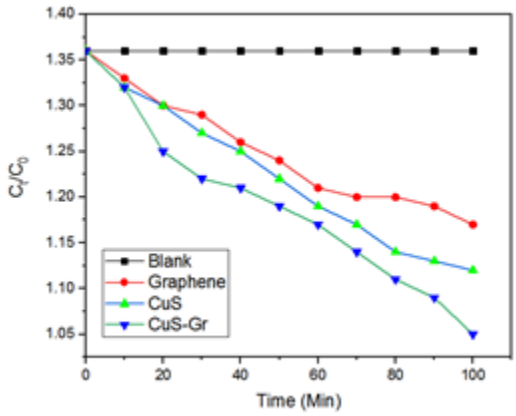

***Figure 7**. Percentage of photo degradation of MO vs solar irradiation time*

***Table 1** Zone of inhabitations against E.Coli with respect to relevant specimens.*

Sl. No.	Types of compound	Zone of inhabitation (Diameter in mm)
1	CuS/90 ^{o}C/EDTA	27
2	CuS/90 ^{o}C/EN	32
3	CuS/70 ^{o}C/EDTA	20
4	CuS/70 ^{o}C/EN	22
5	CuS/50 ^{o}C/EDTA	17
6	CuS/50 ^{o}C/EN	20
7	CuS/Gr/EDTA	0
8	CuS/Gr/EN	20
9	Control 1	---
10	Control 2	---

It should be noted here that in case composite, the amount of CuS is very small in percentage (~30%) and inspite of this it is showing appreciable antibacterial activity towards E-coli bacteria. Moreover it is important to mention here that, the antibacterial activity performed using neat graphene only, does not indicate any inhibition zone. Thus, from above observations it can easily be concluded that the CuS-graphene composite inevitably shows greater antibacterial activity in the present case, which is ascribed due to synergistic effect [26].The CuS prepared with EDTA at temperature 50 ^{0}C had a smallest inhibition zone of 17 mm. While the composite which prepared with EDTA doesn't shows any inhabitation zone.

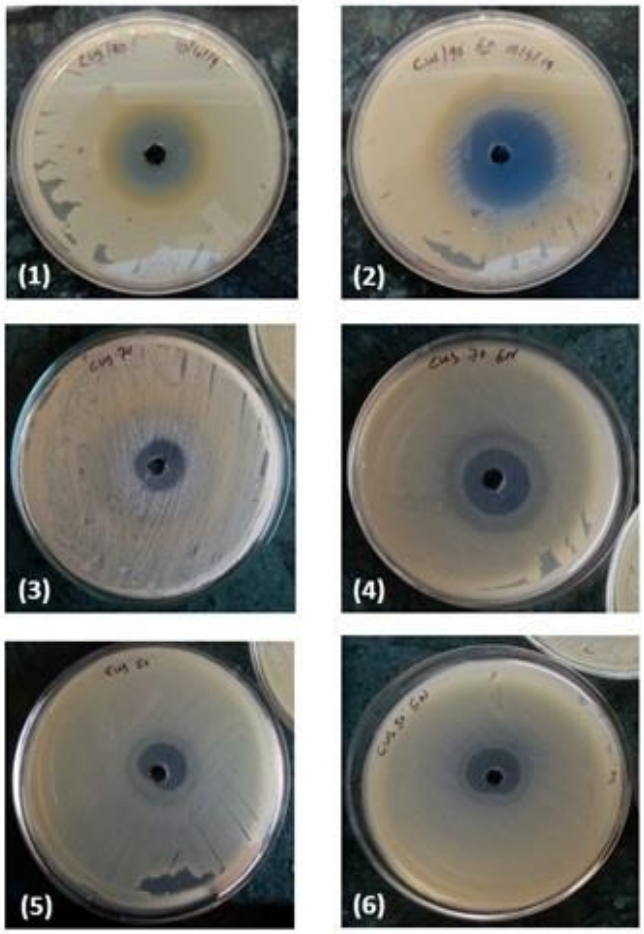

Figure 8 *Zone of inhabitations against E.Coli in presence of CuS prepared with EDTA and EN at different temperatures.*

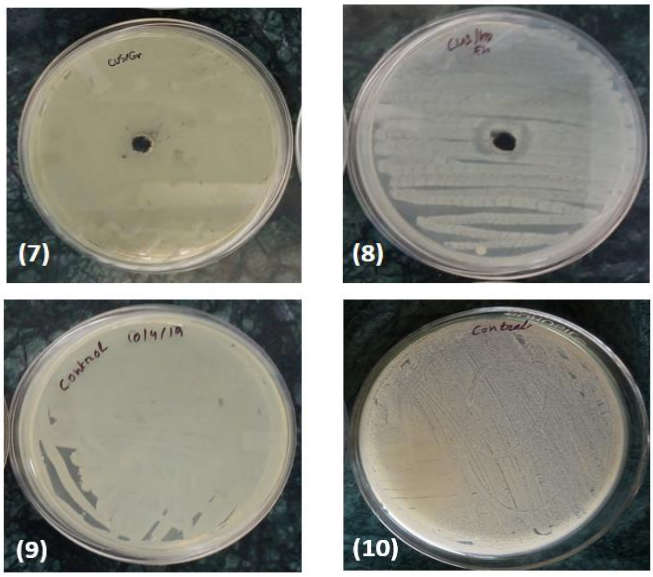

Figure 9 *Zone of inhabitations against E.Coli in presence of graphene composite of CuS prepared EDTA and EN at 90 ^{0}C and controls*

This fact possibly due to formation of some type of organic coating around the sample due to which it inhibits the antibacterial activity and needs further research.

CONCLUSION

CuS nanoparticles was successfully synthesised by wet chemical processes. XRD data and SEM images confirms that particle size varies at different temperatures as increase in temperature particle size increases. The uniformity of distribution of particles on graphene sheets has been confirmed by morphology analysis. It also has been observed that the antibacterial activity also increases with higher particle size as well as in case of the graphene composite in comparison to neat compound. Further, under visible light irradiation the percentage decolorization of the dye follows the order; Graphene (10.5%) <CuS (68.4%) <CuS/Graphene (80%). And Graphene composite of CuS was resulted as a good photo-catalyst.

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