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Studies on biopolymer -Based Nanocomposites reinforced with metallic Nanoparticles

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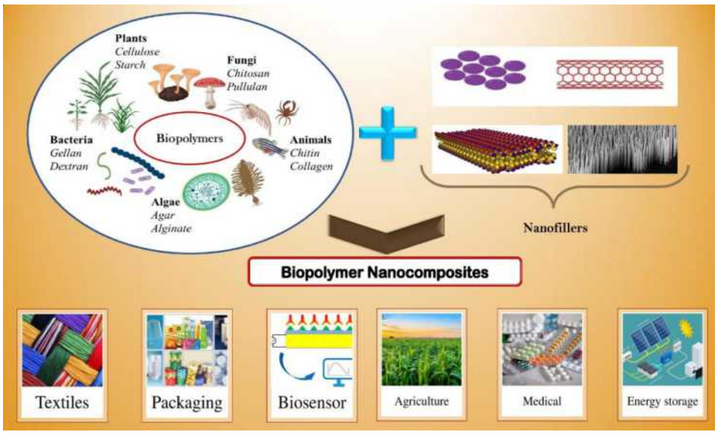
ABSTRACT

Advancements in biopolymer-metallic nanocomposites have led to diverse applications, including drug delivery, biosensing, bone regeneration, solar cells, and supercapacitors. This development supports sustainable progress through a biomimetic approach where the integration of metallic nanoparticles plays a crucial role. This paper reviews how functionalizing metallic nanoparticles using various methods can prevent agglomeration and enhance the thermal, mechanical, and electrical properties of biopolymers. It details the improvements in properties and potential applications achieved by the incorporation of metal-based nanofillers into biodegradable biopolymers. The benefits of metallic nanoparticles such as their high aspect ratio, biocompatibility, low density, and high mechanical strength are highlighted as key factors in boosting biopolymer performance. The review summarizes the mechanism and structural changes in biopolymers to provide researchers with insights into these elements.

Keywords: *Biopolymer-metallic nanocomposites, Drug delivery, Functionalizing metallic nanoparticles, Biodegradable biopolymers, Biomimetic approach*



INTRODUCTION

The size and shape of metallic nanoparticles are the most crucial characteristics that influence their application. The specific uses of metallic nanoparticles depend on their size, shape, and the synthesis method employed. All metallic nanoparticles (MNPs) are particularly appealing due to their unique properties and wide range of applications. It is well established that the size, morphology, dispersity, and physicochemical properties of MNPs are closely linked to their potential applications, all of which are influenced by the synthesis approach used. The phrase "biopolymer nanocomposites" describes biodegradable composites reinforced with natural fibers obtained from plants and animals and with natural or synthetic biopolymers [1-2]. Bio-composites generally exhibit higher stiffness and tensile strength. The adoption of biopolymer composites offers several significant advantages, including sustainability, cost-effectiveness, lightweight characteristics, excellent specific strength, biodegradability, environmental friendliness of renewable resources, and enhanced health and safety for both manufacturers and consumers [3-5].

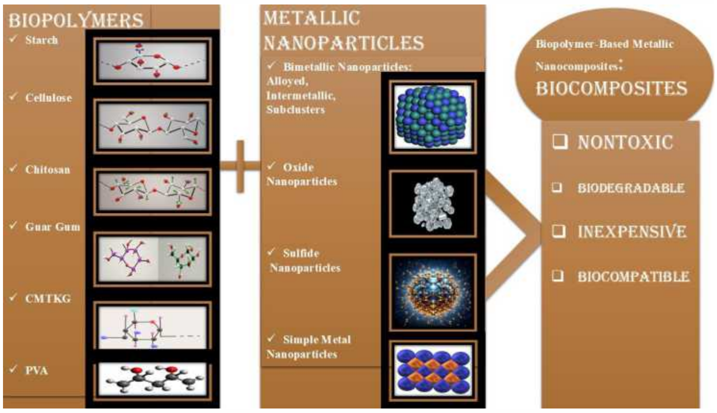


Figure 1: introduction of biopolymer-based metallic nanocomposite

Metal or metal oxide nanoparticles synthesized using biopolymer represent a new class of hybrid inorganic /biopolymer materials possessing distinctive properties and applications that are not present in either inorganic nanoparticles or biopolymer host material [6]. These hybrid materials are known as biopolymer-synthesized nanoparticles (BSNPs). Biopolymers-based nanocomposites, which consist of biopolymers reinforced with nanoparticles exhibit mechanical and barrier properties [7] (Figure 1). However, these properties depend on the type, dispersion level, and concentration of nanoparticles within the polymer matrix. Metal and metal oxide nanoparticles are incorporated into the polymer phase of biopolymer-based nanocomposites using in-situ and ex-situ methods.

Metals and metal oxide nanoparticles possess unique properties including chemical stability and mechanical strength, making them attractive for various applications. However, these nanoparticles often experience a reduction in effectiveness as they convert their high surface area to lower volumes. This review represents the various methods for synthesizing metal precursor nanoparticles, utilizing metal and metallic oxides such as gold, silver, magnetite, cobalt, and zinc. Unique biopolymer-metal nanocomposites (BMNCs) have a wide range of applications, including biosensing [11], drug delivery [8], Novel time-temperature indicators, antimicrobial treatments [9], environmental remediation, chemical-pharmaceutical applications, the food industry uses, DNA carriers, antifouling, wound healing, and the adsorption of organic and inorganic impurities [10].

1. Synthesis of metallic nanoparticles

The term nanoparticles originates from the Greek word meaning **dwarf or small** when used as a prefix it signifies a size of 10^{-9} equivalent to one billionth of a meter or 1 nm. Nanoparticles exhibit properties and characteristics of both solute and separate particle phases. Their surface-to-volume ratio is 35-45 % higher than larger particles or atoms [12]. Metal nanoparticles are entirely synthesized from metal precursors. These NPs exhibit distinctive properties including large surface area, electronic and optical properties, magnetic properties, mechanical properties, and thermal properties. Primarily due to their well-known localized surface plasmon resonance (LSPR) features [13]. Owing to their superior properties, metal nanoparticles are utilized in various research fields, including drug and medication development, manufacturing and materials science, environmentally sustainable products, sensors, heavy metals removal, and energy harvesting [14-16]. Nanoparticle synthesis can be achieved in several methods, broadly classified into two main categories: (1) Bottom-up and (2) Top-down approaches, as shown. These approaches are further subdivided into various subclasses depending on the operations, and reaction conditions **(Figure 2)**.

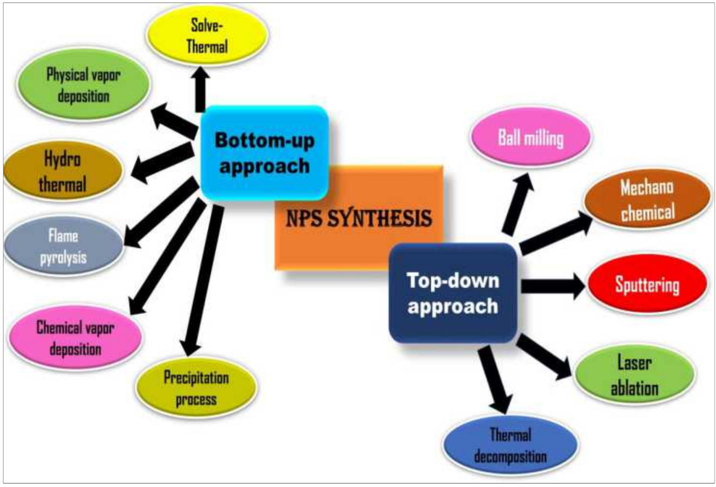


Figure 2: Represents the various methods of metallic NPs synthesis

1.1 Top-down approach for metallic NPs synthesis

In this approach, the bulk material is broken down into nano-sized particles. The process of nanoparticle preparation relies on size reduction of the initial material through various physical and chemical treatments. Top-down methods are straightforward to perform. Along with some benefits, it has some disqualifications as they are not well-suited for creating irregularly shaped or very small particles. A major issue with this method is that it can lead to changes in the surface chemistry and physicochemical properties of nanoparticles [17].

1.2 Bottom-up approach for metallic NPs synthesis

The bottom-up approach to nanoparticle synthesis involves constructing nanoparticles from smaller units, such as atoms, molecules, or tiny particles. In this method, the nanoparticles are formed by first creating nanostructured building blocks, which are then assembled to produce the final nanoparticles. The bottom-up approach, often referred to as the precipitation technique, allows for the stabilization of particles at an early stage of formation and facilitates the production of nanoparticles [18].

Table 1. Overview of metallic nanoparticles preparation method and their applications

Metallic NPs	Method	Size(nm)	Shape	Application	References
Zn	Precipitation	21-25	Hexagonal	Capping and stabilizing agent	**[19]**
Fe	Precipitation	26-42	Semi-spherical	-	**[20]**
Cu	Hydrothermal	12-16	spherical	Antibacterial and antifungal agents	**[21]**
Ag	Hydrothermal	70-192	Spherical	Biomedical devices	**[22]**
Au	Mechano-chemical	-	Triangular	Therapeutic applications	**[23]**
Ti	Chemical deposition method	-	Spherical	Dye degradation	**[24]**

2. Biopolymer Based Matrices

Materials predominantly made of biopolymeric frameworks, with nanofillers dispersed throughout the structure, are termed Biopolymer-based Matrices [25]. These matrices have found widespread use in various applications, such as electronics and biomedical fields, due to their processing flexibility and the competitive cost of the final products [25-26]. Biopolymer-based matrices are crucial in nanotechnology due to their sustainability and biodegradability [27]. Each type of biopolymer, including polysaccharides, proteins, and nucleic acids, has unique features that make them ideal for different uses in nanotechnology [28]. The incorporation of functional nanomaterials into biopolymer matrices improves their physicochemical properties, such as mechanical strength, barrier performance, and biocompatibility. These enhanced characteristics make the matrices well-suited for a wide range of applications, including drug delivery and packaging [29].

Table 2. Overview of Various Synthesized Matrices Incorporating Different filler and their applications

Biopolymer	Nanomaterial Incorporated	Synthesized Matrices	Applications	References
Chitosan	Silver Nanoparticles,Hydroxyapatite, Cellulose Nanocrystals	Chitosan nanocomposites, Chitosan-based hydrogels	Drug delivery, wound healing	**[30]**
Pectin	Silver Nanoparticles (Ag NPs)	Film	Antimicrobial coatings	**[31]**
Alginate	Zinc Oxide Nanoparticles (ZnONps)	Alginate beads, Alginate nanocomposites	Water disinfection	**[32]**
CMGG	-	CMGG nanoparticles	Drug Carrier	**[33]**
Chitosan	-	Chitosan/ZnO nanoparticles	Antimicrobial and UV Protection to Cotton Fabric	**[34]**
Guar Gum	Nanocrystalline Cellulose	Nanocomposite Films	Biodegradability, Food packaging	**[35]**
PVA	Cadmium Sulfide (CdS) nanoparticles	CdS/PVA nanocomposite films	-	**[36]**
CMTKG	ZnONps (Zinc Nanoparticles)	CMTKG/ZnO nanocomposite	Antifungal, hazardous metal removal agent	**[10]**

2.1 Properties And Applications of Biopolymer-based matrices

Biopolymer matrices are distinguished by their biodegradable characteristics, diverse architectures, and effective interaction with cellular environments [37]. They typically exhibit advantageous mechanical properties, including improved tensile strength and flexibility, which render them suitable for a range of applications in tissue engineering and drug delivery [38-40]. Additionally, these matrices demonstrate exceptional biocompatibility, facilitating cell adhesion and proliferation while reducing inflammatory responses [41]. The inclusion of functional additives and modifications can further enhance their properties, enabling customized solutions for biomedical applications [42]. The structural integrity of biopolymer matrices is influenced by their composition and the conditions under which they are formed. For instance, matrices made from chitosan and silk fibroin exhibit specific morpho-functional properties that can be tailored for various applications, particularly in the biomedical field [43-44]. An example of the properties of one such matrix, Biopolymer-based nanocomposites is explained in **(Figure 3)**. Biopolymer matrices are widely applied across numerous fields, particularly in biomedical contexts such as drug delivery, tissue engineering, and wound healing [45]. Their biocompatibility and biodegradability make them ideal for developing scaffolds that promote cell growth and tissue regeneration, aiding in the repair of damaged tissues [46-47]. Moreover, biopolymer matrices are utilized in the creation of hydrogels and microspheres, which function as efficient carriers for therapeutic delivery [48]. In the food industry, they are employed as matrices for encapsulating bioactive compounds, thereby enhancing food preservation and the delivery of nutrients [49]. Overall, these materials hold the potential to transform industries ranging from healthcare to food production due to their versatile properties and functionalities [50].

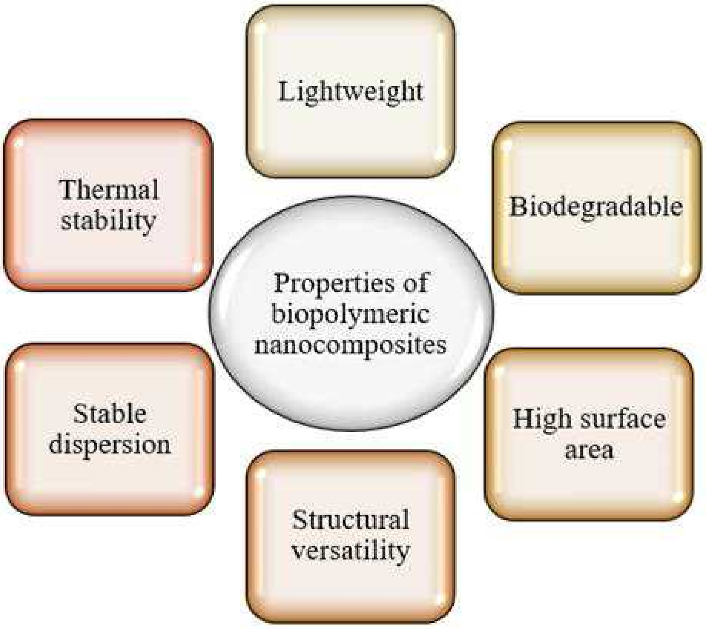


Figure 3. Properties of biopolymer-based nanocomposites

3. Fabrication of metallic nanoparticle-reinforced biopolymer-based nanocomposites:

Biopolymer composites are materials composed of multiple integrated layers, forming a resin reinforced with an appropriate filler [51]. The preparation of high-quality polymer nanocomposite samples using a suitable processing method is essential to attain superior performance in polymer nanocomposites. The preparation technique significantly impacts the thermal, electrical, and mechanical properties of the resulting nanocomposite. Achieving a uniform polymer nanocomposite requires a well-dispersed nanofiller, as these fillers tend to agglomerate, stack, and exhibit incomplete exfoliation when interacting with the matrix [52,53]. The preparation methods for nanocomposites are summarized in **Table 3**, including their associated properties and applications.

Table 3. Overview of nanocomposite preparation methods, properties, and applications

Composite	Preparation method	Properties	Application	References
Polyvinyl alcohol/ZnO/Na-montmorillonite	Melt extrusion	Antimicrobial, water, and oxygen barrier	Packaging	**[54]**
MnO_2 NWs/Chitosan	In-situ polymerization	Excellent compressive strain, smooth evaporation rate, solar-to-thermal energy conversion efficiency	Soar-steam generation	**[55]**
Polyvinyl alcohol (PVA)/Au NPs/ Carboxymethyl chitosan	Electrospinning	Antibacterial	Biomedical Uses	**[56]**
Graphene oxide-Ag-PVA	Solvent casting	Excellent dielectric properties	Charge storage devices	**[57]**
PVA/Guar-gum/Ag	Solution casting	UV-barrier	Food packaging	**[58]**
Guar-gum/$NiWO_4$	Sol-gel	Antioxidant	Dye removal	**[59]**
Cellulose/TiO_2	Precipitation	Antibacterial	Food packaging, Biomedical field	**[60]**

Extrusion

Extrusion is a commonly used technique for processing thermoplastic polymers, valued for its Eco-friendliness (solvent-free) and cost-effectiveness. The process usually involves twin-screw extrusion, applying high temperatures and controlled mechanical energy rapidly. Fine-tuning the extrusion parameters is critical for achieving the specific properties of the material, especially in nanocomposite applications [61].

3.2. In-situ polymerization

This polymerization technique enables the effective dispersion of nanofillers within the polymer matrix by incorporating an initiator or thermal/photocatalyst. It offers a more uniform distribution of nanofillers compared to other methods and is relatively simple. However, intergallary polymerization can be challenging, limiting its applications [63].

3.3. Electrospinning

Electrospinning is highly regarded for its capability to produce structures with random orientations that closely resemble the three-dimensional collagen fibers in the extracellular matrix (ECM) of normal skin. This technique relies on electrical potential to generate nanofibers. The flexibility of electrospinning, including methods like coaxial and emulsion electrospinning, broadens its potential applications [62].

3.4. Solution casting

Solution casting is a simple technique where two or more solutions are mixed and cast onto a Teflon plate for processing. Governed by Stokes' law, it requires minimal processing time. In this method, the polymer matrix is dissolved in the solution, while nanoparticles are dispersed within the same or separate solutions. This technique is primarily used to fabricate films [58,62].

3.5. Sol-gel

The sol-gel process, as the name suggests, involves developing inorganic networks by first creating a colloidal suspension (sol) and then gelating this sol to form a continuous liquid-phase network (gel). It is a widely used chemical method for producing high-purity materials in various forms, including powders, thin-film coatings, fibers, monoliths, and self-supported bulk structures [63].

4. Applicationsof metallic nanoparticle-reinforced biopolymer-based nanocomposites:

Recent advances in biopolymers have sparked significant interest across various fields, primarily due to their enhanced properties and the potential for easy commercialization. Innovations in the synthesis, processing, and functionalization of biopolymers have led to the development of materials with improved mechanical strength, thermal stability, and biodegradability. These advancements have made biopolymers more versatile and suitable for a wide range of applications, from packaging and agriculture to medicine and environmental sustainability [64,65]. The diverse applications of biopolymer nanocomposites reinforced with metallic nanoparticles are particularly significant, as they leverage the distinct properties of both biopolymers and metallic nanoparticles to enhance performance and functionality across a range of sectors [66]. In biomedicine, these nanocomposites are increasingly used for targeted drug delivery systems, allowing for controlled release of therapeutic agents, with metallic nanoparticles such as silver or iron oxide enhancing targeting precision and overall efficacy [67-69]. Their inherent antibacterial properties make them ideal antimicrobial agents in wound healing, where they help prevent infections while promoting tissue regeneration. Additionally, biopolymer nanocomposites are utilized in tissue engineering as scaffolds that provide supportive structures for cell growth, with their mechanical and biological properties being easily tailored through the choice of nanoparticles [70]. Table 4 gives an overview of the application of Biopolymer-based metallic nanocomposites.

Table 4. Overview of the application of Biopolymer-based metallic nanocomposites

Biopolymer matrix	Metallic Nanofiller	Enhanced properties	Application	References
Chitosan	ZnO NPs	Film with Improved hydrophobicity	Antioxidant agent	**[71]**
Cellulose /Sodium alginate	CuO NPs	A film with Improved Antibacterial Properties	Food packaging	**[72]**
Carboxymethyl TKP	Au NPs	Enhanced photo-oxidization ability	Photo catalytical activity of NO removal	**[73]**
Tamarind kernel powder	ZnO NPs	Fim with enhanced mechanical and water vapor barrier	Antimicrobial agent	**[74]**
Guar gum/PAA	Ag NPs	Enhanced catalytic behavior	Antibacterial and catalytic agent	**[75]**
Guar gum	CuO NPs	Photocatalytic property enhanced	Removal of organic pollutants	**[76]**
Guar-gum	Ag-Cu NPs	A film with enhanced thermos mechanical and O_2 barrier properties	Food packaging	**[77]**
PVA	Ag NPs	Enhanced refractive index	Anti-reflective coating agent	**[78]**
PVA	TiO_2	Enhanced optical conductivity and absorption capacity	Electronic devices	**[79]**
TKP	Ce NPs	Enhanced adsorption capacity	Metal removal	**[80]**

Beyond biomedicine, these materials play a crucial role in environmental remediation by effectively removing pollutants due to their high surface area and reactivity [81]. In the food packaging industry, biopolymer nanocomposites offer enhanced barrier properties against moisture, oxygen, and UV radiation, helping to preserve food quality and safety [82]. They also find applications in biosensing and bioimaging, where the incorporation of metallic nanoparticles enhances signal detection, contrast, and image resolution, thereby improving the accuracy and effectiveness of diagnostic techniques [83,84]. Biopolymer nanocomposites enhance agricultural applications by enabling the controlled release of pesticides and nutrients, improving efficacy while reducing environmental impacts [85]. In lithium-ion batteries, these nanocomposites improve thermal stability and ionic conductivity when used as separators, enhancing battery performance and safety [86]. Additionally, as proton exchange membranes in fuel cells, the presence of metallic nanoparticles increases proton conductivity and mechanical strength, leading to more efficient fuel cell operation [87]. Biopolymer nanocomposites are increasingly used to enhance the durability and functionality of textile materials, particularly cotton fabrics. Functionalizing textiles through methods like plasma treatment, grafting, and nanoparticle deposition can impart valuable properties. Incorporating nanoparticles into these fabrics provides antimicrobial activity, ultraviolet (UV) protection, and increased hydrophobicity [88]. (Figure 4) represents some of the important applications of the biopolymer-based metallic nanocomposites.

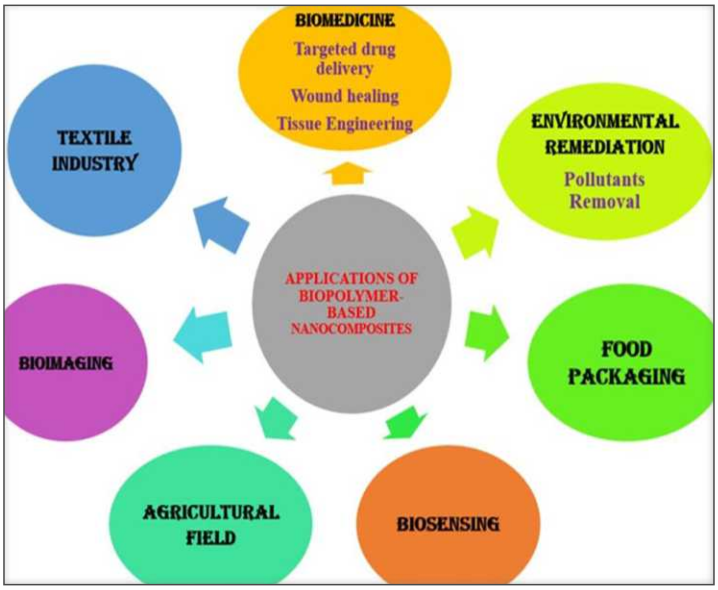


Figure 4. Applications of biopolymer-based metallic nanocomposites

Overall, the recent advancements in biopolymers and their nanocomposites open up new possibilities for innovation across multiple fields, providing sustainable and high-performance alternatives to traditional materials. The ease of commercialization, combined with their environmental friendliness and multifunctional capabilities, positions biopolymer nanocomposites as key materials in the advancement of technology and sustainability initiatives.

5. CONCLUSION

The development of biopolymer-based nanocomposites reinforced with metallic nanoparticles represents a significant advancement in material science, combining the inherent advantages of biopolymers with the enhanced properties provided by metallic nanoparticles. These nanocomposites exhibit improved mechanical strength, thermal stability, and antimicrobial activity, making them highly suitable for a wide range of applications, including packaging, biomedical devices, and environmental remediation. The integration of metallic nanoparticles into biopolymer matrices not only enhances the functional properties of the resulting composites but also introduces new possibilities for tailored materials that can meet specific industrial and environmental requirements. This innovative approach aligns with the growing demand for sustainable materials, offering a pathway to reduce reliance on traditional petroleum-based plastics while enhancing performance characteristics. However, the future success of these materials hinges on overcoming challenges related to scalability, cost-effectiveness, and environmental impact. Continued research and development in this field are essential to optimize fabrication techniques, ensure the safe and effective use of metallic nanoparticles, and explore the full potential of biopolymer-based nanocomposites. As these challenges are addressed, the adoption of such materials is likely to increase, paving the way for a new era of sustainable, high-performance materials in various industries.

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CONFLICT OF INTEREST

There are no conflicts of Interest to declare.

DATA AVAILABILITY

All the data supporting this review are present with the authors and will be provided in case of request is made.

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