Global Journal of Engineering and Technology Advances
eISSN: 2582-5003
Cross Ref DOI: 10.30574/gjeta
Journal homepage: https://gjeta.com/

(RESEARCH ARTICLE)

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SiO_2@Cu core: antibacterial, "shell" active agents synthesized through sol-gel

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Global Journal of Engineering and Technology Advances, 2023, 14(02), 141–149

Publication history: Received on 06 January 2023; revised on 21 February 2023; accepted on 24 February 2023

Article DOI: https://doi.org/10.30574/gjeta.2023.14.2.0034

Abstract

We examined the capacity of SiO_2@Cu core-shell nanoparticles to inhibit *Escherichia coli* and *Streptococcus mutaus*. Before and after the addition of silicate, copper showed a surface plasmon resonance (SPR) with a peak in the 620–630 nanometers' region. SiO_2@cu core-shell nanoparticle manufacturing was further demonstrated to have a spherical shape, as demonstrated in TEM. The crystal structure of the SO_2 @cu we found matches the X-ray diffraction patterns for the nanoparticles, which display Face-Centered Cubic (FCC) copper. The infrared Fourier transform (FT-IR). Explains more about the studied interaction of the produced copper NPs with silica. This demonstrated Cu deposition on the spherical silicate (SiO_2) surface and the mean size of these nanoparticles was 139 nanometers. SiO_2@Cu core-shell nanoparticles were definitely the cause of the inhibitory zone, and they were effective against *Escherichia coli* bacteria and *Streptococcus mutans* within ranges of 12–20 mm and 28–34 mm, respectively.

Keywords: Nanoparticles; Sol-gel; SPR; Antibacterial; Inhibition zone

1. Introduction

Nanoparticles are employed in biomedical and biological applications because nanotechnology is progressively playing a significant role in the field of biomedicine. Recent investigations have discovered that a variety of metallic nanoparticle types, including silver, copper, and zinc, exhibit antibacterial properties [1]. Numerous organizations claim that copper is an effective antibacterial agent; thus, it appears that little copper particles were chosen as the ingredient. Particularly important when administering conventional antibiotics with low damage. For instance, Sol-gel synthesis was used to create mesoporous, copper-doped silica xerogels with antibacterial characteristics. [2]. The antibacterial activity of nanoparticles is correlated with their size and shape. Due to their superior physical and chemical characteristics compared to those of its component parts, core-shell composite structures are a form of new nanoparticle that has garnered considerable interest.

So far, various attempts have been made to produce these peculiar core-shell nanoparticles. [3].Because of their outstanding physicochemical properties, novel metal nanoparticles have received a lot of attention in a variety of fields. Ag and Au's nanoscaled particles have been extensively studied in this area due to their attractive optical characteristics. To create high-performance materials, it is essential to be able to control the particle's size and shape. The materials can be synthesized, which is an important process, using alumina, titanium dioxide, polymer matrices, mesoporous silica, or other supporting materials. [4] These auxiliary components might also serve as inventive hosts to paralyze—Nobel metal nanoparticles. Recently, there has been a great deal of research into these core-shell or hybrid structures, partly because of their unique properties that make them appealing for application in optical and biological sensors and optoelectronic devices. [5] The monolayer coverage is crucial as the shell's chemistry is unique to coating techniques. The monolayer of oxide shell materials is quite complex, requiring a variety of techniques, and scaling up is challenging. For this purpose, oxide nanospheres with almost identical diameters and great compositional flexibility are ideal. A high

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nucleation "rate" but a moderate growth rate are required to create hybrid structures with a high number density of metal nanoparticles without the formation of aggregates. Zeolites and carbon fiber are inorganic supports for antibacterial substances, including silver, as far as is now recognized. [6[Cu has been used as an antibacterial agent for a very long time. This is crucial in conventional antibiotic therapy since it is an efficient medication with low toxicity. A number of techniques, including laser ablation, chemical vapor deposition, Sonochemistry reduction, microemulsion methods, and supercritical techniques, have been used to create the synthesis. [7] These synthetic procedures require expensive equipment and take a lot of time. When made with the aforementioned methods, Cu nanoparticles are easily prone to aggregate, which damages their chemical composition and reduces their antibacterial effectiveness. When chemical persistence is necessary, organic compounds, the cornerstone of many antibacterial treatments, generally perform poorly. However, if Cu is deposited on a supporting material, its release time may be postponed for a long period of time. However, inorganic molecules supported on copper can get around this problem. Cu nanoparticles' antibacterial abilities have not yet been extensively covered in papers. Due to their strong antibacterial activity and superior chemical resistance, metal (Cu or Ag)-supported silica materials such as silica glass and silica thin films are projected to be particularly feasible alternatives for antibacterial materials [8,9]. Understanding the antibacterial effect of nanomaterials requires understanding how nanoparticles adhere to the surfaces of microbes and how these materials are digested within microorganisms. However, research is still required to develop effective antibacterial compounds with unique properties that can provide controlled release of copper ions. Copper-based nanoparticles and nanoparticles' antibacterial properties are largely unknown at this time. [10,11]. This work used the chemical sol-gel technique to create SiO_2@cu core-shell nanoparticles [12]. Before being combined with silica, copper nanoparticles are spread out using ultrasound. Investigating the antibacterial activity of copper nanoparticles against *Escherichia coli* and *Streptococcus mutans* as well as the final spherical SiO2@cu core-shell form.

2. Material and methods

2.1. Materials

Sigma-Aldrich Co. supplied the tetraethyl orthosilicate (TEOS, 99.8%; Aldrich Co., 99 %). In addition, ammonia water (NH3H2O, 25 %) (China) and cetyltrimethylammonium bromide (C T A B) (98 %) were used to increase the pH and speed up the reduction reaction in water. Copper sulfate pentahydrate (CuSO4. 5 H2O, 98 %), Sigma-Aldrich; ethanol (98 %); and cetyltrimethylammonium bromide (C T A B) (98 All of them were bought from Sigma Aldrich. All the trials utilized deionized water.

2.2. SiO_2@Cu core-shell nanoparticle preparation

2.2.1. Method

Table 1 Lists chemicals used in preparation along with their weights

S	Code No.	TEOS ml	Ethanol ml	Cuso4 .5H_2O g.	D.W ml.	NH_4 OH ml.	CTab g.	Fe g.
1	17	0.75	25	2.4	5	2.5	0.05	0.1
2	18	0.75	25	1.2	5	2.5	0.05	0.1
3	19	0.75	25	0.6	5	2.5	0.05	0.1
4	20	0.5	15	2.4	5	2.5	0.05	0.1
5	21	0.5	15	1.2	5	2.5	0.05	0.1
6	22	0.5	15	0.6	5	2.5	0.05	0.1
7	23	0.25	10	2.4	5	2.5	0.05	0.1
8	24	0.25	10	1.2	5	2.5	0.05	0.1
9	25	0.25	10	0.6	5	2.5	0.05	0.1

Tetraethyl orthosilicate (TEOS), tetraethyl orthosilicate (98 %), 0.5 mol, $CuSO_4.5H_2O$ (3 mM), ethanol, Ctab (0.14 mM), and Fe power were used to deposit Cu nanoparticles to the surface of Sio2 spheres (as given in Table 1). The Stobers method was used to create a typical spherical Sio2 [13]. The conventional pre-processing method went as follows: in

the first stage, TEOS (Si(OC2H5)4) and ethanol solutions were blended, Ctab was added, and solution number 1 was assigned. Using deionized water and 2.5 mL of ammonia, solution 2 was created (10 mL). The addition of solution 2 was then made gradually while solution 1 was vigorously agitated for 24 hours at 24 °C. To separate and clean the water-washed particles, they were centrifuged at 10,000 rpm for ten minutes. To create copper-loaded silica nanoparticles, copper sulfate was added to the solution containing SiNPs in step two. The core-shell is made of SiO_2@cu. NPs were cleaned with water after 4 hours of whirling on the magnetic stirrer by centrifugation at 10,000 rpm for 10 minutes.

2.3. Nanoparticle characteristics Equations used X-ray analysis

As a result of XRD examination, the d-spacing (the inter-planar spacing between the atoms) was determined using equation (1) of the Bragg law, and

$$2d \sin \theta = n \lambda \text{ .....(1)}$$

Where d is the inter-planar distance between atoms, n is an integer (n= 1), and

λ = 0.15418 nanometers for Cu Ka.The average crystallite size was determined using equation (2) of the Debye-Scherrer equation.

$$D = \frac{K\lambda}{FWHM \cos\theta} \text{ ..... (2)}$$

λ = 0.15418 nanometers for Cu Ka, FWHM stands for full width at half maximum, λ is the diffraction angle, and D is the mean crystallite size. Where k is a numerical constant factor of (0.89). the equation 3 calculate the lattice parameter (a) [14].

$$\boldsymbol{a = d\sqrt{h2 + k2 + l2}} \text{ ..... (3)}$$

Miller's index serves as the cartesian coordinate representation for cubic crystals (h k l).

2.4. Evaluation of the antimicrobial effect

The diffusion method has been used to test the composite membrane's antibacterial properties against gram-positive Streptococcus mutants and gram-negative *E. coli* bacteria. [15]. Cut into disk shapes with a 10 mm diameter were the test specimen and an untreated control.for the disk diffusion procedure, and both were autoclave sterilized for 15 minutes at 120 °C. They were then put on individual agar plates with cultures of *E. coli* and S. aureus, and they were cultured for 24 hours at 37 °C while the inhibitory zone was being watched.

3. Results and discussion

3.1. FTIR

The FTIR spectra's peaks at 1085 cm-1 and 795 cm-1, respectively, confirmed the traits of Si-O-Si stretching and Si-O bending [16]. Further evidence for the generation of SiO_2 @cu was provided by Fourier transform infrared (FTIR) spectra, as shown in Fig. 1. The peaks at 960 cm-1, 1632 cm-1, and 3436 cm-1, which were connected to the Si-OH, OH bending, and OH stretching on SiO_2 surfaces, respectively, showed that the hydroxyl group was adsorbed on SiO_2 surfaces. The peaks were relocated to larger waves, such as 2916 cm-1 and 1423 cm-1 to 1438 cm-1. The outcomes could be proof that Cu NPs developed in the silica matrix created by Stober's technique. The coordination with Cu nanoparticles is revealed by the change in wave numbers brought on by C=C stretching. A peak also shows a 628 cm-1 peak. Copper nanoparticles are perhaps susceptible.[16, 17].

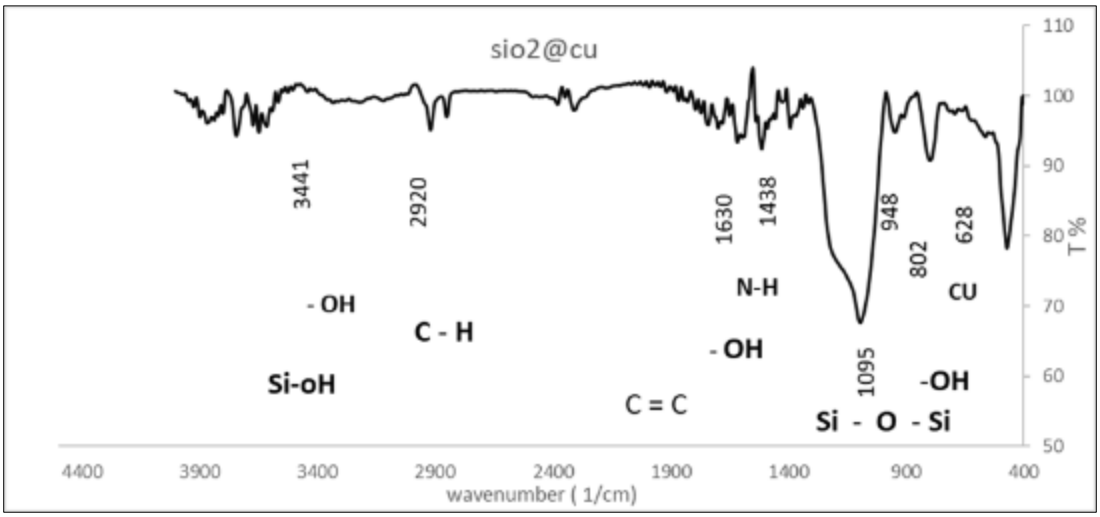

Figure 1 The FTIR spectrum of Sio2@cu core-shell nanoparticles

3.2. UV-visible spectrum

Qualities of light Because of the free electron, Nobel Metals Nanoparticles (NMNP) have been given the name Surface Plasmon Resonance (SPR), which characterizes it as a widespread oscillation of the electrons in the conduction band with frequency in the visible range [18]. As a result, plasma-restricted NMNP exhibits large fluctuations due to the electromagnetic field produced by the incoming light. The Plasmonic of NP has a wide electromagnetic spectrum absorption band that extends from UV to IR. Following when copper ions are exposed to the reducing and capping agent, they are reduced to Cu NPs.color changes and spectroscopic methods like UV-visible may occur. The color began to change when the reducing agent was added to the copper ions' aqueous solution as a result of the surface plasmon resonance, which pointed to development of copper nanoparticles. According to UV-visible spectroscopy, A dark brown hue with a wavelength of around 620 nanometers quickly replaced the solution's initial bright color.It is also visible that the peak of the wavelengths shifted to a higher wavelength (630 nanometers) as a result of the copper-loaded silica nanoparticles. (Fig. 2).

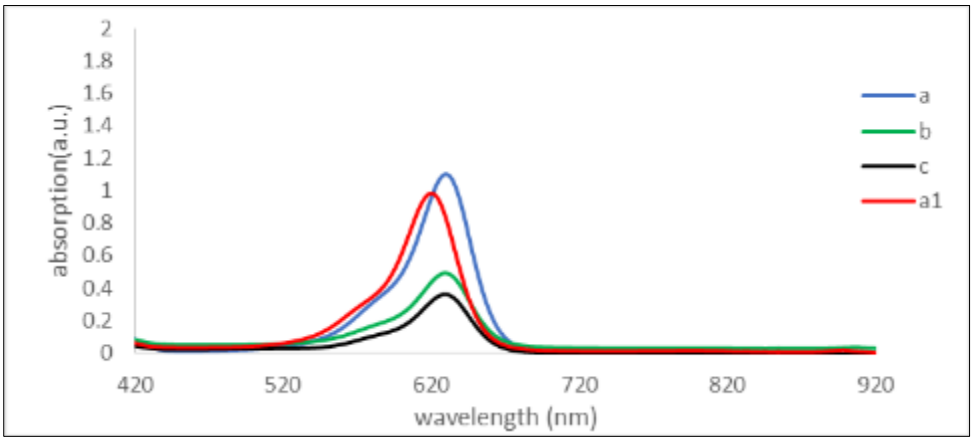

Figure 2 UV-vis absorption spectra for(a1, a, b, and c) different concentrations of **SiO_2** @cu core-shell

3.3. X-Ray Diffraction

XRD was used to confirm the nanoparticles' size and crystal structure. Figure 3 displays the XRD pattern of the sol-gel generated SiO_2@cu core-shell nanoparticles. The metallic Cu's (111), (200), and (220) planes are connected to peaks at 2 values of 43.29, 50.39, and 74.27, respectively. According to the XRD analysis, the copper nanoparticles produced have a face-centered cubic structure (FCC). Pure FCC (Face-Centered Cubic) sample peaks resembled those of the normal JCPDS Card No. 04-0836 quite a bit. In addition to the copper peaks, other X-ray diffraction peaks appear after the metal has been covered with silica. Figure 4 displays the XRD pattern of the SiO_2@cu core-shell nanoparticles made by the sol-gel technique. Peaks are observed at 2 values of 23.41, 41.65, 43.6, 45.28, 48.75, and 50.28, which are, respectively,

SiO_2@cu planes of 100, 110, 111, 200, 003, and 200. (102). These peaks were associated with the usual JCPDS Card Nos. 01-081-0069 and 00-001-1241 for SiO2 and copper, respectively [18, 19].

Using the JCPDS (Joint Committee on Powder Diffraction Standards) database, the mean size of nanocrystals was calculated from the broadening of the diffraction peaks corresponding to the strongest reflections. The crystallite size was calculated from the nanoparticle XRD diffraction pattern using the Scherrer equation. The results of the X-ray diffractometer study demonstrate that the synthesized Cu-NPs have a face-centered cubic (FCC) crystal structure of Cu with a lattice constant of 0.36 nanometers measured by equations 1 and 3, which is in good agreement with the standard lattice parameter (a = 0.3615 nanometers). According to calculations using Scherrer equation 2 and JCPDS card number 04-0836, the mean size of the crystalline copper and SiO_2@cu nanoparticles (D) was roughly 47.08 and 133.3 nanometers, respectively.

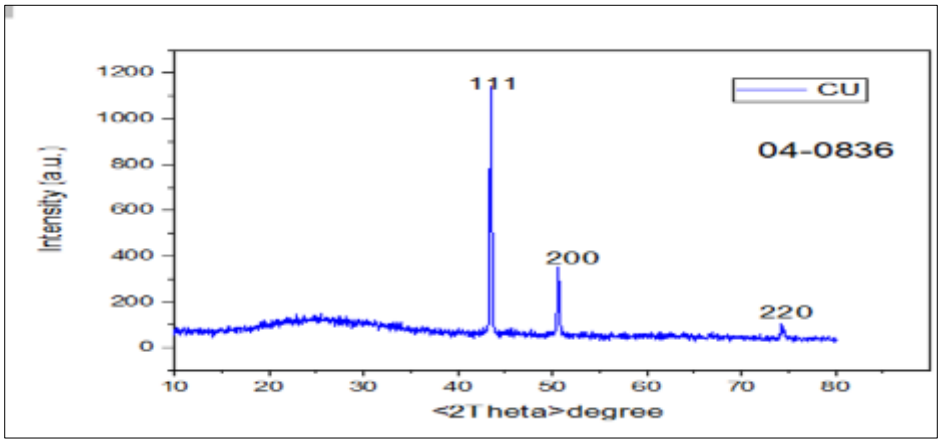

Figure 3 CuNps' XRD patterns

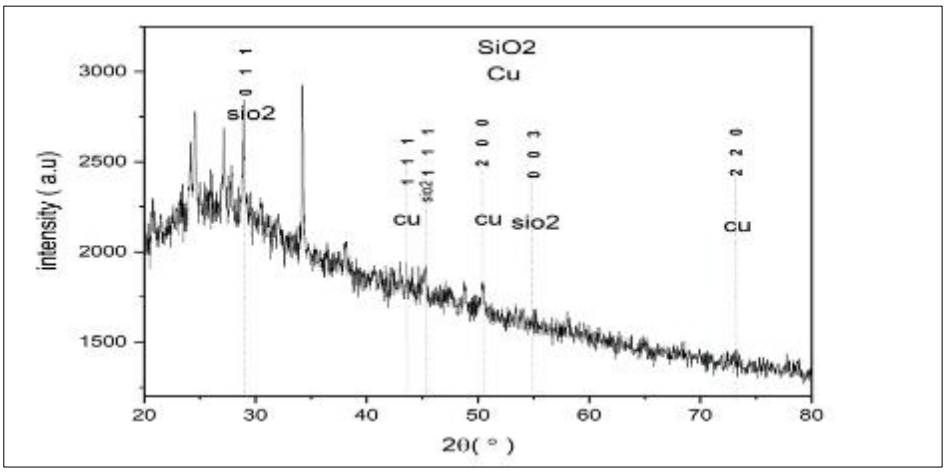

Figure 4 A **SiO_2**@cu core-shell XRD patterns

3.4. TEM and EDX

TEM image analyses are helpful tools for determining the size and form of the produced SiO_2@cu core-shell NPs, which have a spherical appearance with copper loaded around them. It should be emphasized that the copper-metal NPs used in the TEM pictures were loaded with silicate. The particle size distribution is shown in Fig. 5, and the histogram in Fig. 6 reveals that the mean size of SiO_2@Cu core-shell NPs is 157 nanometers, and also has a wide size range; the SiO_2@cu core-shell diameter ranges from 110 to 188 nanometers. The EDX measurement in Fig. 7 demonstrates how copper is produced and how it is deposited on the surface of silicate (SiO_2) nanoparticles.

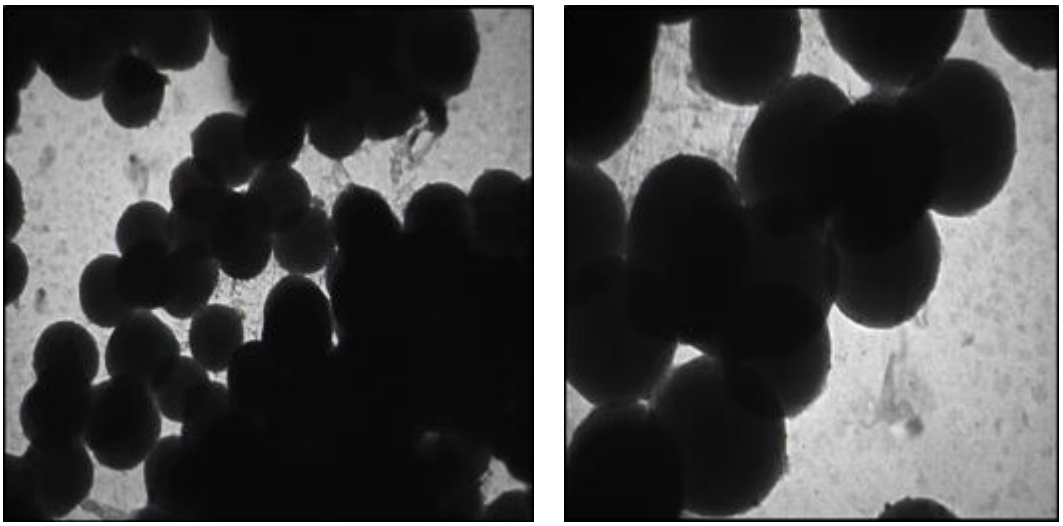

Figure 5 TEM pictures of **SiO_2** @cu core-shell nanoparticles

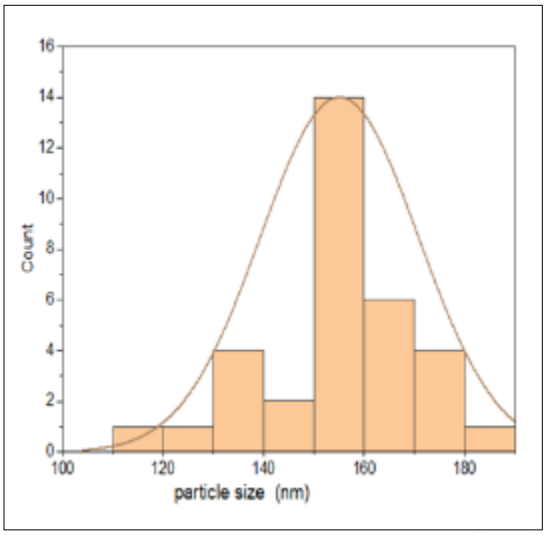

Figure 6 Particle size histograms of Sio2@cu core-shell NPs

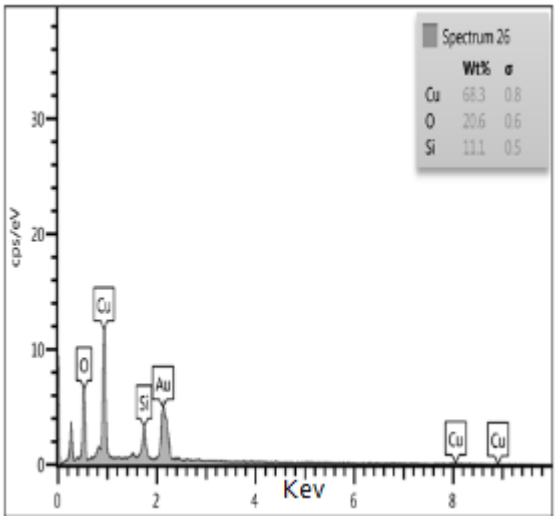

Figure 7: EDsDiagram showing the presence of copper Nps and silica

3.5. Evaluation of Antibacterial of SiO_2@cu core shell

Inhibitory zones are employed to qualitatively assess the antibacterial capabilities of SiO_2@Cu core-shell nanoparticles against the microorganisms tested.Table 2 displays the inhibition zones and antibacterial effects of SiO_2@cu nanoparticles as determined by the disk diffusion experiment. The range of inhibition zones of different concentrations of SiO_2 @ cu (12–20) and (26-34)mm against *Escherichia coli* and *Streptococcus mutans*, respectively, are shown in Figures 9 and 10, a 10-mm-diameter well was created and filled with antimicrobial fluid. The zones of inhibition show that all concentrations are effective against the two varieties of bacteria, with the *Escherichia* type of bacteria being more resistant to treatment. High concentrations of copper nanoparticles also show total cytotoxicity toward the bacteria. [21] Free radical synthesis has been demonstrated to be the process by which bacteria are poisoned by copper.By destroying intracellular and extracellular components that block the electron transport pathway, the resulting radicals harm DNA and RNA. These nanoparticles enter the bacterial cell membrane and stick to the cell wall. Copper ions damage the bacterial cell wall, causing it to thicken and become coarse. Subsequently, the cytoplasm deteriorates and disappears, ultimately leading to cell death. The high adsorption of copper ions to bacterial cells is credited with the antibacterial process, which confers antibacterial activity in a concentration-dependent way. The size,

shape, and number of copper nanoparticles have a high surface-to-volume ratio. The synthesis procedure and other parameters have an impact on the antibacterial capabilities of SiO_2@cu core shell. [22 -24]

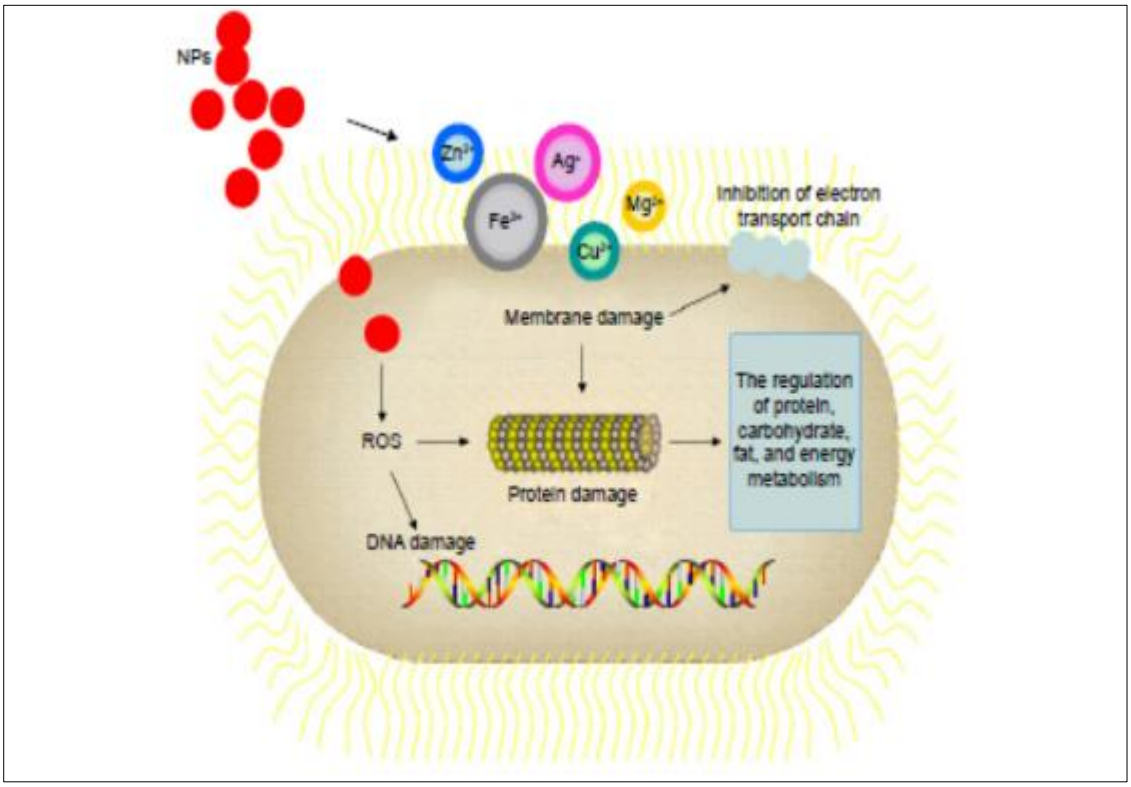

Figure 8 Mechanisms of metals NP activity, In bacteria cells

Table 2 The effectiveness (inhibition zone) of nanoparticles against *S.mutans* and *E. coli*

Sr. No	code	*S. mutants*(mm)	*E. coli*(mm)	ph
1	17	34	17	8
2	18	30	14	9
3	19	28	14	9
4	20	28	16	10
5	21	30	14	9
6	22	26	20	9
7	23	30	13	10
8	24	30	14	10
9	25	28	12	10

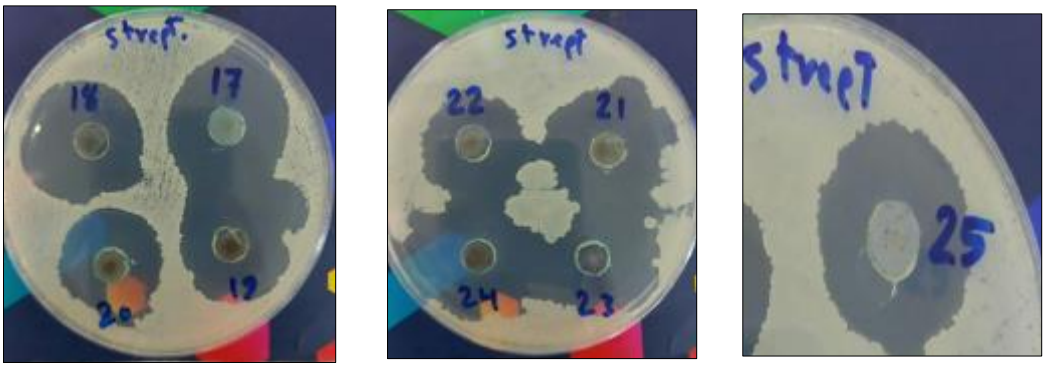

Figure 9 The inhibition zones SiO_2@cu against *streptococcus mutants*

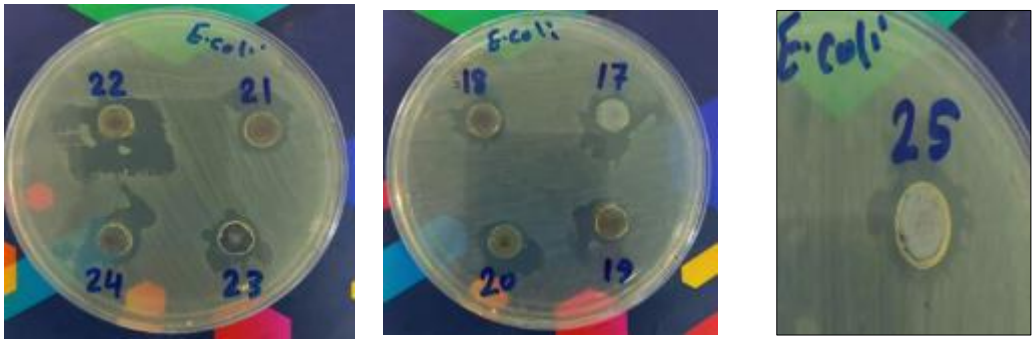

Figure 10 Zones of inhibition for SiO_2 @cu core shell against *E.coli* bacteria

4. Conclusion

The SiO_2@Cu core-shell NPS, which includes SiO_2 as the core and Cu nanoparticles as the shell, was made using chemical sol-gel. Using XRD, UV-VIS, FTIR, TEM, and EDD techniques, the chemical compositions and morphologies of SiO_2@Cu were identified and examined, and the effectiveness of their antibacterial characteristics was evaluated using the paper disk-agar diffusion experiment. The objective of the study was to validate the antibacterial activity of SiO_2@copper nanoparticles against mutant strains of Streptococcus and Escherichia coli. The action against Escherichia coli that was negative was substantially less than that against positive germs.

Compliance with ethical standards

Acknowledgments

All authors listed have significantly contributed to the development and the writing of this article .I extend my thanks and gratitude to my technical colleagues in the Baghdad university laboratories for helping me accomplish this work.

Disclosure of conflict of interest

The authors declare no conflict of interest.

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