

Transparent glass coated with silver colloid nanoparticles candidate as an anti-Coronavirus surface - Perspective

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Silver nanoparticles have a wide range of anti-bacterial, anti-fungal, and anti-viral effects due to their unique properties. In this work, citrate reduction has been employed to fabricate silver colloidal nanoparticles with 12 nm. The plasmon resonance spectra of nanoscopic silver particles adsorbed onto transparent electrodes in contact with various electrolyte solutions and concentrations of NaClO₄, KPF₆, and NaCl were studied. Potentials were controlled with a galvanostat, and UV/visible spectrophotometer was employed to obtain the optical spectra. The results showed the electrolyte identity, potential-induced redshifts, and damping is most pronounced for NaCl, whereas spectral changes are weaker in the cases of NaClO₄ and KPF₆ solutions. Hence, due to the noble physical and biological properties of silver colloid nanoparticles, it becomes a great candidate and promising in the future to be used as an anti-coronavirus surface.

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1. Introduction

Human coronaviruses have been discovered six times since the 1960s when the first one was found. Currently, SARS-CoV-2, a highly contagious version of the Coronavirus family, attacks the human body [1]. Despite this fast propagating virus's low infection fatality rate (IFR) (ranging from 0.00% to 1.54%) [2]. Pandemic conditions are being created because of increased diseases and mortality throughout the world. Public health has been seriously threatened by Coronavirus disease 2019 (COVID-19) caused by SARS-coV-2 (SARS-CoV-2). Coronavirus disease 2019 (COVID-19) is presently considered a severe threat to human health worldwide [3]. The World Health Organization (WHO) announced a public health emergency of international concern at the end of January of the year 2020[4]. Droplets of respiratory fluid and somatic contacts are the main spread mechanisms of this novel virus. The new virus transmits primarily via respiratory drizzle, runny nose, and bodily contact [5]. Patients who are critically ill are likely to suffer complications as their disease progresses. Pathological analysis revealed the presence of various organs and symptoms characteristic of severe respiratory stress disorder [5]. Structural analysis revealed four kinds of proteins exist in all coronavirus forms, including spike, envelope, membrane, and nucleocapsid. A positive sense single-strand RNA is present as well. Spike protein is considered the only part of a viral body that is able to bind to a receptor. As of now, COVID-19 has no known particular medication other than palliative care [7]. There is a need to perform medical examinations to evaluate whether antivirals, convalescent plasma transfusions, and tocilizumab are helpful [8-9]. The clinical administration of COVID-19 has enhanced immensely in recent years [10]. However, despite significant progress, the disease still presents unique biological characteristics, clinical symptoms, and imaging manifestations. In spite of notable

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improvements, the disease exhibits unusual biological properties, physiological signs, and imaging findings [11]. Historically, silver has had many uses in the medical fields, such as preserving drinking water and milk from bacterial contamination [12-13]. Medicinal uses of silver have existed since the eighth century. With the discovery of antibiotics at the beginning of the twentieth century, silver in medicine waned [14]. However, due to the emergence of so-called antibiotic-resistant superbugs, interest in studying the effects of silver with antibiotics has returned. A colloidal silver solution consists of silver nanoparticles suspended in water with antibacterial properties [15]. Colloidal silver displays antibacterial properties because of the silver oligodynamic behavior and the large surface area capable of better interacting with bacteria [16-17]. This work aims to design a transparent glass surface coated with silver nanoparticles to be a candidate for an anti-coronavirus surface.

2. Materials and method

2.1. Materials

All chemicals were high purity and recrystallized three times using distilled water NaClO_4 (Fluka), KI (JANSSEN and KPF6 (UORSICH, MERCH, while sodium citrate and silver nitrate were used without any purification.

2.2. Experimental procedure

The solution of colloidal silver was obtained by following Graber protocol with some alterations in the amounts of $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ and AgNO_3 (Graber et al). In our study, silver colloids been prepared using the following procedures: In 250 ml of triply distilled water, about 45 gm of AgNO_3 was dissolved and vigorously stirred, allowing it to boil. Silver salt was reduced by adding 2.5 ml (1%) $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ in one-step. As a result of the reaction, the greenish-yellow colloid was produced by boiling the solution for an hour. Silver colloids were analyzed using the UV/ visible spectrophotometer.

2.3. Setup for electrochemical assay

Figure(1) illustrates the spectroelectrochemical setup. This set-up has only Pyrex components (including the windows). Throughout each investigation, silver chloride coated silver wire submerged in 4 M KCl was used as the reference electrode. The counter electrode always consisted of a strip of platinum foil. A range of 0.05-0.65 V was used as a precaution against silver oxide formation on SnO_2 electrodes. Potentials were controlled with a galvanostat and UV/visible spectrophotometer was employed to obtain the optical spectra. The electrode used in this experiment was a diaphanous glass slide 20x75x3 mm painted with antimony modified tin oxide. The solution of the silver colloid was evaporated on the electrode at room temperature for a short time, and the dried physisorbed colloid was washed three times with distilled water. Afterward, the working electrode was dipped three times in distilled water for 5-15 minutes before being applied to the electrochemical cell. Following washing the deposited Ag layer three times in distilled water, the layer was not allowed to dry before being used. In a typical experiment, spectral data is collected with a potential of 0.05 V versus SSCE. Then, another spectrum was recorded after changing the applied potential to 0.65 V. One more spectrum was collected at that potential of 0.05 to verify reproducibility. After that, intermediate possibilities 0,55 V versus SSCE was collected. Spectral scanning was carried out after two minutes of applying the cell potential.

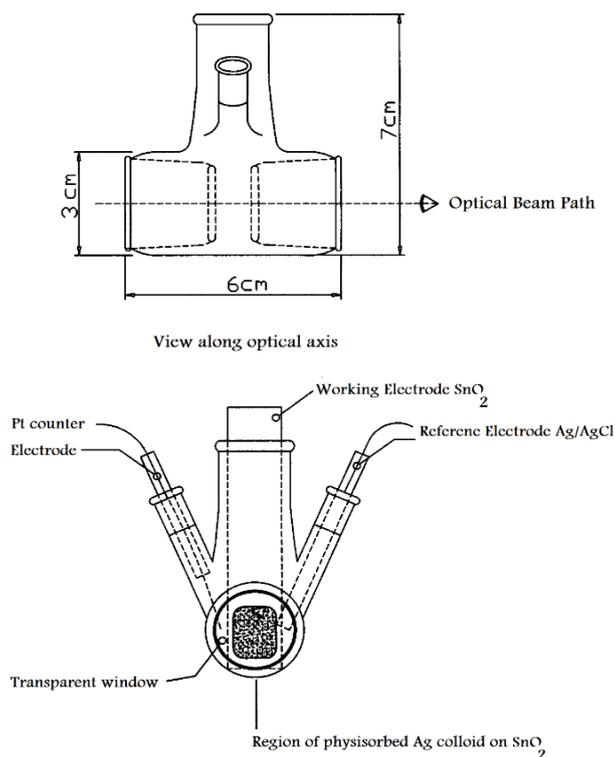
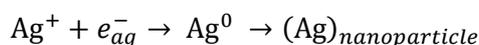
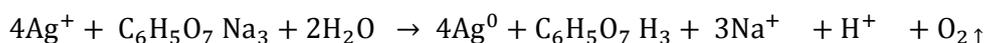


Fig. 1. Setup of spectroelectrochemical test

3. Results and discussion

3.1. Synthesis of colloidal silver nanoparticles

Citrate reduction has been employed in this work to fabricate silver colloidal nanoparticles due to its benefits of producing huge nanomaterials at a low economic cost and distinctive characteristics (free of aggregation) [18]. Moreover, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ acts as a reducing agent and stabilizer that prevents the aggregation of silver nanoparticles by the electrostatic repulsion caused by negatively charged surfaces. The chemical reaction to obtain colloidal silver nanoparticles using citrate reduction technique described below.



As a result of photo oxidation of citrate and water, aquatic electron electrons changed from Ag^+ to Ag^0 . The aquatic electrons are powerful reductants; the Ag^+ ions are strongly and rapidly reduced during reduction reaction. Among the three carboxylic groups in citrate, two will attach to the silver surface [19]. At the same time, the third remain to the surface and act as a stabilizer for the colloid by the electrostatic repulsion. [20]. Several studies indicate that the mechanisms governing silver colloid nanoparticle formation are affected by heating, stirring rate, and reagent concentrations. On the other hand, the color of a colloid depends on only its size and shape [21].

The spectra of UV-VIS absorption of the synthesized silver colloid is shown in Figure 2. Two peaks characterize these spectra, one of them an intense peak centered at 415nm and the second a small and large peak at ~426 nm, showing the presence of predominantly relatively tiny and regular spherical nanoparticles with a few irregular shapes in the colloid. These happen because of the surface plasmonic vibration occurs at the same frequency as the light entering. The

absorption peak position indicates the formation of fine nanoparticles in the colloid with size of 12 nm. Nevertheless, the frequency of plasmonic vibration depends on the size and shape of the nanoparticle. Therefore, the intensity of the absorbance spectra is proportional to the number density of the particles present in the colloid. Furthermore, spheres usually exhibit a single resonance peak as their greatest symmetry [22]. Therefore, an intense single absorption peak in the spectrum reveals the existence of regular and spherical nanoparticles with relatively high density [23].

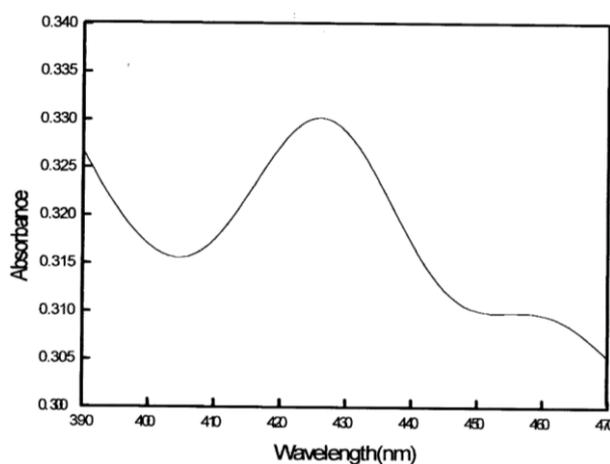


Fig. 2. Absorption spectra of silver colloids in solution.

3.2. Study of electrolyte identity and concentration on potential-induced spectroscopic shifts

Spectroscopic studies of colloidal silver particles adsorbed on SnO₂ transparent electrodes were done with the electrode in contact with a variety of aqueous electrolyte concentration in order to examine the effects of electrolyte identity and concentration on potential – induced spectroscopic shifts. SnO₂ electrodes containing silver colloid particles were immersed in two different electrolytes sodium perchlorate (NaClO₄) and potassium hexafluoride phosphate (KPF₆). For the electrolyte identity and concentration effect studies, NaClO₄, KPF₆ and NaCl have been chosen, because they showed the most pronounced dependence on the applied potential. For a given salt spectroscopic studies of silver colloid particles were done at 5 different concentrations (1 x 10⁻⁵M, 1 x 10⁻³M, 1 x 10⁻²M, 5 x 10⁻²M, 7.5 x 10⁻²M). Figures 3 show the absorption spectra of adsorbed silver colloid nanoparticles in contact with (5) concentration of NaClO₄ at the two limiting potentials (0.05V and 0.55V). The absorption peak shows that the colloid exhibits a moderate redshift of the most intense absorbance peak to the previous one, with the peak centered at ~430 nm. The intensity increases with increasing concentrations at 0.05 volts. On the other hand, 0.55 volts shows less intensity at high concentrations, and there is no change observed at low concentrations. Thus, the redshift of the prominent plasmonic absorbance peak may be due to the formation of larger-sized NPs in the colloid.

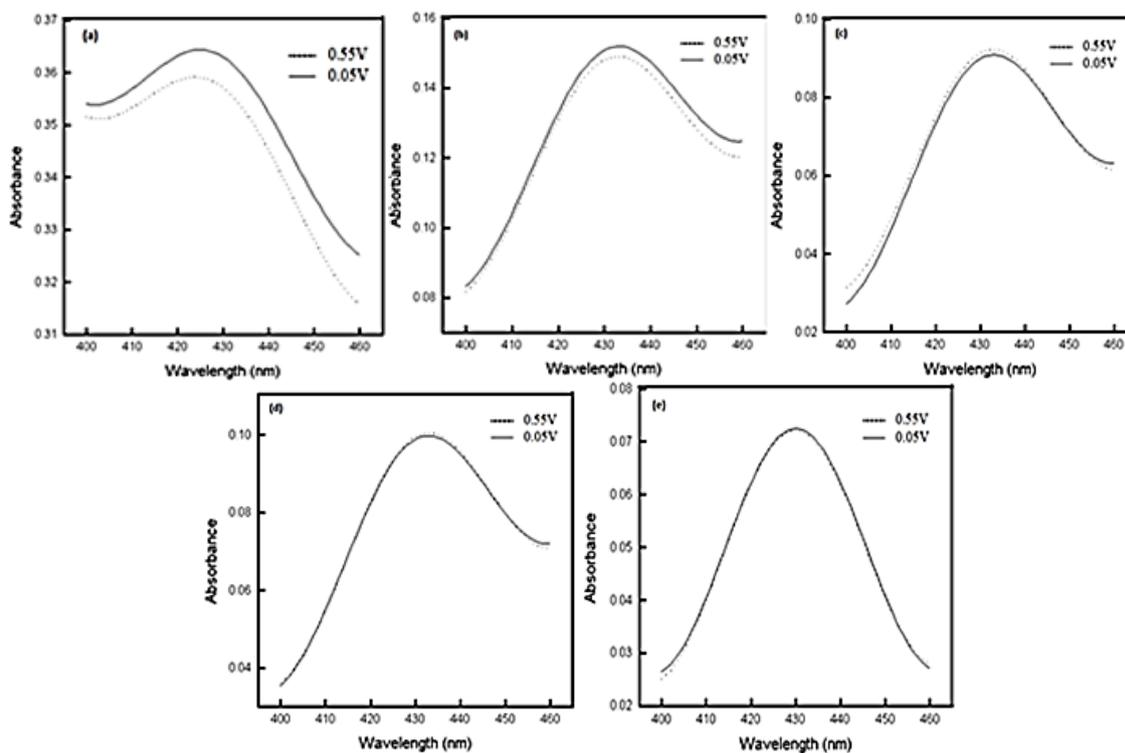


Fig. 3. Absorption spectra of adsorbed Ag particles in contact with (a) $7.5 \times 10^{-2}M$ (b) $5 \times 10^{-2}M$ (c) $1 \times 10^{-2}M$ (d) $1 \times 10^{-3}M$ (e) $1 \times 10^{-5}M$ of $NaClO_4$ solution at two limiting potentials (0.05V and 0.55V).

Figures 4 display the absorption spectra of adsorbed Ag particles in contact with (5) concentration of KPF_6 at the two limiting potentials (0.05V and 0.55V).

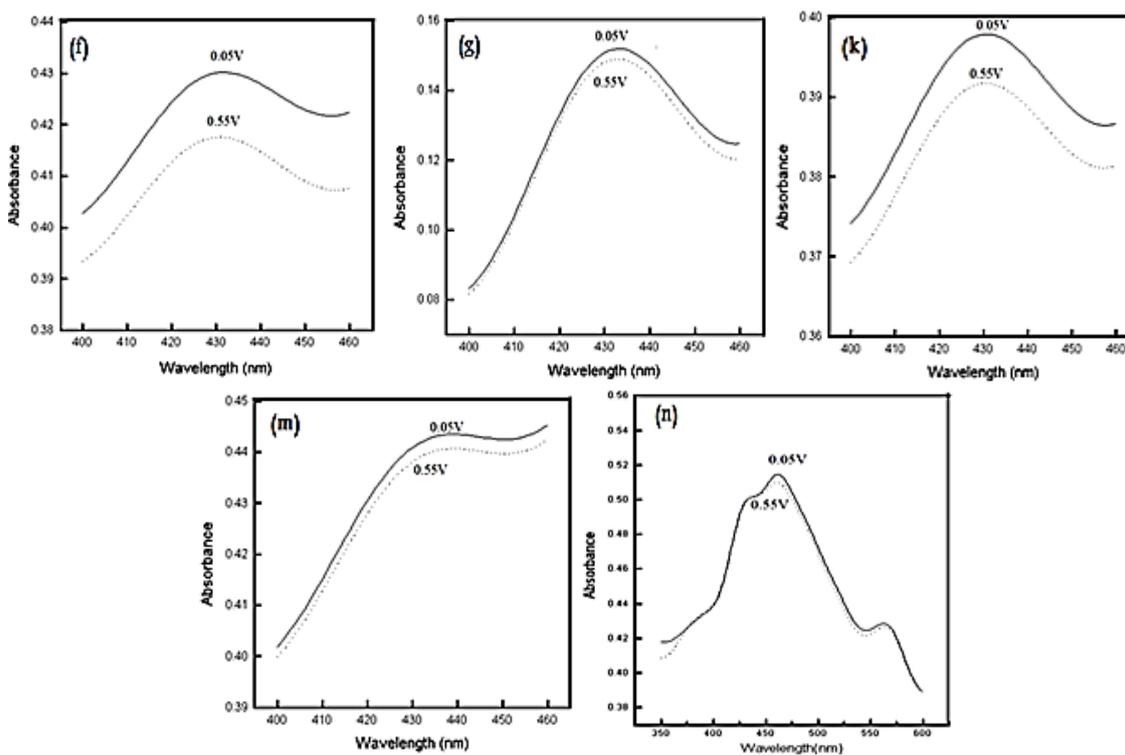


Fig. 4. Absorption spectra of adsorbed silver colloidal particles in contact with (f) $7.5 \times 10^{-2}M$ (g) $5 \times 10^{-2}M$ (k) $1 \times 10^{-2}M$ (m) $1 \times 10^{-3}M$ (n) $1 \times 10^{-5}M$ of KPF_6 solution at two limiting potentials (0.05V and 0.55V).

A measurement of the absorbance peak indicates a redshift with the peak centered at ~ 410 , 450 and 557 nm. These peaks might be due to presence of very fine spherical NPs together with larger NPs in the colloid or because of the quadrupole resonance caused by the nonuniform incident of light across the sphere or due to the development of low-dimensional nonspherical features in the colloid [24]. The intensity does not have a regular behavior, as it appears at a concentration of $1 \times 10^{-5} M$ increments greater than all other concentrations. The applied voltage has no effect on absorption and intensity except at the $1 \times 10^{-5} M$ concentration.

Figures 5 illustrate the absorption spectra of adsorbed Ag particles in contact with (4) concentration of NaCl at the two limiting potentials ($0.05V$ and $0.55V$). The absorption peak reveals that the colloid displays a redshift of the most intense absorbance peak to the previous one, with the peak centered at ~ 430 nm. No increases in the intensity were observed due to increases in concentrations at 0.05 and 0.55 volts.

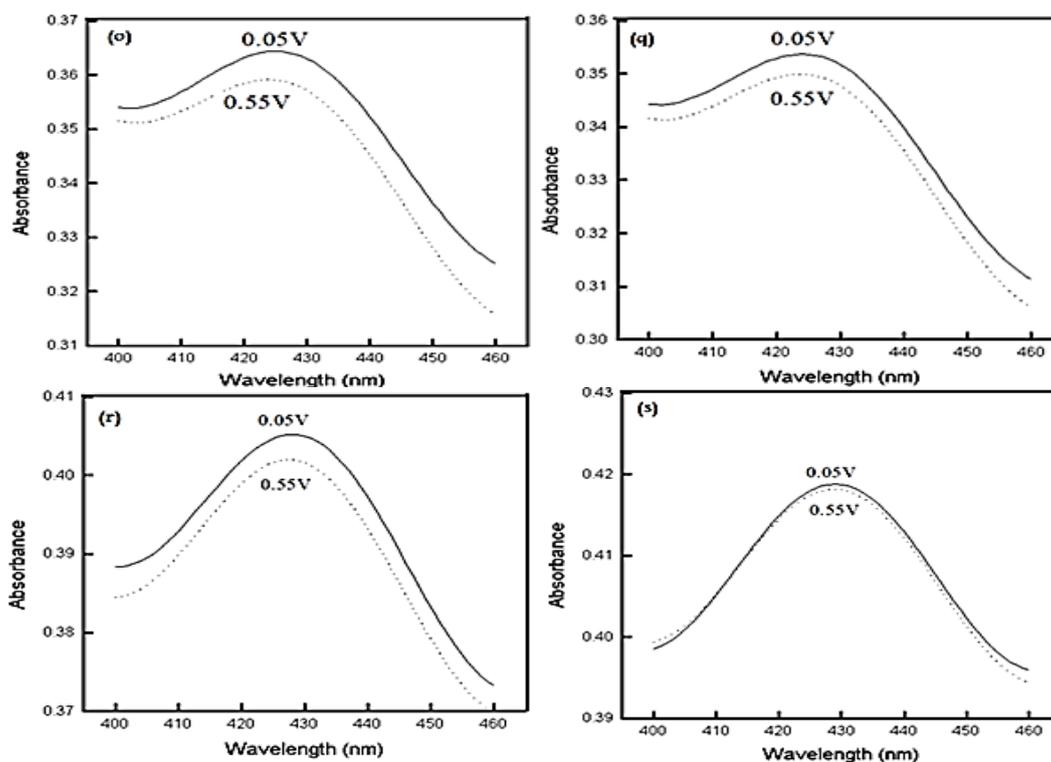


Fig. 5. Absorption spectra of adsorbed silver colloidal particles in contact with (o) $7.5 \times 10^{-2} M$ (q) $1 \times 10^{-2} M$ (r) $1 \times 10^{-3} M$ (s) $1 \times 10^{-5} M$ of NaCl solution at two limiting potentials ($0.05V$ and $0.55V$).

Figure (6) shows spectra for all potential values from 0.0 to $0.65V$ of $NaClO_4$, KPF_6 at concentration of $7.5 \times 10^{-2} M$ KPF_6 and $NaCl$. From the results obtained it was shown that the plasmon resonance band of nanoscopic silver particles on SnO_2 electrode is red-shifted and generally decreased in intensity as the electrode potential is made more positive. The extent of the red shift and damping are dependent on the electrode potential, the identity and concentration of the electrolyte, and the size of the silver particle. The most obvious results concern the electrolyte identity, potential-induced red shifts and damping is most pronounced for $NaCl$, whereas spectral changes are weaker in the cases of $NaClO_4$ and KPF_6 solutions as shown table (1). No correlation have been recorded with concentration in $NaClO_4$ and KPF_6 solutions. However, a marked concentration dependence of the $\Delta\lambda_{max}$ and the intensity damping were observed when the silver particles were in contact with $NaCl$ solutions. Hence, due to the noble physical and biological properties of silver colloid nanoparticle, it becomes a great candidate and promising in the future to be used as an anti-coronavirus surface.

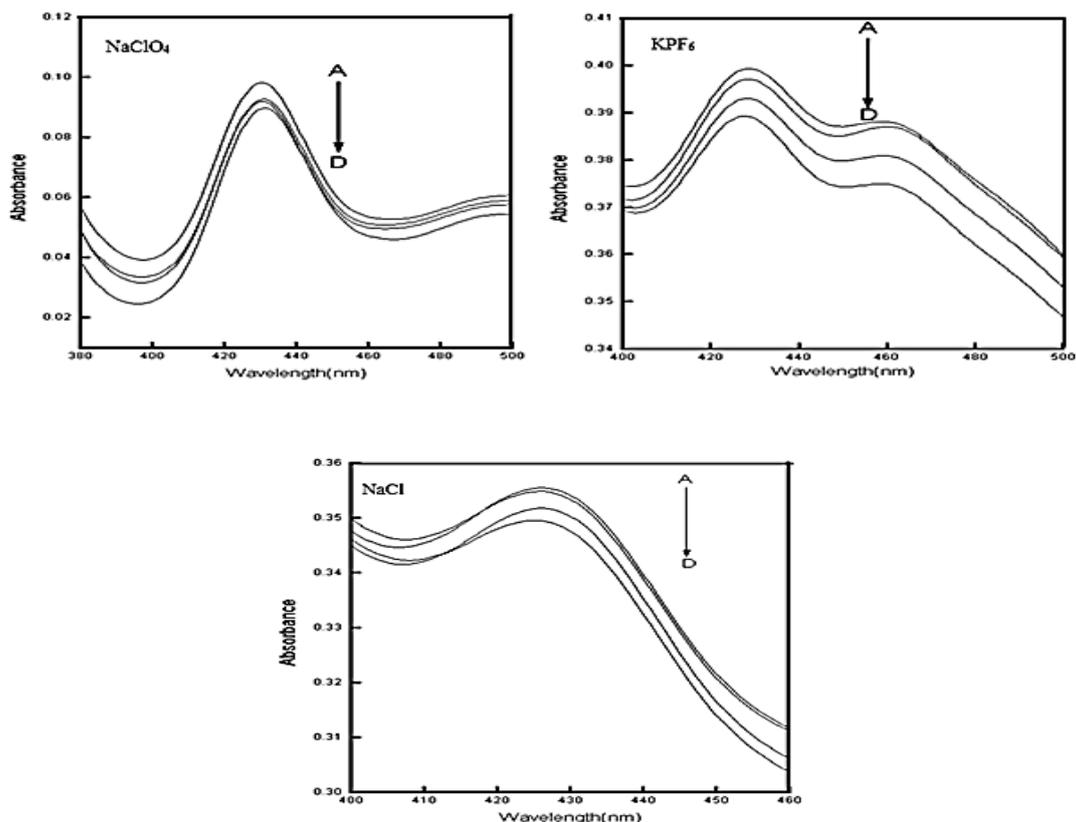


Fig. 6. Absorption spectra colloidal silver in contact with NaClO_4 ($7.5 \times 10^{-2} \text{M}$), KPF_6 ($7.5 \times 10^{-2} \text{M}$) and NaCl ($1 \times 10^{-3} \text{M}$) at two limiting potentials at all voltage. (A 0.0 V) (B 0.05V), (C 0.55V) and (D 0.65V).

Our hypothesis is based on using transparent glass-coated silver colloid nanoparticles as an antiviral surface as shown in figure 7. First, the silver-coated surface harvests the light, and then the surface becomes hot; this increases the properties of silver in the prevention of coronavirus. Several studies have suggested that temperature increases and humidity increases reduce transmission of the severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2) [25]. Silver has multi uses as antimicrobial activity, which includes bacteria, fungi, and viruses [26]. Due to their multiple benefits, silver nanoparticles have recently become popular as a disinfectant for biological surfaces in numerous forms, such as wound dressings, medical equipment, deodorant sprays, and textiles. Many investigations have revealed the powerful antiviral properties of silver nanoparticles against various human diseases caused by SARS-CoV-2[27].

Table 1. The changes in plasmon absorption maxima for two limiting potentials (0.05V and 0.55V) in contact with NaClO₄, KPF₆ and NaCl electrolytes of different types and concentrations.

Salt	Concentration	$\Delta\lambda_{max}$ nm
NaClO ₄	7.5x10 ⁻² M	0.24
	5x10 ⁻² M	0.0
	1x10 ⁻² M	0.3
	1x10 ⁻³ M	1.8
	1x10 ⁻⁵ M	0.24
NaCl	7.5x10 ⁻² M	0.25
	5x10 ⁻² M	0.51
	1x10 ⁻² M	0.0
	1x10 ⁻³ M	0.25
	1x10 ⁻⁵ M	0.51
KPF ₆	7.5x10 ⁻² M	0.25
	5x10 ⁻² M	0.3
	1x10 ⁻² M	0.02
	1x10 ⁻³ M	0.5
	1x10 ⁻⁵ M	0.0

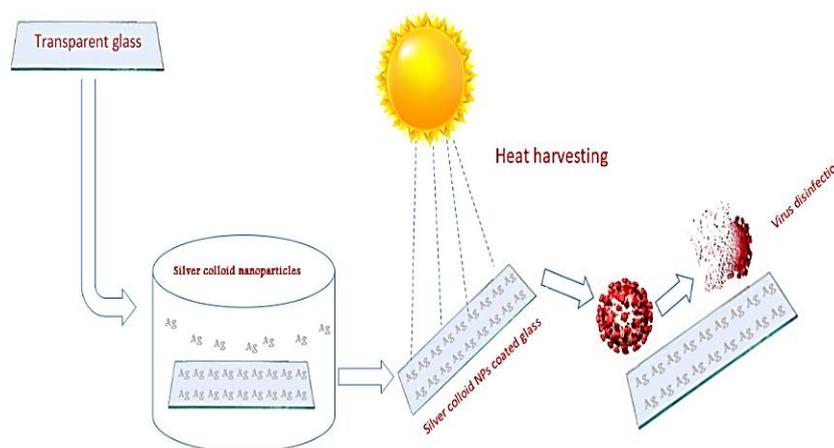


Fig. 7. Mechanism of eliminating the Coronavirus through the silver nanoparticles-coated glass surface.

4. Conclusion

In summary, it can be noted that the citrate reduction technique is reliable, simple, and practical to produce silver colloid nanoparticles. The plasmon resonance spectra of nanoscopic silver particles adsorbed onto transparent electrodes in contact with various electrolyte solutions and concentrations of NaClO₄, KPF₆, and NaCl were studied. The results showed the electrolyte identity, potential-induced redshifts, and damping is most pronounced for NaCl, whereas spectral changes are weaker in the cases of NaClO₄ and KPF₆ solutions. The study outcomes propose that the glass-coated silver colloid nanoparticles act as anti-coronavirus surfaces due to their unique physical and biological activity.

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