Metallic Nanoparticles: A Novel Approach in Nanotechnology

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***Abstract*- Metallic nanoparticles are metals that range in size from 1 to 100 nm in length, width, and thickness. Faraday conducted the first investigation into metallic nanoparticles in solution in 1857. A numerical explanation for their colours was provided by Mie in 1908. They can now bind to medicines, ligands, and antibodies thanks to the ability to create and modify these nanomaterials with different chemical functional groups. Numerous medical, biotechnological, and drug delivery uses exist for metallic nanoparticles. The advantages, disadvantages, and characteristics of metal nanoparticles are outlined in this review. It gives the readers in-depth details on synthesis using different methods and characterization, with an emphasis on application and its adverse effects. Recent advances have made it possible for these metallic nanoparticles to transport drugs and target specific sites.**

Keywords: **Metal Nanoparticles, Gold, Silver, Platinum, Radiotherapy.**

I. Introduction:

The focus of the science and engineering discipline known as "nanotechnology" is on substances that are 100 nm in size or less. Even though the expression is new, it has been widely used to create technology that is more useful. Due to its use in fields like targeted drug delivery, magnetic separation and pre-concentration of target analytes, electronic storage systems, biotechnology, and vehicles for the delivery of genes and medications, nanotechnology has recently gained the support of many industrial sectors. [1-3]

The discovery of nanoparticles was foreseen by Cal Tech physicist Richard P. Feynman in 1959, which represents a crucial turning point in the development of nanomaterials. "There is plenty of room at the bottom," he said in one of his seminars, suggesting that scaling down to the nanoscale and starting from the very bottom would be the key to future technological advancement.[4] As nanotechnology developed, new nanostructures with distinct features from their larger counterparts started to emerge. The high surface-to-volume ratio of nanomaterials is responsible for their distinctive physiochemical properties. Due to the fact that a variety of biological processes occur at nanoscales, these unique characteristics make them ideal candidates for biomedical applications.

The many sizes, structures, and geometries of the metal nanostructures, such as gold, silver, and iron, are designed. Metal NPs often have a smaller size and more distinct physical, chemical, and biological properties. One of the most often studied gold nanoparticles (NPs) comes in a variety of shapes, including nanospheres, nanorods, and nanoshells.[5] These metal nanomaterial structures have enormous potential for use as drug delivery systems, in enhancing radiation-based anticancer therapy, in supporting molecular imaging, and in supplying photothermal transforming effects for thermal therapy, in addition to being substances with bactericidal, fungicidal, and antiviral properties.[6-7]

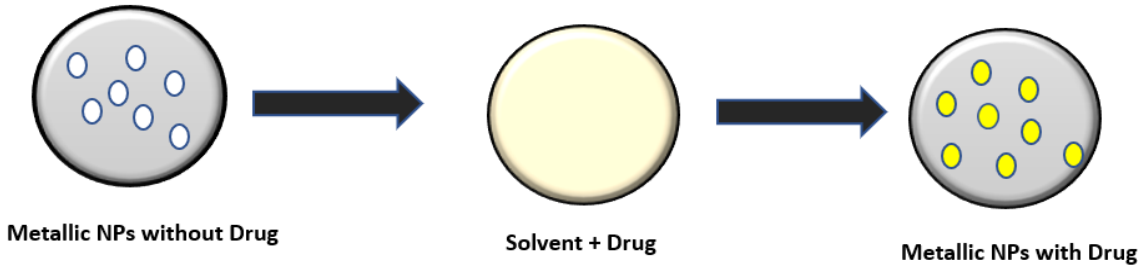

Figure number 1: Formation of NPs

II. Advantages of metallic nanoparticles [8]

1. Rayleigh scattering enhancement.
2. Surface-enhanced Raman Scattering.
3. A significant plasma absorption
4. Imaging a biological system
5. Analysing chemical data on a metallic nanoscale substrate.

III. Disadvantages of Metallic Nanoparticles:

a. Particles instability: Nanomaterials can change because they are located in the vicinity of high-energy local minima and are thermodynamically unstable. This causes quality to decline; the materials used have poor corrosion resistance, and maintaining the structure becomes more challenging.

b. Contaminants: The production of nitrides, oxides, and nanoparticles can be increased in a polluted environment. Due to their strong reactivity, nanoparticles also have a high risk of contamination. Nanoparticles should be created as encapsulated particles in solution form. Therefore, eliminating contaminants in nanoparticles becomes difficult.

c. Biologically harmful: Nanomaterials are thought to be toxic, cancer-causing, and irritating due to their translucency to the cell dermis.

d. Explosion: Due to the powerful explosive properties of small metal particles, exothermic combustion might result in an explosion.

e. Difficulty in synthesis: It is quite difficult to maintain the nanoparticle size in solution form; hence, it is recommended to encapsulate nanoparticles when synthesising them.[9]

IV. Characteristics of Metallic Nanoparticles [10]

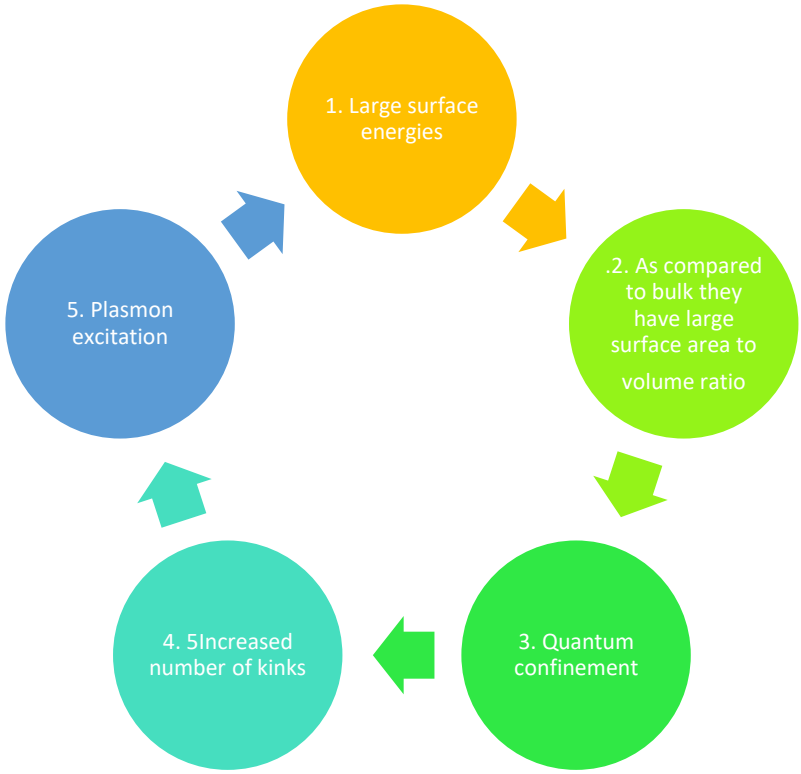

Figure number 2: Characteristics of Metallic NPs

V. Synthesis of Metallic Nanoparticles:

1] Gold Nanoparticles: The term "colloid" describes a suspension of gold nanoparticles, often known as "coloidal gold" or "gold nanoparticles." Since the Roman era, when they were used to create stained glass decorations, these colloidal solutions have had a lengthy history.[11] However, the current scientific analysis of colloidal gold dates back to Michael Faraday's study from the 1850s, when he discovered that the properties of the colloidal gold solutions were distinct from those of the bulk gold.[12,13]. As a result, the colloidal solution is either brilliant red (for particles smaller than 100 nm) or yellowish (for larger particles) [14,15]. These gold nanoparticles' intriguing optical characteristics are the result of a special interaction they have with light[16] In the presence of the fluctuating electromagnetic field of light, the free electrons of metal nanoparticles fluctuate with respect to the metal lattice. [17-18]. Localised surface plasmon resonance (LSPR) is a mechanism that is resonant at a certain light frequency. After absorption, the surface plasmon decays either non-radiatively (by converting the absorbed light to heat) or radiatively (by scattering light). Gold nanospheres with particle sizes of roughly 10 nm show a considerable absorption maximum in aqueous solution due to their LSPR. These nanospheres demonstrate a Stokes shift as their size grows due to electromagnetic retardation in larger particles..[19,20].

2] Silver Nanoparticles: Silver nanoparticles are extremely small silver particles with diameters ranging from 1 to 100 nm. Because of the large proportion of surface to bulk silver atoms, some materials, despite being often referred to as "silver," include a significant quantity of silver oxide. Ionic silver, like gold nanoparticles, has a long history and was first used to yellow-stain glass. There is currently work being done to include silver nanoparticles in a variety of medical products, such as surgical masks, bone cement, and other items. Additionally, it has been demonstrated that using ionic silver to cure wounds in the proper dosages.[21-23]. In fact, silver nanoparticles have taken over from silver sulfadiazine as the preferred method for treating wounds. On the surfaces of home appliances, Samsung has also developed and sold a substance called Silver Nano that contains silver nanoparticles. Furthermore,

due to their appealing physiochemical properties, these nanomaterials have sparked a great deal of interest in biological imaging using SERS. Individual silver nanoparticles are good candidates for molecular tagging because of their surface plasmon resonance and large effective scattering cross-section. A plethora of tailored silver oxide nanoparticles are presently being produced.[24].

They are commonly made by reducing a silver salt with a reducing agent such as sodium borohydride while a colloidal stabiliser is present. The most commonly used colloidal stabilisers include polyvinyl alcohol, polyvinyl pyrrolidone, bovine serum albumin (BSA), citrate, and cellulose. Ion implantation is a more recent creative strategy that uses d-glucose as a reducing sugar and starch as a stabiliser to produce silver nanoparticles.[25] It is critical to note that not all nanoparticles are created equal. It has been established that its size and shape have an impact on its effectiveness. According to Elechiguerra et al., silver nanoparticles interact with HIV-1 in a size-dependent way, with particles only in the 1–10 nm range sticking to the virus.[26] They further believe that silver nanoparticles' preferential attachment to the gp120 glycoprotein knobs mediates their interaction with the HIV-1 virus. Similarly, Furno and Co. researchers developed biomaterials by impregnating silicone with silver oxide nanoparticles. These cutting-edge biomaterials were developed in order to reduce antimicrobial infections. Despite inconsistencies in the findings, the approach enables the first-ever silver impregnation (rather than coating) of therapeutic polymers and offers the promise of generating an antibacterial biomaterial.[27]

Despite not being as well-known as gold nanoparticles and sand nanoshells, these particles have had a substantial impact on medical research in recent years. The possibility of continuing to use noble metals as new applications and protocols are developed is an attractive feature of these materials..[27].

3] Iron Oxide Nanoparticles: One of the three principal oxides of iron—the other two being FeO and FeO—is iron (III) oxide, usually known as FeO. It is an inorganic substance that is reddish-brown in colour and paramagnetic. Superparamagnetic materials include the mineral magnetite, which also appears naturally as FeO. A few biomedical applications that superparamagnetic iron oxide nanoparticles (SPION) have shown promise for include enhanced resolution contrast agents for MRI, targeted drug delivery and imaging, hyperthermia, gene therapy, stem cell tracking, molecular/cellular tracking, magnetic separation technologies (e.g., rapid DNA sequencing), and early detection of inflammatory diseases, cancer, and diabetes.[28-29] For any of these biomedical applications to provide high-resolution MR images, the nanoparticles must have high magnetization values. Superparamagnetic nanoparticles are generally good imaging probes for use as MRI contrast agents because they considerably change MR signal intensity while maintaining in vivo stability.[30] In general, all contrast agents reduce the T1 and T2 relaxation durations of the water protons around them, which affects the signal strength of the imaging tissue.[31]

Converging advances in the knowledge of the molecular biology of many diseases led to the proposal of homogenous and targeted imaging probes with a constrained size distribution between 10 and 250 nm in diameter. The synthesis of magnetic nanoparticles in this diameter range is a difficult process, and several chemical techniques have been proposed. These procedures include sol-gel synthesis, microemulsions, sol-gel reactions, sonochemical reactions, hydrothermal reactions, hydrolysis and thermolysis of precursors, and flow injection synthesis[32-33] The most popular approach for creating magnetite nanoparticles is a chemical co-precipitation process that uses iron salts.[34] The key benefit of the co-precipitation approach is the ability to synthesise a lot of nanoparticles with only a little control over size distribution. This is mostly caused by the kinetic variables driving crystal formation. Thus, tiny particles of iron oxide (SPIO) (60–150 nm) and ultra-small particles of iron oxide (USPIO) (10–40 nm) are among the particulate magnetic contrast agents that can be produced utilising these techniques. Monocrystalline USPIOs are also referred to as monocrystalline iron oxide nanoparticles (MIONs), but when MIONs are coupled to dextran, they are referred to as cross-linked iron oxide nanoparticles (CLIO, 10–30 nm).[35–37] A shorter blood clearance half-life is caused by the carboxylation modification of the dextran coating.[38] As a result, the carboxyalkylated polysaccharide-coated iron oxide nanoparticle ferumoxytol (AMAG Pharmaceuticals) is already well recognised as an efficient first-pass contrast agent. To facilitate uptake in macrophage-rich plaques, macrophage uptake is unspecific and happens too soon.[39]

To boost their capacity to link with drugs, proteins, enzymes, antibodies, or nucleotides and to target an organ, tissue, or tumour, these particles can be given a unique surface coating. However, iron oxide nanoparticle-based, customised molecular imaging probes have been developed that directly target biological tissue or cells. Traditional contrast agents have a tendency to disperse somewhat randomly.[40] For instance, Conroy and colleagues created a biocompatible iron oxide nanoprobe called a chlorotoxin (CTX) nanoprobe that may specifically target glioma tumours with a surface-bound targeting peptide.[41] Additionally, MRI research revealed that the nanoprobe accumulated preferentially within gliomas. Apopa et al. created iron oxide nanoparticles in a different study that can improve cell permeability by stabilising microtubules and producing reactive oxygen species (ROS).[42]

These investigations provide new insights into the bioreactivity of synthetic iron nanoparticles, which may be useful for medication delivery or imaging applications. The further creation and modification of iron oxide complexes in association with dendrimers, polymeric nanoparticles, liposomes, and solid lipid nanoparticles have been the subject of numerous investigations. However, given that certain neuronal cell types are susceptible to the toxicity of these magnetic nanoparticles, there is still cause for concern.[43]

4] Platinum Nanoparticles: The precursor platinum metal, either in an ionic or molecular state, is used to create platinum nanoparticles. The precursor is chemically changed into platinum metal atoms by the reducing agents. The resulting nanoparticles are created when these metal atoms combine with stabilisers or supporting elements. For instance, in chemical reduction, Zn or NaBH4 convert H2PtCl6 to produce platinum nanoparticles. NaBH4 + H2PtCl6 = Pt and other reaction products The most frequent precursor for creating platinum nanoparticles is H2PtCl6. Typically, H2PtCl6 dissolves in aqueous or organic liquid phases. Electrochemical mechanisms, including breakdown, displacement, and reducing agents, can be used to convert the dissolved metal precursor into solid metal. The radiolytic, sonochemical, or electrochemical approaches can all use physical mixing to initiate a chemical reaction. For mixed metal nanoparticles, two different reactivates are commonly employed, such as PtCl2 and RuCl3, H2PtCl6 and Na6Pt (So3)4, and RuCl3 and Na6Ru (So3)4.[44].

VI. Characterization of Metallic Nanoparticles [45]:

a) Absorbance Spectroscopy: Metal nanoparticles have a vivid hue that is apparent to the naked eye, making spectroscopy effective for characterising them. This method can be used to get qualitative data about the nanoparticle. It is possible to quantify absorbance by using Beer's law. Path length (l), nanoparticle concentration (c), and extinction coefficient (A) can all be calculated.

b) Infrared Spectroscopy: This technique can provide details about the biological layers that cover metallic nanoparticles. It also provides important details for comprehending the surface structure of metal nanoparticles.

c) TEM: Nanomaterials are often characterised using transmission electron microscopy to learn about the size, shape, crystallinity, and inter-particle interactions of the particles. TEM is a technology for chemical and structural characterization with great spatial resolution. It can directly image atoms in crystalline specimens at resolutions of about 0.1 nm, which is smaller than the interatomic distance. Additionally, a single nanocrystal can be employed for quantitative chemical analysis when an electron beam is concentrated to a diameter less than 0.3 nm.

d) SEM: With a resolution of only a few nanometers, it is an effective technique for photographing the surface of any material. An incident electron beam interacts with the object to produce secondary electrons with energies below 50 eV. Regarding the sample's nanoparticle purity, SEM can offer specifics.

e) XRD: This technique works well and is widely used to determine the crystal structures of crystalline materials. The size, distribution, and strain of nanocrystals are strongly associated with their diffraction line widths. The lack of long-range order in relation to the bulk causes the line width to broaden as the size of the nanocrystal decreases. The Debye-Scherrer method can be used to determine the particle size using the XRD line.

$D = 0.9 \lambda / b \cos \Theta$ Where,

D= nanocrystal diameter λ=light wavelength

b=full width half at max. Of the peak (radians)

Θ=Bragg angle

f) FTIR: In contrast to IR spectroscopy, it is a technique that is commonly used. Different FTIR patterns are displayed by functional groups bound to the metallic nanoparticle surface compared to free groups.

VII. Application of Metallic Nanoparticles: [46-50]

1. Thermal Function

The melting point is lower than that of bulk metal when the nanoparticle diameter is less than 10nm. Nanoparticles can be used to create electronic wire because of their low boiling point.

2. Mechanical Function

The mechanical characteristics of polymers loaded with nanotubes improve. And this development only depends on the kind of filler and how the filing is handled. The qualities achieved are worse the larger the filler's particle size. Excellent mechanical qualities are provided by the components' polymer matrix and defoliated phyllosilicate composition. By combining metallic nanoparticles with metals or ceramics, one can enhance the mechanical properties of the nanoparticles.

3. Magnetic Function

Although they are not magnetic in their bulk forms, platinum and gold nanoparticles are magnetic at the nanoscale. By capping, the interaction of the nanoparticle's surface and bulk atoms with other chemical species can be changed. Therefore, capping with the appropriate molecules offers the chance to modify the physical properties of nanoparticles.

4. Catalysis

For a wide range of processes, metallic nanoparticle-based catalysts are highly active, selective, and long-lasting. The two types of catalysts that are immobilised on inorganic support are heterogeneous and homogeneous catalysts. Applications include the oxidation, water gas shift, hydrogenation, and H2O2 production processes. Homogeneous catalysts are composed of metallic nanoparticles that have been stabilised. Olefin and nitrile hydrogenation applications.

5. Elimination of Pollutants

Metallic nanoparticles are very active in terms of their physical, chemical, and mechanical properties, making them ideal for use as catalysts to reduce air pollution from burning coal and gasoline. because of how they interact with dangerous gases like carbon monoxide and nitrogen oxide.

6. In Tumour Therapy

According to studies, VEGF-induced angiogenesis in vivo as well as heparin-binding proteins, including VEGF165 and bFGF, were both reduced by bare gold nanoparticles. More studies have shown that heparin-binding proteins are absorbed and subsequently denatured on the surface of AuNPs. The researchers also showed that surface size has a substantial impact on AuNPs' therapeutic effects. The effect of gold nanoparticles on VEGF-mediated angiogenesis was examined using a mouse ear model that had been injected with an adrenovirus vector of VEGF by Mukherjee and colleagues (Ad-VEGF replicates the subsequent angiogenic response seen in tumours). One week after Ad-VEGF injection, mice treated with AuNPs developed less edoema than mice treated with the same drug. The anti-tumour properties of 50-nm AgNps were discovered by Eom and colleagues both in vitro and in vivo.

7. In Leukaemia

Apoptosis resistance is the main characteristic of the incurable illness known as B-chronic lymphocytic leukaemia (CLL). More apoptosis was reportedly elicited when anti-VEGF antibodies were co-cultured with CCL B cells. Gold nanoparticles were used in CLL therapy to increase the potency of these medications. Gold nanoparticles' biocompatibility, enormous surface area, surface functionalization, and ease of characterization were all taken into account. To see if VEGF antibodies could kill CLL B cells, they were attached to gold nanoparticles.

8. In Rheumatoid Arthritis

Australian researchers at the University of Wollongong have created a novel anti-arthritic drug that may be combined with gold nanoparticle therapy and has fewer potential side effects. When the immune system is out of whack and attacks the sufferer's joints, an autoimmune disease called rheumatoid arthritis develops. Recent research suggests that gold particles can infiltrate macrophages without really killing them, preventing them from generating inflammation. According to research published in the Journal of Inorganic Biochemistry, it is possible to reduce the gold's toxicity while increasing the amount that immune cells absorb by converting it into smaller nanoparticles (50 nm).

9. In Photo Thermal Therapy

Light is strongly absorbed by gold nanoparticles, which efficiently and swiftly transform photon energy into heat. An invasive therapy called photo-thermal therapy (PTT) uses photon energy to create heat in order to kill cancer.

10. In Radiotherapy

Gold is a great X-ray absorber, so tumours that are laden with gold absorb more X-rays. As a result, a local dose that increases exclusively for cancer cells arises from the deposition of increased beam energy. The ability of gold nanoparticles to treat cancer has become greater.

VIII. Side Effects of Metallic Nanoparticles:

One of the adverse consequences observed in patients from prolonged exposure to or consumption of silver salts is argyria. The skin and mucous membranes are stained grey and black in argyria due to the deposition of silver. Silver may accumulate in the skin as a result of industrial exposure or silver salts included in pharmaceuticals. According to one study, a patient who consumed colloidal silver three times annually over a two-year period developed diabetes, hypertension, and hyperlipidemia. [51]. Nanosilver exposure caused apoptosis and gene regulation in mouse brains.[52]. Workers also have tarnished corneas and conjunctiva as a result of inhaling [53]. Gold colloid has been used for centuries in the medical field with no known adverse effects. Additionally, thrombosis, immunogenic responses, and hemolysis have all been linked to gold nanoparticle exposure. Salivary enzymes can change gold (0) into gold (I), which is then ingested by immune cells.[54]

IX. Currently available marketed nanoparticles:

Table No 1: Currently available marketed nanoparticles Formulations

Brand	Generic Name	Indication	Company	Innovator
Tricor	Fenofibrate	Hypercholesterolemia	Abbott Lab.	Abbott
Triglide	Fenofibrate	Hypercholesterolemia	IDD-P Skyepharma	Sciele Pharma Inc.
Rapamune	Rapamycin, Sirolimus	Immunosuppressant	Elan Nanosystem	Wyeth
Megace ES	Megestrol	Anti-anorexic	Elan	Par Pharmaceuticals
Emend	Aprepitant	Anti-emetic	Elan Nanosystems	Merck & Co.
Paxceed	Paclitaxel	Anti-inflammatory	Angiotech	-

X. Some novel antihypertensives with their development phase and mechanism of action:

Table No 2: Novel antihypertensives with their mechanism of action

MOA	Brand	Development phase	Company
Aldesterone Receptor Blocker	Eplerenone	Marketed	Pfizer, USA
Phosphodiesterase 5 inhibitor	TadalafilKD027	MarketedPhase II	Eli Lilly, USAKadmon Pharmaceuticals
Dopamine βhydroxylase inhibitor	Etamicastat	Phase I	Bial,
ACE 2 modulator	APN01 (rhACE2)	Phase II	Apeiron-biologics

Aldosterone synthase inhibitor	ASI LCI699	Phase II	Novartis, Switzerland
AT2R agonist	Compound 21	Phase I	Vicore, Sweden
Combined AT1R blocker and NEP inhibitor	LCZ696Daglutril	Phase III Phase II	Novartis, SwitzerlandSolvay, Belgium
Renin inhibitor	AliskirenVTP27999	MarketedPhase II	Novartis, Switzerland, and Speedel SwitzerlandVitae Pharmaceuticals, USA

XI. Conclusion:

Due to their versatility in terms of synthesis methods, metallic nanoparticles are in great demand in the twenty-first century. Metallic nanoparticles are used in a variety of fields, including radiotherapy, rheumatoid arthritis, and thermal, mechanical, and magnetic functions. Enhancing the therapeutic effectiveness of nanoparticles while lowering their level of toxicity is one of the main difficulties facing the field of nanobiotechnology. Individualised treatment can greatly benefit from the use of nanotechnology. However, additional study is required for that. Noble metal nanoparticles exhibit novel features at the atomic and supramolecular scales (1–100 nm), which make them useful as therapeutic and diagnostic agents.

It is true that there is an increasing need for the use of nanomaterials in the healthcare, cosmetics, and industrial sectors. As a result, safety measures must be adopted to protect both the environment and human health. This clearly shows the need for more in-depth investigation into the safety profiles of metallic nanoparticles before their use in healthcare. Further research is necessary for any potential application of metal nanoparticles to humans. Overall, gold, silver, and platinum nanoparticles are in a good position to transition from the slab bench to the clinical setting in the very near future.

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