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Photothermal effect of Ag nanoparticles deposited over poly(amidoamine) grafted carbon nanotubes

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Abstract

This paper illustrates the potential of Ag nanoparticles based nanocomposites to use as effective agents in photothermal therapy apart from their traditional employment as antimicrobial materials. Herein an Near- Infrared active photothermal agent was fabricated by deposition of Ag nanoparticles over aromatic poly(amidoamine) grafted carbon nanotubes. Thus prepared CNTs-PAMAM-Ag possessed strong photothermal effect under exposure to 980 nm laser system and prominent photothermal stability. The photothermal conversion efficiency of CNTs-PAMAM-Ag was found to be higher than readily used Au and CuS based photothermal agents. The photothermal effect of CNTs-PAMAM-Ag was substantial in presence of 980 nm laser compared to 808 nm laser and a linear dependence of photothermal effect on its concentration was identified. The maximum temperature attained by CNTs-PAMAM-Ag during assessment of its photothermal effect was about 66.0 °C, which is significantly higher than the survival temperature level of cancer cells. So CNTs-PAMAM-Ag could be a promising photothermal agent to apply in future photothermal hyperthermia therapy to treat cancer. Moreover CNTs-PAMAM-Ag can synchronous trigger by a single wavelength (980 nm) laser system, so it could simplify the future therapeutic process.

Keywords

Carbon nanotubes; Poly(amidoamine); Silver nanoparticles; Photothermal effect; Near-Infrared

1. Introduction

Compared to rest of electromagnetic radiations, near-infrared (NIR) radiations are primarily important and effective in several biomedical therapies owing to their deep penetration into body tissues and low absorption by water and hemoglobin [1]. The NIR radiations persists with weak scattering ability from biological soft tissues [2]. Accordingly, NIR equipped emerging technique used in the treatment of various cancers known as photothermal hyperthermia therapy (PHT) has gained special attention because of its advantages such as selective destruction of cancer cell tissues without harming to normal cells [3]. This categorized therapy is executed by conversion of radiation or light energy into thermal

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Appendix A. Supplementary data

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energy for heat-up and kill cancer cells using NIR resonant nanomaterials [3,4]. The process of PHT involve with injection of photothermal transducers into cancer cells and their exposure to NIR radiations to produce localized cytotoxic heat for ablation of cancer cells [5]. The vital benefit of PHT is prevention of collateral damaging of healthy cells. Hence, PHT persists with many important benefits compared to traditional radiation therapies in those healthy cells are unavoidably excised [6,7]. Hence PHT is a safe and advanced therapeutic procedure for selective and effective treatment of cancer. Nevertheless success of PHT is exclusively depends on photothermal agent employed in therapy and that agent should able to generate temperature which can lead to death of cancer cells. It is revealed that the survival temperature level of cancer cells is lower than 50 °C, so photothermal agent, executed in PHT should able to produce the temperature beyond 50 °C, in that condition only destruction of cancer cells is achievable [8,9]. Therefore, photothermal efficiency of agents is a decisive factor in success of PHT. So that modulating the photothermal agents as NIR active is crucial for PHT, however it is challenging. Under this guideline, many efforts have been dedicated to explore different nanomaterials having high absorption ability to NIR radiations as photothermal agents and readily translated them into clinical settings [10,11].

So far, silver and its comprised nanomaterials have been broadly explored as antimicrobial agents without considering their strong SPR in NIR region [12,13]. Nonetheless assessment of photothermal effect (PTE) of silver and its containing nanomaterials is completely ignored. However silver nanomaterials could be excellent PHT agents and its investigation is critically needed. Identical to gold, silver is also a high- Z element that has potential of enhancing the photothermal ablation of cancer cell in radiation enhanced therapy [14]. Recently, few efforts have been made to scrutinize the ability of silver nanomaterials to administer as PHT agents [15–18]. Interestingly, Cui et al. found low toxicity and higher inhibition (90.2%) rate in the growth of tumor by administering albumin stabilized Ag nanodots [15]. The single-light-triggered indocyanine green loaded PEGylation silver nanoparticle core/polyaniline shell nanocomposites prepared by Tan et al. demonstrated augmentation in photoacoustic/NIR fluorescence imaging guided photothermal therapy (PTT) and photodynamic therapy (PDT) [16]. In this study instead of individual PTT or PDT, single wavelength laser (808 nm) triggered, combined therapy of PTT/PDT showed superior lethality of HeLa cells and inhibited the growth of tumor. Kleinauskas et al. reported the synthesis of silver nanoshells with carbon core and testified their potentiality in photothermal ablation therapy or radiation-enhanced therapy [17].

Carbon nanotubes (CNTs), reside one or more seamless, cylindrical graphitic sheets of sp^2 carbon atoms bonded together in an edgeless, hexagonal network have gained great deal of attention due to their combined electrical, thermal and spectroscopic properties [19]. The unique physical and chemical properties of CNTs offer the possibility to engineer multiple diagnostic and therapeutic functions into a single particle [19,20]. CNTs provide an exceptional combination of attributes for development of future photothermal agents due to their ability in efficient conversion of NIR radiations into heat energy [21]. In this arena, CNTs have emerging as promising next generation material to apply in PHT. Under this significance, tremendous efforts have been devoted in development of CNTs based heat transduction nanomaterials [19]. However, practical application of CNTs in PHT is hindered by their hydrophobic nature, rendering CNTs as incompatible with living organisms or

biological systems. To modify CNTs as hydrophilic and biologically attuned, range of functionalization methods have been reported [22–25]. Among them, surface modification of CNTs with biocompatible polymers is important and hold a decisive role in improving the solubility and stability of CNTs, and custom them to execute in PHT [19]. To functionalize CNTs various polymers were used, in which poly(amidoamine) (PAMAM) is leading one as it holds series of important properties and excellent biocompatibility [26,27]. While merely accentuating over its cytotoxicity, PAMAM has been extensively administered as an antibacterial agent [28,29]. Interestingly, PAMAM could be an interesting NIR responsive material to apply in PHT. However, PTE of PAMAM and its comprising nanomaterials has been least explored [30]. Therefore, we revealed the PTE of PAMAM in combination with CNTs and Ag nanoparticles.

In consideration of their distinction in absorption of NIR radiations, integration of these three brilliant materials viz., Ag nanoparticles, CNTs and PAMAM could lead to formation of an interesting nanohybrid that might persist with high excellence in absorption of NIR radiation and their conversion to thermal energy. On this deliberation to design an excellent NIR active nanomaterial for PHT, herein, we covalently grafted the PAMAM to CNTs and consequently deposited the Ag nanoparticles. Prior to deposition of Ag nanoparticles, CNTs were covalently functionalized with fourth generation (G4), NH_2 -terminated aromatic PAMAM by Michel addition using *p*-phenylenediamine and methylmethacrylate. The PTE of thus produced CNTs-PAMAM-Ag was evaluated under exposure to 980 nm laser system and compared with its individual components, viz., CNTs and CNTs-PAMAM. Moreover, PTE of CNTs-PAMAM-Ag was investigated with 808 nm laser by replacement of 980 nm laser and effect of concentration over its PTE was also deliberated.

2. Experimental

2.1. Materials

CNTs prepared by CVD process were received from Carbon Nanotechnology Laboratory at Rice University, Houston TX, USA. The H_2SO_4 (Fischer), HNO_3 (Fischer), toluene (sigma-aldrich), SOCl_2 (Sigma-Aldrich), *p*-phenylenediamine (Sigma-Aldrich), tetrahydrofuran (Sigma-Aldrich), methylmethacrylate (Sigma-Aldrich), methanol (Fischer) and AgNO_3 (Sigma-Aldrich) were used as received. The aqueous solutions were prepared using ultrapure water obtained by Milli-Q Plus system (Millipore).

2.2. Preparation of CNTs-PAMAM-Ag

The CNTs-PAMAM-Ag was prepared using reported method [31]. In brief, 100 mg of CNTs-PAMAM, obtained by Michael addition process were dispersed in 15 mL of DI water by sonication and 10 mL aqueous solution of AgNO_3 (0.01 mol/L) was slowly added. The resulting suspension was allowed to stir under ambient conditions for 8 h and centrifuged. Thus formed CNTs-PAMAM-Ag was purified by successive washings with DI water and ethanol, followed by drying under vacuum.

2.3. Photothermal effect

The photothermal effect of samples was evaluated using 980 and 808 nm NIR diode laser systems (Armlaser Inc. USA) with an output power of 2 W/cm². In each experiment, 1 mL aqueous dispersion of the sample was transferred into 1 × 1 × 4 cm³ quartz cuvette and illuminated with NIR laser. The resulting elevation in temperature mediated by exposure to NIR radiations was measured using Hanna precision digital thermometer (Model: HI93510) carrying a thermocouple that was immersed in aqueous dispersions during experiment.

2.4. Characterization

UV-vis-NIR absorption spectra were recorded on a Varian Carry 50 Bio UV-vis spectrophotometer and FTIR spectra were acquired using Thermo-Nicolet IR 2000 spectrometer with KBr. Raman spectra were measured with Raman System (R-3000QE) in the backscattering configuration using an Argon ion laser having wavelength of 85 nm. The XRD were recorded on a Scintag X-ray diffractometer, model PAD X, equipped with Cu K α photon source (45 kV, 40 mA) at scanning rate of 3°/min. Scanning electron microscopy (SEM) measurements were carried out on a JEOL JXA-8900 scanning electron microscope and transmission electron microscopy (TEM) images were obtained with Hitachi H-8100 microscope at 200 kV. The x-ray energy dispersive spectroscopy (EDS) measurements were made using ThermoNoran EDS System 6 equipped with SEM.

3. Results and discussion

The FT-IR spectrum of CNTs-PAMAM (Fig. 1) displayed an absorption band related to N–H stretching frequency at 3427 cm⁻¹ and the band corresponding to carbonyl stretching of amide (–CO–NH) was found at 1621 cm⁻¹. The presence of the band at 1031 cm⁻¹ is additional characteristic signal originated from –CO–NH absorption. The absorption consisting to symmetric and asymmetric stretching of –CH₂ are appeared at 2851 and 2922 cm⁻¹, respectively. Moreover, the absorptions associated with aromatic C–C and C–H para-aromatic out of plane vibration were observed at 1515 and 826 cm⁻¹, respectively. Also, aromatic –CH was projected at 1031 and 1113 cm⁻¹ [31]. Comparatively, the spectrum of CNTs-PAMAM-Ag exhibited the strong absorptions associated with important characteristic bands of CNTs- PAMAM. The position of absorption bands in CNTs-PAMAM-Ag were varied compared to CNTs- PAMAM. To insist, N–H stretching was found at 3341 cm⁻¹, and the symmetric and asymmetric stretching of –CH₂ was generated at 2855 and 2924 cm⁻¹. The absorption originated by –CO–NH was found at 1605 cm⁻¹ and bands from aromatic ring were displayed at 1509 (aromatic C–C), 1016 and 1162 (–CH) and 831 cm⁻¹ (C–H para-aromatic out of plane vibration). The obvious modifications observed in the spectrum of CNTs-PAMAM-Ag compared to CNTs-PAMAM could be related to deposition of Ag nanoparticles and their strong interaction with CNTs and PAMAM chains.

The XRD of pristine CNTs shown in Fig. 2 has emerged with two characteristic peaks at 2θ value of 25.7 and 43.5° corresponding to (0 0 2) and (1 1 0) reflections of graphite, respectively [32]. In CNTs-PAMAM, these reflections were found at 25.5 and 43.8°. The minute dispersion observed in the graphitic reflections of CNTs and CNTs- PAMAM was accounted for successful grafting of PAMAM over the surface of CNTs. The diminutive

variation observed in the position of the reflections in CNTs-PAMAM compared to CNTs indicates inherent structure of CNTs was not affected by grafting of PAMAM. The XRD of CNTs-PAMAM-Ag promoted the high intense diffractions indexed to (1 1 1), (2 0 0) and (2 2 0) Bragg's reflections of silver with face centered cubic (fcc) symmetry at 38.0, 44.2 and 64.3°, respectively [31,33]. While, the diffractions of graphitic shells in CNTs were barely detectable in CNTs-PAMAM-Ag due to high intensity of Ag reflections. However, magnified display of XRD of CNTs-PAMAM-Ag, presented in Fig. S1, shows distinct (0 0 2) reflection of CNTs at 25.5° and the (1 1 0) reflection was not distinctly visible as it is merged with (2 0 0) reflection of Ag nanoparticles and appeared as a single peak at 44.2°.

The SEM images of CNTs-PAMAM-Ag (Fig. 3), clarifies perfect exfoliation of CNTs by effective grafting of PAMAM over their entire surface. It demonstrates the strong interaction persists between CNTs and PAMAM chains by providing the dispersing ability to CNTs-PAMAM-Ag in aqueous media, which is a primary requirement to employ CNTs-PAMAM-Ag as a photothermal agent. The presence of Ag nanoparticles are not obviously visible in SEM images due to low resolution of instrument and it was successfully accomplished in TEM images shown in Fig. 4. The TEM images bring the attention of Ag nanoparticles decorated over PAMAM grafted CNTs. It is clearly distinguishable the existence of PAMAM chains over surfaces of CNTs. The graphitic frame of CNTs is noticeable underneath of PAMAM layers, and the thickness of these PAMAM layers was found to be non-uniform. In general, a kind of core-shell structure formed between CNTs and PAMAM chains. The presence of PAMAM layers could help in effective nucleation of Ag seeds during in-situ deposition and the abundant population of Ag nanoparticles in CNTs-PAMAM-Ag. The in-situ deposition of Ag nanoparticles employed in the preparation of CNTs-PAMAM-Ag could leads to strong adherence of Ag nanoparticles, since sequential washings applied during purification of CNTs-PAMAM-Ag could not detach Ag nanoparticles. The absence of any free standing or unbounded nanoparticle in TEM images demonstrates the strong binding of Ag nanoparticles. The Ag nanoparticles are densely packed and have resemblance with spherical shape. Further, EDS of CNTs-PAMAM-Ag (Fig. S2) suggests the presence of C, Ag and Cu in the sample. Among these, the peak for C is generated mainly by enormous amount of CNTs with small contribution from PAMAM chains. The Ag is produced by Ag nanoparticles and Cu is originated by copper grid used in TEM measurement. The ratio of C to Ag in CNTs-PAMAM-Ag is found to be approximately 1.

The Raman spectrum of pristine CNTs (Fig. 5) displayed the typical G-band corresponding to Raman active E_{2g} at 1587 cm⁻¹ and D-band associated with the defective sites exists in hexagonal framework of graphite layers at 1306 cm⁻¹ [34]. While, G- and D-bands in CNTs- PAMAM were appeared at 1597 and 1315 cm⁻¹, respectively and in CNTs-PAMAM-Ag were at 1587 and 1311 cm⁻¹, respectively. The more details about position of Raman bands and their intensity ratio have been summarized in Table 1. Compared to CNTs, G- and D-bands in CNTs-PAMAM were shifted towards higher frequency side and this modification was attributed to defects created in graphite structure of CNTs due to harsh treatment of CNTs using strong acid mixture implemented prior to grafting of PAMAM. The G- and D-bands in CNTs- PAMAM-Ag were repositioned towards low wavenumber side compared to CNTs-PAMAM, which indicates that defective density in CNTs- PAMAM-Ag

has reduced by anchoring of Ag nanoparticles. The reduction in the defects of CNTs-PAMAM-Ag was ascribed to occupancy of Ag nanoparticles in defective sites of CNTs-PAMAM. Furthermore, intensity ratio of D- to G-band (I_D/I_G) provide an important information about degree of functionalization in measured samples. The value of I_D/I_G calculated for CNTs was found to be 0.40 and it was 1.44 for CNTs-PAMAM (Table 1). The substantial ratio found for CNTs-PAMAM could be narrated to presence of sever number of defective sites generated in CNTs by disordering of intrinsic structure of nanotubes. The value of I_D/I_G in CNTs-PAMAM-Ag was reduced to 1.35, it could be related to internal disordering graphite structure in CNTs-PAMAM was diminished by successful deposition of Ag nanoparticles. It could say that, herein, size of Ag nanoparticles was smaller than the size of defective sites persists over CNTs-PAMAM, hence the Ag nanoparticles have occupied defective sites.

The UV-vis-NIR spectrum of CNTs (Fig. 6) displayed the typical characteristic band at 235 nm [31,34]. In the spectrum of CNTs- PAMAM, the characteristic band is repositioned to 273 nm. The displacement observed for characteristic band in CNTs-PAMAM compared to CNTs was accounted grafting of PAMAM over CNTs. The CNTs- PAMAM-Ag revealed the strong absorption at 370 nm, owing to surface plasmon excitation of Ag nanoparticles and a shoulder band at 266 nm, attributed for the characteristic band found in CNTs-PAMAM. Compared to CNTs-PAMAM, the typical band was slightly shifted to 266 nm in CNTs-PAMAM-Ag, which implies the structure of CNTs-PAMAM was not altered by the deposition of Ag nanoparticles. Moreover, prominent absorption was observed for CNTs-PAMAM-Ag in NIR region. The strong absorption of CNTs-PAMAM-Ag persists in NIR region could make it as a promising photothermal agent [1,35,36]. In this insight, PTE of CNTs-PAMAM-Ag has been revealed in detail to verify its potentiality for employment in future photothermal therapy.

The PTE of CNTs-PAMAM-Ag was accessed by subjecting its aqueous dispersion at concentration of 1 mg/mL under continuous exposure to 980 nm laser for 7 min. The illumination process led to raise in temperature as shown in Fig. 7. The temperature attained by the samples during measurement of PTE is presented in Table 2. The elevation found for water was just 7.6 °C, since it was 30.2 °C for CNTs. The rise of 36.6 °C was observed in CNTs-PAMAM and it was 45.4 °C was in case of CNTs-PAMAM-Ag. The difference of 8.9 °C found in CNTs-PAMAM-Ag compared to CNTs-PAMAM is accounted for presence of Ag nanoparticles that could leads to enhancement in dissipation of thermal energy of CNTs-PAMAM-Ag. Obviously, the PTE of CNTs- PAMAM was improved by anchoring of Ag nanoparticles. In the same manner, PTE of CNTs was enhanced after grafting of PAMAM, therefore, an escalation of 8.9 °C was observed for CNTs-PAMAM compared to pristine CNTs. Henceforth, PTE of CNTs was methodically improved through grafting of PAMAM chains and sequential decoration with Ag nanoparticles. Overall, the PTE found in CNTs, CNTs-PAMAM and CNTs-PAMAM-Ag was caused by sample itself with very minute contribution from water, which was employed to prepare the samples for PTE. However, PTE of CNTs-PAMAM-Ag was found to be concertation dependent and linearly dropped by reducing the concentration level from 1 to 0.5, and 0.25 mg/mL (Fig. S3). The PTE of CNTs-PAMAM-Ag was further reveled in detail by evaluating its photothermal

conversion efficiency (η) with help of Roper's method using the equation given below [35,37,38],

$$\eta = \frac{hS(T_{\max} - T_{\text{surr}})Q_{\text{dis}}}{I(1 - 10^{-A_{980}})}$$

where h is heat transfer coefficient and S is the surface area of the sample holder. The value of hS was calculated with the help of Figs. 8 and 9 (see the Supporting Information for detailed calculation). $T_{\max}$ is the maximum temperature attained by sample and T_{surr} is the surrounding temperature. I is the incident power of laser source (2000 mW) and A_{980} is absorbance of the sample at 980 nm (1.18 for CNTs-PAMAM and 1.21 for CNTs-PAMAM-Ag). The Q_{dis} is the rate of heat dissipated due to absorption of light by solvent and sample holder, and it was measured independently using quartz cuvette containing DI water without any sample (25.9 mW). Thus, value of photothermal conversion efficiency (η) calculated for CNTs-PAMAM-Ag was found to be 21%, which is significantly higher than the value estimated for CNTs-PAMAM (16%). So, incorporation of Ag nanoparticles with CNTs-PAMAM, considerably improved the PTE of CNTs-PAMAM-Ag. The value of η calculated here for CNTs-PAMAM-Ag was found to be significantly higher than the value reported for well know Au and CuS based photothermal agents [8,35,39–41]. Apart from its substantial PTE, CNTs-PAMAM-Ag showed the dramatic anti-photobleaching and corrosive property. After application in three consecutive cycles, PTE of CNTs-PAMAM-Ag was not reduced and it retained virtually constant (Fig. S4). Moreover, the XRD of CNTs-PAMAM-Ag employed in three cycles of PTE measurement could not show structural rupture (Fig. S5). As evidenced by UV–vis-NIR spectrum of CNTs-PAMAM-Ag (Fig. 6), it is more responsive towards the radiations having wavelength around 1000 nm was experimentally verified. It was found that the PTE @ 980 nm was higher than that of 808 nm (Fig. S6). Overall, the temperature sustainability of cancer cells is lower than 50 °C, while the maximum temperature attained by CNTs-PAMAM-Ag during PTE measurement under illumination to 980 nm laser was 65.8 °C [8,9]. Under illumination to 980 nm laser, maximum temperature attained by CNTs-PAMAM-Ag was 65.8 °C, which is significantly higher than the survival level of cancer cells, so that CNTs-PAMAM-Ag could be a rationale agent to administer in future PHT.

4. Conclusions

In conclusion, CNTs-PAMAM-Ag is an excellent NIR photo-absorbing material with significant photothermal stability. The covalent grafting of PAMAM chains to CNTs and subsequent decoration of Ag nanoparticles has provided a step-wise improvement in the PTE of CNTs and CNTs-PAMAM-Ag could be an admirable photothermal agent. The exposure of CNTs-PAMAM-Ag to 980 nm laser possessed higher PTE compared to 808 nm. Moreover, the photothermal conversion efficiency of CNTs-PAMAM-Ag was found to be higher than the value reported for Au and CuS based photothermal agents. The final temperature attained by CNTs-PAMAM-Ag during its PTE measurement was is 65.8 °C, which is significantly higher than the temperature tolerance level of cancer cells. In

consideration of its efficient photothermal conversion ability and photothermal stability, CNTs-PAMAM-Ag could be a great potential for efficient destruction of cancer cells by light-induced heat. The CNTs- PAMAM-Ag was synchronously triggered by a single 980 nm laser, hence it could simplify the current therapeutic process. Overall, this work demonstrates the real potential of Ag nanoparticles to cross the regulatory barrier as antimicrobial agents into clinical use as effective therapeutics.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
FT-IR spectra of CNTs-PAMAM and CNTs-PAMAM-Ag.

Fig. 2.
XRD of CNTs, CNTs-PAMAM and CNTs-PAMAM-Ag.

Fig. 3.
SEM images of CNTs-PAMAM-Ag.

Fig. 4.
TEM images of CNTs-PAMAM-Ag.

Fig. 5.
Raman spectra of CNTs, CNTs-PAMAM and CNTs-PAMAM-Ag.

Fig. 6.
UV-vis-NIR spectra of CNTs, CNTs-PAMAM and CNTs-PAMAM-Ag.

Fig. 7.

Rise in temperature found for aqueous dispersions as a function of illumination time under illumination to 980 nm laser.

Fig. 8.

Temperature variation found for aqueous dispersions of CNTs-PAMAM and CNTs-PAMAM-Ag under exposure to 980 nm laser followed by its shut off.

Fig. 9.

The plot of time from cooling period versus negative natural logarithm of driving force temperature obtained for CNTs-PAMAM and CNTs-PAMAM-Ag using the data shown in Fig. 8.

Table 1

Frequency of Raman bands and their intensity ratio.

	<u>Position of bands (cm⁻¹)</u>		<i>ID/IG</i>
	D-band	G-band	
CNTs	1306	1587	0.40
CNTs-PA	1315	1597	1.44
CNTs-PA-Ag	1311	1587	1.35

Table 2

Temperature of samples measured during photothermal effect.

Sample	Laser System (nm)	Concentration of aqueous dispersion (mg/mL)	Initial temperature before irradiation with 980 nm laser (°C)	Final temperature after irradiation with 980 nm laser for 7 min (°C)	T (T _{final} -T _{initial}) (°C)
Water	980	–	20.8	28.4	7.6
CNTs	980	1.00	20.8	51.0	30.2
CNTs-PA	980	1.00	20.7	57.2	36.5
CNTs-PA-Ag	980	1.00	20.4	65.8	45.4
CNTs-PA-Ag	980	0.50	20.2	60.9	40.7
CNTs-PA-Ag	980	0.25	20.7	50.3	29.6
CNTs-PA-Ag	808	1.00	20.1	59.7	39.6