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Ag₂S nanocrystallites deposited over polyamidoamine grafted carbon nanotubes: An efficient NIR active photothermal agent

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Abstract

A novel NIR (near infrared) active photothermal agent, CNTs-PAMAM-Ag₂S has been synthesized by covalent grafting of polyamidoamine (PAMAM) to carbon nanotubes (CNTs) and subsequent deposition of Ag₂S nanocrystallites. The potential of CNTs-PAMAM-Ag₂S as a NIR active photothermal agent was preliminarily accessed by its electronic absorption spectrum measured in UV–vis–NIR region. The CNTs-PAMAM-Ag₂S exhibited excellent photothermal effect and photothermal conversion efficiency of 26% under illumination with 980 nm laser, the efficiency was found to be higher than popular gold and copper based photothermal agents. Temperature attained by CNTs-PAMAM-Ag₂S during measurement of its photothermal effect was 64.7 °C at 1 g/mL, which far exceeds the temperature tolerance level of cancer cells. So that CNTs-PAMAM-Ag₂S could destroy the cancer cells in an effective manner. Furthermore, it was found the linear dependence of photothermal effect of CNTs-PAMAM-Ag₂S over its concentration. CNTs-PAMAM-Ag₂S possessed excellent stability against photo-bleaching and photo-corrosiveness. In consideration of its outstanding photothermal effect and photothermal conversion efficiency, CNTs-PAMAM-Ag₂S could be a promising photothermal agent to employ in future photothermal therapy.

Keywords

Carbon nanotubes; Polyamidoamine; Ag₂S; Photothermal effect; Near infrared

1. Introduction

Currently it is highly desired to develop the novel therapeutic strategies with high efficiency, specificity and precision to treat cancer as cancer has become one of the major threats to human. The conventional clinical therapies presently in use to destroy cancer cells such as surgical removal, chemotherapy and radiotherapy persist with series of critical barriers like lower efficacy and higher toxicity [1,2]. On account of sequenced challenges associated with classical therapies use of near infrared (NIR) light-triggered therapy (photothermal therapy, PTT) has gained recent attention owing to its uncompromised benefits viz., non-invasiveness, safety, and efficiency, [3–8]. The PTT consists of conversion of photon energy

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Appendix A. Supplementary data

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into thermal energy in presence of a photo-absorbing agent called photothermal agent under exposure to NIR radiations [9–11]. After delivery of photothermal agent into tumor or cancerous cells results in transfer of NIR radiations into thermal energy, elevate local temperature of cancer cell, and ablaze [12, 13]. PTT is a promising therapeutic method to treat cancer owing to its efficiency, accuracy and safety [3–8]. Additional is use of NIR radiations as this light is considered to be safer light source imposing negligible damage to normal tissues, deeper tissue penetration, and higher precise spatial/temporal resolution of body tissue [3,14,15]. Therefore, success of PTT relies exclusively on photothermal agent executed in therapy. To this contest, series of nanomaterials have been designed and their suitability as photothermal transducers in terms of photothermal effect (PTE) under exposure to NIR radiations were reported [3–8,16]. Among reported photothermal agents, carbon nanotubes (CNTs) are especially interesting due to their unique physical and chemical properties, and excellent biocompatibility [17–20]. Due to photothermal efficiency and deep penetration ability through biological tissues, CNTs have been extensively applied in PTT [17–20]. The benefit in use of CNTs is ease of surface functionalization for customized target. While several polymers have been explored to functionalize CNTs, however, we are more inclined to explore the use of polyamidoamine (PAMAM) due to its unique structure and excellent biocompatibility [21,22]. Nevertheless, application of PAMAM in PTT has been least explored, so its further exploration as a photothermal agent is a current critical requirement.

Ag₂S is an important class of chalcogenide, which exhibit narrow band gap and strong absorption coefficient [6,23]. Ag₂S persist with needful vital properties such as low cytotoxicity and high stability in aqueous solution that prevents the release of silver ions into biological surroundings [6]. Moreover, Ag₂S absorbs strongly to the NIR radiations, high *anti*-photobleaching, elevated photoconversion efficiency and ideal inertness [5]. However, irregular morphology and nonhomogeneous size distribution of Ag₂S has restricted its amazing photo-responsive properties and hampered its wide range of applications in biomedical field, especially as photothermal agent. Therefore acute challenge still persisting with rational design to produce homogeneous Ag₂S nanocrystallites having efficient absorption of NIR radiations and their elevated photothermal conversion efficiency. In this consideration, herein we report the modification of Ag₂S nanocrystallites for their effective absorption of NIR radiations and impressive conversion to thermal energy by depositing them over nanostructured framework of PAMAM grafted to CNTs. Thus created CNTs-PAMAM-Ag₂S demonstrated exceptional PTE and photothermal conversion efficiency by illuminating to 980 nm NIR laser.

2. Experimental section

2. 1. Materials

All reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise noted and the aqueous solutions were prepared using ultrapure water obtained from Milli-Q Plus system (Millipore).

2.2. Preparation of CNTs-PAMAM-Ag₂S

Pristine CNTs were modified to carboxylated and acylated form before grafting of PAMAM [24]. Then acylated CNTs were utilized in covalent grafting of fourth generation PAMAM by repeated process of Michael addition using methylmethacrylate to the surface amino groups and amidation of terminal ester groups with ethylenediamine [24]. Followed by Ag₂S nanocrystallites were deposited over PAMAM grafted CNTs (CNTs-PAMAM) by dispersing them in 25 mL methanol and addition of silver nitrate (0.01 mol L⁻¹). Then 20 mL of Na₂S in methanol (0.01 mol L⁻¹) was added and the resulting mixture was stirred under ambient condition for 6 h to yield CNTs-PAMAM-Ag₂S.

2.3. Preparation of Ag₂S nanocrystallites

The Ag₂S nanocrystallites were prepared according to similar procedure mentioned for CNTs-PAMAM-Ag₂S without using CNTs-PAMAM.

2.4. Photothermal effect

The photothermal effect (PTE) of the samples was evaluated using 980 nm NIR diode laser system (Armlaser Inc. USA) with an output power of 1 and 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 the exposure to NIR radiations was measured using Hanna precision digital thermometer (Model: HI93510) with a thermocouple immersed in aqueous dispersion of sample during experiment.

2.5. Characterization

The XRD patterns were recorded by Scintag X-ray diffractometer, model PAD X, equipped with a Cu K α photon source (45 kV, 40 mA) and the TEM images were perceived with JEOL 2010 microscope. The UV-vis-NIR absorption spectra of samples were recorded using Jasco V-770 spectrophotometer.

3. Results and discussion

The XRD of CNTs-PAMAM-Ag₂S (Fig. 1) demonstrated the peak corresponding to (0 0 2) plane of graphitic shells of CNTs at 26.3°. In addition, it displayed the distinct peaks resolved at 22.4°, 26.0°, 29.0°, 31.5°, 33.6°, 34.4°, 36.8°, 37.8°, 40.7°, 43.5°, 46.2°, 47.7°, 48.8°, 53.3° and 63.8° owing to (-101), (-111), (111), (-112), (120), (-121), (121), (-103), (031), (200), (-123), (-212), (014), (-213) and (-134) planes of acanthite structured Ag₂S nanocrystallites, respectively (JCPDS 14-0072). The TEM image of CNTs-PAMAM-Ag₂S shown in Fig. 2 exhibit the deposition of Ag₂S nanocrystallites and their uniform distribution over the surface of PAMAM grafted to CNTs. The binding of PAMAM to the surface of CNTs is definable in Fig. 2. The strong adherence of Ag₂S nanocrystallites over the surface of PAMAM is perceptible in TEM image. The shape of Ag₂S nanocrystallites exists in CNTs-PAMAM-Ag₂S was found to be spherical and their diameter was around 9 nm.

The suitability of CNTs-PAMAM-Ag₂S as a NIR active photothermal agent was preliminarily accessed by its electronic absorption spectrum measured in UV-vis-NIR region. The spectrum of CNTs (Fig. 3) has exhibited a shoulder band around 231 nm, which is ascribed to C=C bonds of CNTs [25]. After covalent grafting of PAMAM, the characteristic absorption of CNTs has turned to clear band and its position has shifted to 237 nm in CNTs-PAMAM (Fig. 3). The shifting of 6 nm found in the characteristic band of CNTs-PAMAM compared to CNTs is accounted for strong adherence of PAMAM chains to the surface of CNTs. The spectrum of CNTs-PAMAM-Ag₂S (Fig. 3) displayed the characteristic band of CNTs at 237 nm, in addition, it demonstrated an absorption tail between 470 and 530 nm corresponding to monoclinic Ag₂S nanocrystallites [6,25]. Compared to CNTs-PAMAM, the characteristic band of CNTs has not shifted in CNTs-PAMAM-Ag₂S, which reveals that structure of CNTs-PAMAM has not been affected by deposition of Ag₂S nanocrystallites. The significant absorption of aqueous dispersion of CNTs-PAMAM-Ag₂S in NIR region is a primary assessment to employ it as a NIR active photothermal agent.

In consideration of its significant absorbance in NIR region, PTE of CNTs-PAMAM-Ag₂S was measured with its aqueous dispersion of 1 mg/mL and compared with PTE of water, CNTs and CNTs-PAMAM (Fig. 4). The total rise in temperature (ΔT) of 8.1 °C was found for water under its continuous irradiation for 7 min with 980 nm laser (Table 1). CNTs and CNTs-PAMAM exhibited the elevation in temperature of 30.2 and 36.5 °C, respectively. PTE of CNTs-PAMAM was 6.3 °C higher than the value measured for CNTs, so, absorption rate of CNTs to NIR radiations and their conversion to thermal energy was significantly improved by conjugation with PAMAM in CNTs-PAMAM. PTE of CNTs-PAMAM was further enhanced by anchoring of Ag₂S nanocrystallites. After deposition of Ag₂S nanocrystallites over surface of CNTs-PAMAM, PTE of CNTs-PAMAM-Ag₂S has increased. Nevertheless, PTE measured for Ag₂S nanocrystallites was lower than the PTE of CNTs-PAMAM-Ag₂S and higher than that of CNTs.

Further the ΔT value recorded for CNTs-PAMAM-Ag₂S was 44.2 °C, while it was 30.2, 36.5 and 40.5 °C for CNTs, CNTs-PAMAM and Ag₂S nanocrystallites, respectively. So that, systematic enhancement in PTE of CNTs was attained by grafting of PAMAM and successive deposition of Ag₂S nanocrystallites. However, PTE measured for water was considerably low, therefore contribution of water in PTE accounted for CNTs, CNTs-PAMAM, Ag₂S nanocrystallites and CNTs-PAMAM-Ag₂S was negligible. Overall a systematic enhancement in the PTE of CNTs was attained by grafting of PAMAM, and consecutive immobilization of Ag₂S nanocrystallites. Therefore, synergetic combination of CNTs, PAMAM and Ag₂S was significantly enhanced the PTE of CNTs-PAMAM-Ag₂S compared to its individual components.

Further to verify the excellence in PTE of CNTs-PAMAM-Ag₂S, its photothermal conversion efficiency (η) was calculated using equation (1) [25–30],

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

where η is photothermal efficiency, h is heat transfer coefficient and S is surface area of the sample container. $T_{\max}$ is maximum temperature attained by sample and T_{surr} is surrounding temperature (Table 2). I is power of laser source (2000 mW) and A_{980} is absorbance of aqueous dispersion of samples at an excitation wavelength of 980 nm. Q_{dis} is rate of heat dissipated due to absorption of light by solvent and container.

To calculate the value of hS , a dimensionless driving force of temperature, θ is introduced and scaled using the maximum system temperature, $T_{\max}$ and the surrounding temperature, T_{surr}

$$\theta = \frac{T - T_{surr}}{T_{\max} - T_{surr}} \quad (2)$$

and the sample system time constant, τ_s was evaluated using the following equation (3)

$$t = -\tau_s \ln(\theta) \quad (3)$$

The value of τ_s was calculated by Figs. 5 and 6, and using its value, the unknown parameter, hS was evaluated with the help of following equation (4).

$$hS = \frac{m_D C_D}{\tau_s} \quad (4)$$

where m_D is mass of DI water (1.01 g) and C_D is its heat capacity. The value of Q_{dis} was measured separately using quartz cuvette containing only DI water without any sample and it was found to be 25.9mW.

On basis of above calculation, the value of photothermal conversion efficiency (η) estimated for CNTs-PAMAM-Ag₂S was 26%, while it was 23% for CNTs-PAMAM. By anchoring of Ag₂S nanocrystallites over CNTs-PAMAM an increment of 3% in the value of η was observed for CNTs-PAMAM-Ag₂S. Overall, CNTs-PAMAM-Ag₂S exhibited exceptional photothermal conversion efficiency and it is found higher than the value reported for popular Au and Cu based photothermal agents *viz.*, Au nanoshells (25 and 18%) [28,31], Au nanorods (22%) [32], Au nanoparticles (21 and 22%) [17], Cu_{2-x}Se nanoparticles (22%) [33], Cu₉S₅ nanoparticles (25.7%) [34] and hollow-structured CuS (18%) [7]. Moreover, photothermal conversion efficiency of CNTs-PAMAM-Ag₂S was more than Ag₂S quantum dots (23.8%) [6].

Furthermore stability of CNTs-PAMAM-Ag₂S was monitored by measuring its PTE for subsequent five cycles and found that it was constant for all five cycles (Fig. 7). Therefore, CNTs-PAMAM-Ag₂S possessed excellent stability against photo-bleaching and photo-corrosiveness. Then to identify the influence of concentration over PTE of CNTs-PAMAM-Ag₂S, its PTE was measured in additional two lower concentrations *viz.*, 0.5 and 0.25 mg/mL. It was observed that PTE is linearly dependent on its concentration in such a manner that it improved with increase in concentration (Fig. S1). The T value determined for concentration of 1, 0.5 and 0.25 mg/mL was 44.2, 42.6 and 40.3 °C, respectively.

Generally, the survival temperature level of cancer cells is below 50 °C [34,35]. This temperature was attained by CNTs, CNTs-PAMAM and Ag₂S at 6, 4.5 and 3.5 min of irradiation, respectively. However, CNTs-PAMAM-Ag₂S conquered the desired temperature of 50 °C within 3 min of exposure to laser. Compared to CNTs, CNTs-PAMAM and Ag₂S, CNTs-PAMAM-Ag₂S accomplished the needful temperature within a short period of 3 min of irradiation. Nonetheless, rest of the samples were unable to attain the temperature of 50 °C within 3 min of exposure. Therefore, CNTs-PAMAM-Ag₂S could produce a strong absorption and heat transfer effect from laser, and this heat could lead to direct destruction of cancer cells. The CNTs-PAMAM-Ag₂S can deliver enormous heat within short period to cancer cells and succeed in ablating them in an efficient manner. Overall, CNTs-PAMAM-Ag₂S possess strong absorption of 980 nm radiations with large light harvesting ability. In addition, CNTs-PAMAM-Ag₂S is feasible at low energy level of laser like 2 W/cm². Therefore, if CNTs-PAMAM-Ag₂S is employed in PTT, it could be viable under low energy of 2 W/cm² and therapy can complete within short time of about 3 min. So that CNTs-PAMAM-Ag₂S persists with strong optical absorption and high efficiency of photothermal conversion, critically needed for success of cancer therapy. In addition, target is also easily perusable using CNTs-PAMAM-Ag₂S.

Moreover, to reveal the effect of power of laser source over PTE of CNTs-PAMAM-Ag₂S, its PTE was measured under illumination of 980 nm laser having power of 1 W/cm² and compared it with value obtained with 2 W/cm² laser (Fig. S2). It was found that PTE of CNTs-PAMAM-Ag₂S was reduced by reduction in the power of laser. In particular, T estimated for 1 and 2 W/cm² laser was 41.7 and 44.2 °C, respectively (Table 1). PTE of CNTs-PAMAM-Ag₂S was reduced by 2.5 °C by replacing 2 W/cm² laser with 1 W/cm². Hence, PTE of CNTs-PAMAM-Ag₂S was found to be dependent on power of laser source and it can be controlled to desired amount by varying the power of laser. In general, due to its significant PTE, CNTs-PAMAM-Ag₂S can cause irreversible destruction of cancer cells by denaturation of their protein and damage of cell membrane, led in growth suppression, and ablation of tumors. Hence, CNTs-PAMAM-Ag₂S could be a promising photothermal agent to implement in future PTT.

4. Conclusions

In conclusion, an intelligent NIR active photothermal agent, CNTs-PAMAM-Ag₂S has been fabricated by immobilization of Ag₂S nanocrystallites over the framework of covalently grafted PAMAM to CNTs. The UV-vis-NIR spectrum of CNTs-PAMAM-Ag₂S revealed its significant absorption in NIR region and it was verified by its excellent PTE and photothermal conversion efficiency under exposure to 980 nm laser. The rational improvement in PTE of CNTs was achieved by grafting of PAMAM and successive anchoring of Ag₂S nanocrystallites. The CNTs-PAMAM-Ag₂S exhibited higher photothermal conversion efficiency than popularly known gold and copper based photothermal agents. Moreover, PTE of CNTs-PAMAM-Ag₂S measured for consecutive five cycles was found to be constant, so it persists with notable antiphotobleaching and antiphotocorrosiveness properties. The linear dependence of PTE over the concentration was observed in CNTs-PAMAM-Ag₂S. Overall maximum temperature attained with CNTs-PAMAM-Ag₂S by illuminating to 980 nm laser for 7 min was far exceeded the temperature

tolerance level of cancer cells. Therefore, on basis its outstanding properties, viz., PTE, photothermal conversion efficiency, antiphotobleaching and antiphotocorrosiveness, CNTs-PAMAM-Ag₂S could be a promising candidate to advance the current PTT.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1.
XRD of CNTs-PAMAM-Ag₂S.

Fig. 2.
TEM image of CNTs-PAMAM-Ag₂S.

Fig. 3.
UV-vis-NIR spectra of CNTs, CNTs-PAMAM and CNTs-PAMAM-Ag₂S.

Fig. 4.

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

Fig. 5. Temperature variation found for aqueous dispersion of CNTs-PAMAM and CNTs-PAMAM-Ag₂S under exposure to 980 nm laser followed by its shut off.

Fig. 6.
The plot of time from cooling period versus negative natural logarithm of driving force temperature obtained for CNTs-PAMAM and CNTs-PAMAM- Ag_2S using the data shown in Fig. 5.

Fig. 7.
Temperature variation measured for the aqueous dispersion of CNTs-PAMAM-Ag₂S (1mg/mL) for five cycles under irradiation by 980 nm laser.

Table 1
Temperature of samples measured during measurement of photothermal effect using 980 nm laser.

Sample	Power of laser (W/cm ²)	Concentration of aqueous dispersion (mg/mL)	Initial temperature before irradiation (°C)	Final temperature after irradiation for 7 min (°C)	T (T _{final} -T _{initial}) (°C)
Water	2	–	20.8	28.9	8.1
CNTs	2	1.00	20.8	51.0	30.2
CNTs-PAMAM	2	1.00	20.7	57.2	36.5
Ag ₂ S	2	1.00	20.4	60.9	40.5
CNTs-PAMAM-Ag ₂ S	2	1.00	20.5	64.7	44.2
CNTs-PAMAM-Ag ₂ S	2	0.50	20.2	62.8	42.6
CNTs-PAMAM-Ag ₂ S	2	0.25	20.7	61.0	40.3
CNTs-PAMAM-Ag ₂ S	1	1.00	20.7	62.4	41.7

Table 2

Properties used in calculation of photothermal conversion efficiency.

Sample	$T_{\max}$ (°C)	T_{sur} (°C)	$T_{\max} - T_{\text{sur}}$ (°C)	A_{980}	η (%)
CNTs-PAMAM	62.1	20.3	41.8	1.021	23
CNTs-PAMAM-Ag ₂ S	64.1	20.7	43.4	1.129	32