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Antibacterial and release properties of Ag nanoparticles on dopamine coated carbon nanotubes

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ABSTRACT

The multi-wall carbon nanotube (MCNT) was selected to combine with nanosilver in order to increase the mechanical properties and reduce the releasing rate of nanosilver in solutions. The higher dispersion of Ag nanoparticles (AgNPs) was in-situ prepared on the dopamine coated carbon nanotubes by a mild and environmentally friendly method. The antibacterial activity of hybrid material was investigated by the disk-diffusion test against Gram-negative bacteria. Compared with the MCNT/Ag composites, the introduction of polydopamine (PDA) on the MCNT surface obviously improves the deposition of AgNPs and increased the long-term antibacterial property, and the Ag/PDA/MWCNTs hybrid materials exhibited excellent antibacterial ability.

INTRODUCTION

As Ag nanoparticles (AgNPs) have unique thermal, magnetic and engineering applicability due to their high surface energy and high chemical activity, they are being extensively studied in various fields[1, 2, 3]. It has been widely applied in the fields of antistatic materials, biosensors materials and antibacterial materials[4, 5, 6]. AgNPs are attributed to a kind of representative antibacterial materials which possess a broad-spectrum antibacterial property, no drug resistance and a low cytotoxicity[7]. However, AgNPs are readily being released in practical application, resulting in the decline of antimicrobial properties. For the purpose of obtaining long-lasting antibacterial performance, we take advantage of reservoirs to fix the AgNPs. Carbon nanotubes can be regarded as an excellent candidate for the AgNPs carrier due to their certain inhibitory performance, high chemical stability and higher specific surface area. The adhesion strength of adult barnacles was significantly reduced by the addition of low amounts of multiwall carbon nanotubes (MWCNTs) to the silicone-based coatings[8]. Stable AgNPs supported on MWCNTs have been successfully synthesized by calcinations of the complexes of Ag cation and acid-treated MWCNTs[9]. Whereas MWCNTs may lose the excellent physical properties after being acid-treated, therefore other methods are applied we attempt to employ other methods to modify MWCNTs. Dopamine (DA), a biomolecule that contains catechol and amine functional groups, was proved to have the abilities to reduce metal ions to metal nanoparticles, such as Au^+ and Ag^+ [10]. Additionally, the polydopamine (PDA) has an aromatic structure with catechol groups and versatile functions[11]. Inspired by the versatile capabilities of PDA, hypothesized DA can be an alternative to modify MWCNTs.

In this work silver nanoparticles/polydop-amine/ multi-walled carbon nanotubes composites (Ag/ PDA/MWCNTs) was prepared. Meanwhile the inhibition zone method provides the evidence that Ag/ PDA/MWCNTs composites have a long-term bacteriostatic effect.

EXPERIMENTAL

Sample preparation: firstly 30 mg pristine MWCNTs were dispersed in 50 mL Tris-HCl (pH=8.5) by sonication for 10 min. Then 30 mg DA were added to the mixture, which was magnetically stirred at 25 °C for 24 h. The coated MWCNTs were filtered and washed with deionized water followed by vacuum drying at 50 °C overnight. And then, 10 mL aqueous solution (0.01 M) of $AgNO_3$ and 5 mL PVP solution (5 wt%) were mixed with vigorous stirring at 25 °C for 2 h. 20 mg dopamine modified MWCNTs (PDA/MWCNTs) were added into the mixture after sonicating for 10 min. Then the mixture was magnetically stirred under ultraviolet irradiation for 4 h. Ag/PDA/MWCNTs composites were obtained after filtering and sufficient washing,

Surface characterization: The surface morphologies of PDA/MWCNTs and Ag/PDA/MWCNTs composites were characterized by transmission electron microscope (TEM Hitachi. H-7000, Japan). XPS measurement was performed on an ESCALAB-MKII spectrometer (VG Co., United Kingdom) with

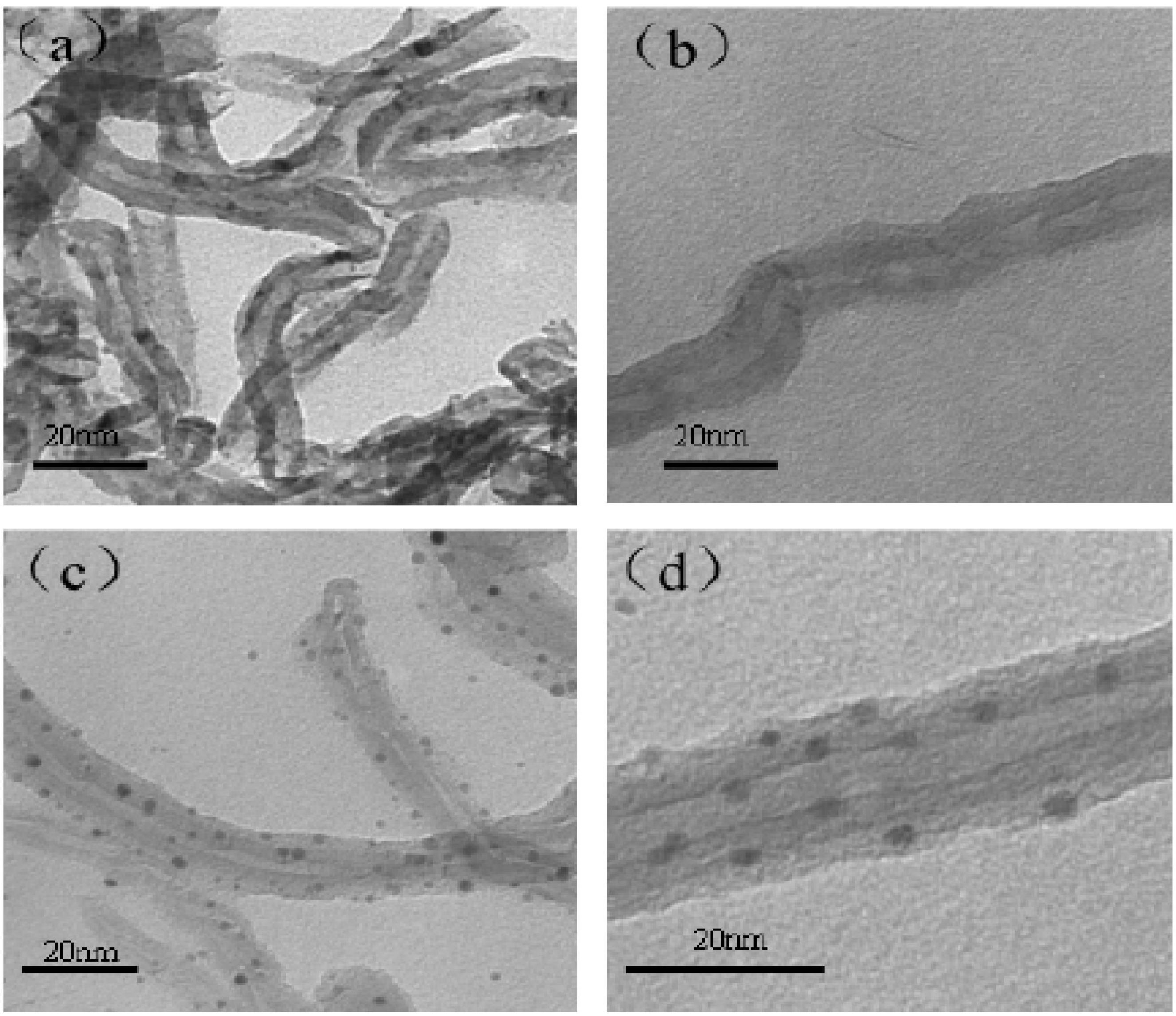

Figure 1 : TEM of composite materials; a pristine MWCNTs; b PDA/MWCNTs; c and d Ag/PDA/MWCNTs composites

Al KaX-ray radiation as the X-ray source for excitation. The sample for XPS characterization was deposited onto a Si slide. The release-rate of Ag/PDA/MWCNTs composites was characterized by the conductivity of the suspension. The conductivity was measured by a HANNA instruments HI 98188 portable conductivity meter.

Antibacterial assessments: All materials and disks were sterilized at 121 °C in an autoclave before the experiment according to the CLSI, 2000. The antimicrobial susceptibility test in LB agar plates was conducted E. coli was cultured in LB medium in a shaking incubator (120rpm) at 37 °C for overnight to grow a primary culture, which was further diluted with LB medium to obtain a approximate concentration of 10^7 cfu/mL. E. coli was spread onto LB agar plates with a cotton swab from bacterial suspensions. After filter paper disks with diameter of 10 mm were immersed in different composites suspension, they were placed on the agar plates for incubating at 37 °C for 12 h, respectively. Subsequently, the zone of inhibition was obtained and measured.

RESULTS AND DISCUSSION

The surface morphologies of the composite materials were examined by TEM. As shown in Figure 1a-b, the MWCNTs were uniformly coated with PDA. The interface of MWCNTs sidewall and PDA is clearly observed. Compared to the smooth and flat surface of PDA/MWCNTs, AgNPs were clearly observed across the surface of the coated nanotubes (Figure 1c-d). Figure 1c shows a typical TEM image of Ag/PDA/MWCNTs, where the cross-sectional view indicates that the average diameter of AgNPs is about 6 nm. In general, the nanoparticles prepared have a narrow size distribution and present spherical shape.

Further evidence was provided with XPS analysis for covalent modification of Ag/PDA/MWCNTs composites. The C1s binding energy is at 286.4 eV,

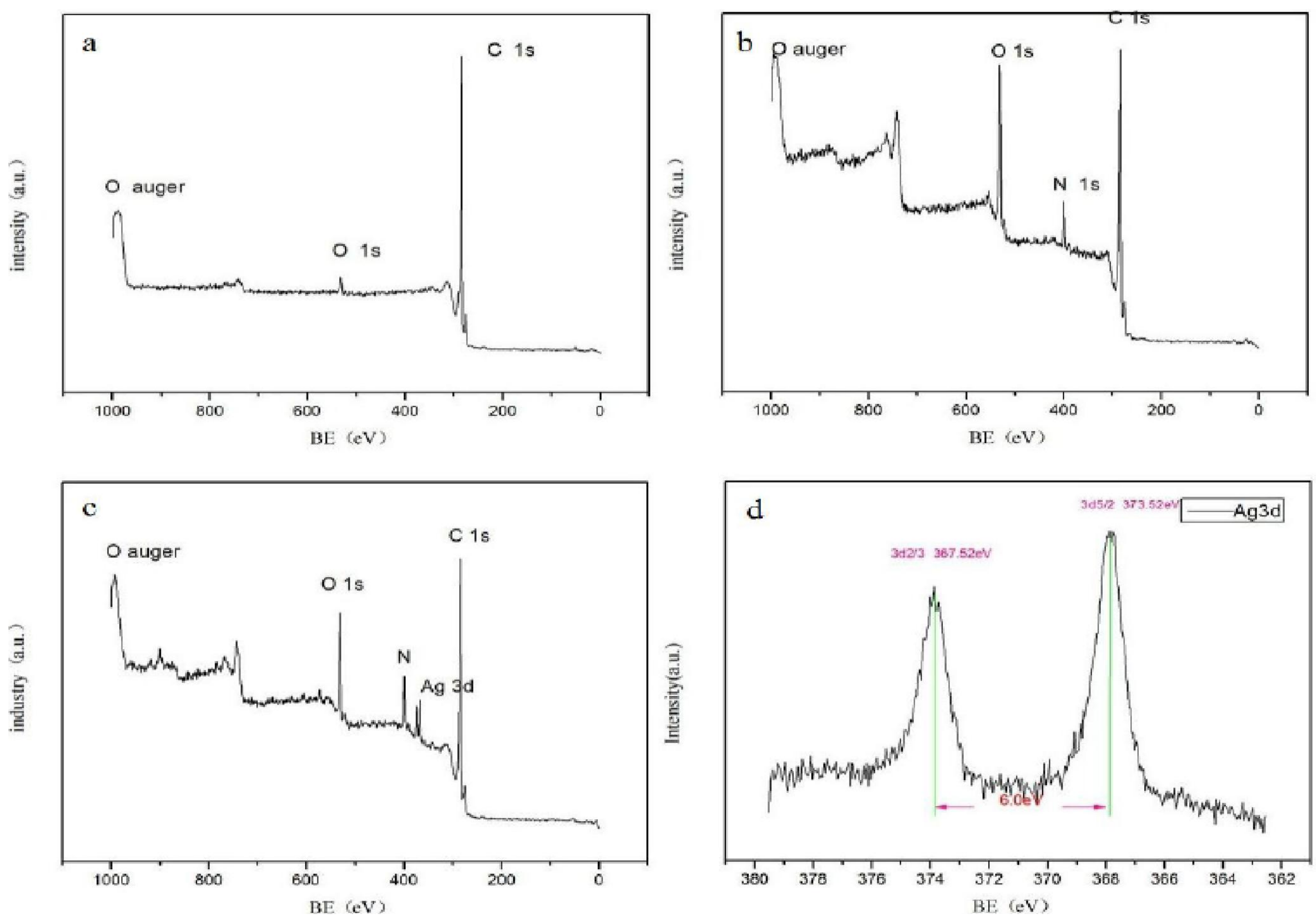

Figure 2 : XPS of composite materials; a pristine MWCNTs; b PDA/MWCNTs; c and d Ag/PDA/MWCNTs composites

corresponding to the value (284.5 eV)[12]. The oxygen signal is probably caused by mixed acid or air absorption. The spectrum of the Ag 3d core level of the Ag/PDA/MWCNTs (Figure 2d), clearly proved that the Ag 3d5/2 component is at a binding energy of 368.3 eV, which is a characteristic peak of the metallic Ag oxidation state[13]. Several reports have demonstrated that metal-support interaction makes the XPS peaks shift to higher values[14, 15]. There is a shift occurring at the binding energy of Ag 3d5/2 component, which indicates that the AgNPs are mainly deposited on the surface of MWCNTs with chemical adsorption.

AgNPs owning strong bactericidal effect have been used as antibacterial agents in many fields[16, 17]. However, the practical applications are often limited by the problem of their low stability, which is important parameter for determining the antibacterial activity of AgNPs. Furthermore, AgNPs interactions with bacteria are dependent on the size and shape of the nanoparticles. The antibacterial activity of the silver nanoparticles decreases with an increase of the particle size[18, 19]. Therefore, we assume that the Ag/PDA/MWCNTs hybrid materials possess excellent bactericidal property because of their suitable particle size (5-7 nm). For this superiority, AgNPs can easily reach the nuclear content of bacteria and they present greater surface area; therefore the contact with bacteria is greater[20].

In order to demonstrate this conjecture, we apply to the method of the disk-diffusion test for evaluating the bactericidal activities of the pristine MWCNTs, Ag/MWCNTs composites and Ag/PDA/MWCNTs composites against E. coli respectively. As shown in Figure 3a, we assume that the nonfouling effects were due to leakage of AgNPs from the coatings in the solution for the Ag/MWCNTs composites barely have an inhibition zone. Compared with Ag/MWCNTs composites, Ag/PDA/MWCNTs composites have a larger inhibition zone, indicating that Ag/PDA/MWCNTs composites have better antibacterial activity than Ag/MWCNTs composites. The growth of E. coli was fully inhibited during the whole 12 h culture period when the concentration of the Ag/PDA/MWCNTs was 0.3 mg/mL (Figure 3b). After being stored for 3 months (Figure 3c), the inhibition zone containing Ag/MWCNTs composites decreases evidently, however the other inhibition zone containing Ag/PDA/MWCNTs composites still remain comparatively large, which further supports the conclusion that the Ag/PDA/MWCNTs composites can prevent Gram-negative bacterial growth obviously and enduringly. We assume that the AgNPs in the composites are fixed on the PDA layers, which further improve the stability of AgNPs.

To further validate the stability of AgNPs on the surface of PDA/MWCNTs, the release-rate test was used to estimate the conductivity of the composite materials. As shown in Figure 4, the polyvinylpyrrolidone/Ag nanocomposites (PVP/Ag, PVP serve as dispersant) solution conductivity increased rapidly. It approximately rose to the maximum in the first two days, proving that silver ions had been completely released. Compared with the PVP/Ag nanoparticles, the conductivity of Ag/MWCNTs composites increased more slowly, the first few days into a curve upward trend, seven days later, as a smooth curve slightly upwards trend. These results demonstrate that the release of AgNPs was controlled effectively by adding to the synthesis of Ag/MWCNTs composites. Furthermore, the addition of the PDA layers significantly increased the slow-release ability of the Ag/PDA/MWCNTs composites. Ten days later the silver ions still had not been completely released and the back of the curve still had a

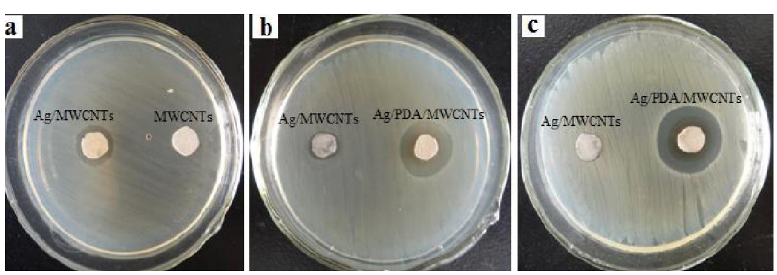

Figure 3 : Antibacterial activities of composite materials toward gram-negative bacteria E. coli cells; a Ag/MWCNTs and the pristine MWCNTs; b Ag/MWCNTs and Ag/PDA/MWCNTs; c Ag/MWCNTs and Ag/PDA/MWCNTs after being stored for 3 months

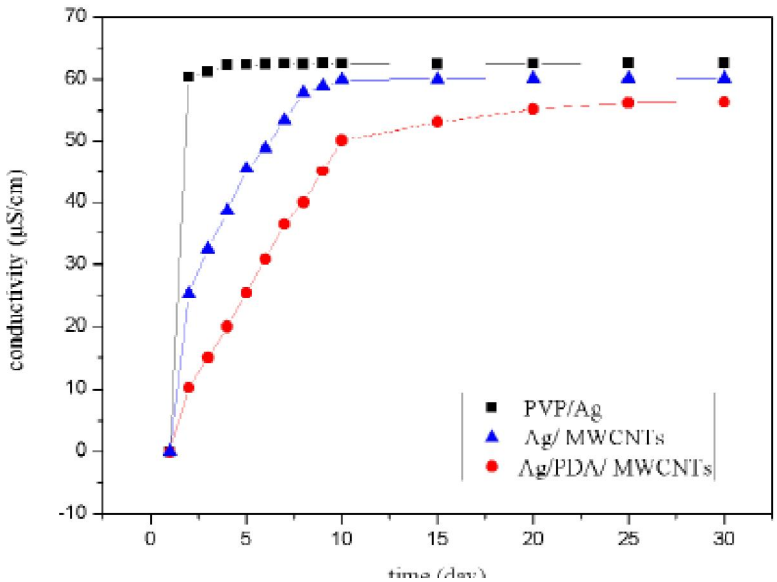

Figure 4 : Conductivity of PVP/Ag, Ag /MWCNTs and Ag/PDA/MWCNTs composite materials

certain upward trend which proved that the releasing of the silver ions were controlled in a certain degree. To incorporate the results of the disk-diffusion test, the conclusion is that the Ag/PDA/MWCNTs composites possess strong antimicrobial activity and sustained-release performance.

CONCLUSIONS

In summary, a simple, flexible and effective biocompatible antifouling strategy is applied to prepare Ag/PDA/MWCNTs hybrid materials using the pre-synthesis PDA layer as a nanoscale guide to form uniform AgNPs on the surface of PDA/MWCNTs. The bactericidal activities showed that Ag/PDA/MWCNTs nanocomposites have a good inhibitory effect on bacteria and release property superior to Ag/MWCNTs composites. We believe that the Ag/PDA/MWCNTs hybrid materials have great potential for anti-fouling coatings and environmental applications.

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REFERENCES

[1] P.Dibro, J.Dzioba, K.K.Gosink, C.C.Hase; Antimicob. Agents and Chemother, **46**, 2668-2670 **(2002)**.

[2] Q.L.Feng, J.Wu, G.Q.Chen, F.Z.Cui, T.N.Kim, J.Q.Kim; J Biomed.Mater.Res., **52**, 662-668 **(2000)**.

[3] C.N.Lok, C.M.Ho, R.Chen, Q.Y.He, W.Y.Yu, H.Z.Sun et al.; Journal of Proteome Research, **5**, 916-924 **(2006)**.

[4] K.C.Bhol, P.J.Schechter; British Journal of Dermatology, **152**, 1235-1242 **(2005)**.

[5] M.Rai, A.Yadav, A.Gade; Biotechnology Advances, **27**, 76-83 **(2009)**.

[6] S.Mazumder, P.K.Ghosal, C.A.Pujol, M.J.Carlucci, E.B.Damonte, B.Ray; International journal of biological macromolecules, **31**, 87-95 **(2002)**.

[7] B.Matsuhiro, A.F.Conte, E.B.Damonte, A.A.Kolender, M.C.Matulewicz, E.G.Mejias et al.; Carbohydr.Res., **340**, 2392-2402 **(2005)**.

[8] A.Beigbeder, P.Degee, S.L.Conlan, Q.Y.Zhang, S.S.J.Leong, C.Y.Tang et al.; Biofouling, **24**, 291-302 **(2008)**.

[9] P.Gunawan, C.Guan, X.Song, Q.Zhang, S.S.J.Leong, C.Tang et al.; Acs.Nano., **5**, 10033-10040 **(2011)**.

[10] K.Yoosaf, B.I.Ipe, C.H.Suresh, K.G.Thomas; J Phys.Chem.C., **111**, 12839-12847 **(2007)**.

[11] T.A.Morris, A.W.Peterson, M.J.Tarlov; Anal.Chem., **81**, 5413-5420 **(2009)**.

[12] F.Wang, S/Arai, M.Endo; Electrochemistry Communications, **7**, 674-678 **(2005)**.

[13] S.X.Ren, H.F.Yang, X.S.Tian, Y.F.Li; Advanced Materials Research, **79**, 965-968 **(2009)**.

[14] A.A.Khassin, T.M.Yurieva, V.V.Kaichev, V.I.Bukhtiyarov, A.A.Budneva, E.A.Paukshtis et al.; Journal of Molecular Catalysis, **175**, 189-204 **(2001)**.

[15] J.Radnik, C.Mohr, P.Claus; Phys.Chem.Chem.Phys., **5**, 172-177 **(2003)**.

[16] H.Wang, J.Fang, T.Cheng, J.Ding, L.T.Qu, L.M.Dai et al.; Chem.Commun., 877-879 **(2008)**.

[17] A.Kumar, P.K.Vemula, P.M.Ajayan, G.John; Nature materials, **7**, 236-241 **(2008)**.

[18] J.R.Morones, J.L.Elechiguerra, A.Camacho, K.Holt, J.B.Kouri, J.T.Ramirez et al.; Nanotechnology, **16**, 2346–2353 **(2005)**.

[19] Martinez G.A.Castanon, Nino N.Martinez, Martinez F.Gutierrez, Martinez J.R.Mendoza, F.Ruiz; J.Nanopart Res.,**10**, 1343-1348 **(2008)**.

[20] C.N.Lok, C.M.Ho, R.Chen, Q.Y.He, W.Y.Yu, H.Z.Sun et al.; J Proteome Res., **5**, 916-924 **(2006)**.