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RESEARCH ARTICLE

A study on the bactericidal properties of Cu-coated carbon nanotubes

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Abstract A Cu layer was coated on carbon nanotubes (CNTs) by ion beam-assisted deposition (IBAD). Standard agar dilution method was used to evaluate the bactericidal rate against E. coli and S. aureus bacteria. The structure and chemical states of the Cu-coated CNTs were investigated by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The results show that the Cu-coated CNTs possess a very high bactericidal rate. In comparison with the Cu-coated pyrolytic carbon sample, the Cu-coated CNTs show much stronger bactericidal property.

Keywords bactericidal property, Cu-coated carbon nanotubes, ion beam assisted deposition (IBAD)

1 Introduction

With the development of biomedical materials, more and more artificial organs and parts are used in clinics to ease the patients' agony and prolong their lives. Biomedical materials are those materials that can be used to assist or substitute for human beings' tissue and organs. Because of the contact with tissue, blood, cells and protein, their biocompatibility is a very important factor. Biomedical materials can be divided into metal and non-metal materials. Metal biomaterials are used as frame plates and screws in orthopedics [1]. Non-metal biomaterials are used as heart valves and artificial tubes [2]. Recently, pyrolytic carbon has been used to make artificial heart valves due to its fantastic mechanical property and biocompatibility [3,4]. It is essential for materials used as artificial heart valves, not only to have good mechanical properties such as wear and fatigue resistance, but also to possess strong bactericidal properties. It is well known that Ag is the only heavy metal that is harmless to the human body and shows strong bactericidal properties. Because silver is an expensive metal and oxidizes easily, researchers have been looking for another candidate. In terms of antibacterial properties, Cu is just ranked second after Ag and is stable and harmless for the human body [5]. Therefore, Cu has been chosen as the research object. Materials with Cu doping have already been used in medical instruments and sanitary facilities. In order to enhance the bactericidal property of an artificial valve, a Cu-implanted pyrolytic carbon was reported in our previous work [6]. On the other hand, carbon nanotubes (CNTs) have been widely used in the biomedical area due to their unique structure, excellent mechanical and electrical properties, and high surface area [7]. Our interest is to combine the advantages of both CNTs and Cu doping.

In this paper, CNTs were grown on a pyrolytic carbon substrate by the chemical vapor deposition (CVD) method and the Cu coating was deposited on the surface of CNTs by ion beam-assisted deposition (IBAD). The bactericidal property of the Cu-coated CNTs was evaluated by using a standard agar dilution method with E. coli and S. aureus bacteria. In addition, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) analyses were performed to investigate the Cu distribution and chemical states as well as their relationships to bactericidal properties.

2 Experimental details

The pyrolytic carbon plate was cut into circular pieces with a diameter of 13 mm and a thickness of 4 mm. The samples were ground and polished to a mirror finish and sputter-etched by argon ions prior to growing CNTs by CVD.

The CNTs were grown on pyrolytic carbon by decomposing ethylene on Ni/Co catalyst nanoparticles at 850°C during the CVD process at the University of Western Ontario, Canada. The experimental details were described in a

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previous report [8]. The CNTs were directly used without further treatments.

After growing the CNTs, the samples were coated with Cu by IBAD in our group using a multifunctional thin film deposition facility. The IBAD facility has two Kaufmann ion sources that can provide ion beams of low and high energy. An argon beam can be used to sputter the Cu target providing the Cu atoms simultaneously. Another a nitrogen ion beam is used to assist the Cu deposition to enhance the adhesion. The experimental condition of the IBAD is listed in Table 1. All the sample descriptions are shown in Table 2.

Table 1 Experimental parameters of Cu coated CNTs samples by IBAD

Parameters	Value
Base vacuums	3.0×10^{-4} Pa
High energy Ar ions bombarding energy	1.4 keV
High energy Ar ions beam current	20 mA
Low energy Ar bombarding energy	100 eV
Low energy Ar ions beam current	5 mA
Working vacuums	2.1×10^{-2} Pa
Working temperature	Room temperature

Table 2 Describing and numbering of the samples

Number	Substrate	Number	Substrate	Deposition time /min
A0	CNTs	B0	Pyrolytic carbon	0
A1	CNTs	B1	Pyrolytic carbon	5
A2	CNTs	B2	Pyrolytic carbon	10
A3	CNTs	B3	Pyrolytic carbon	30
A4	CNTs	B4	Pyrolytic carbon	60

The bactericidal properties of the Cu-coated CNTs on the pyrolytic carbon substrate and the Cu-coated pyrolytic carbon samples were measured using Gram positive S. aureus and negative E. coli as the test bacteria, because these two kinds of bacteria are very common and are typical infections to the human body. The bactericidal experimental procedures were described in detail in our previous work [6]. The bactericidal rate K can be calculated by the following formula

$$K = \frac{(A-B)}{A} \times 100\%$$

where A and B are the numbers of bacteria colonies corresponding to the reference sample and Cu-coated samples, respectively.

X-ray photoelectron spectroscopy analysis was performed using an XPS analyzer (PHI5300, USA). It operates at 250 W and 1256.6 eV with Mg Kα radiation. The working pressure in the XPS chamber was approximately 4×10^{-7} Pa. Charging effects of the samples during analyses were corrected using a value of 285.0 eV for the binding energy of the main C 1s peak. SEM characterization was conducted by a SEM instrument (LEO 1530 VP made in Germany).

3 Results and discussion

3.1 Bactericidal effects

The specimens with E. coli and S. aureus were incubated at 25°C for 24 h. The number of live bacteria and the antibacterial rate were measured by the standard agar dilution method.

Figure 1 presents the breeding status of E. coli on the Cu-coated CNTs sample (A1), Cu-coated pyrolytic carbon sample (B1), and CNTs sample without Cu-coating (A0) and pyrolytic carbon sample (B0). After the E. coli had been cultivated for 24 h, only a few bacteria were present on the surface of the Cu-coated pyrolytic carbon sample (B1) compared to the sample without Cu coating (B0). There were only a few bacteria present on the surface of the Cu-coated CNTs (A1) compared to the sample without Cu coating (A0). Furthermore, the bacteria colonies on the Cu-coated CNTs sample (A1) were fewer than those on the Cu-coated pyrolytic carbon (B1) under the same condition. This result shows that Cu-coated CNTs can greatly improve the antibacterial ability.

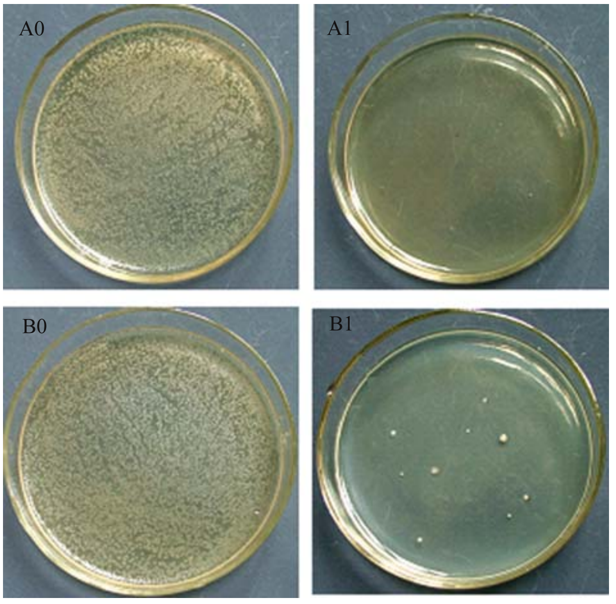

Fig. 1 The breeding status of E.coli on the samples: CNTs sample without Cu coating (A0); pyrolytic carbon without Cu coating (B0); CNTs sample with Cu coating (A1); pyrolytic carbon with Cu coating (B1)

The bactericidal rate K depends on the thickness of the Cu film, which is associated with the deposition time. The dependence is shown in Fig. 2 where two scales are used to show the different effects on Cu-coated CNTs samples and Cu-coated pyrolytic carbon samples. It can be observed that the bactericidal rate K increases with the thickness of Cu film on both samples. However, under the same thickness, the bactericidal rate K of Cu-coated CNTs is much higher than that of the Cu-coated pyrolytic carbon sample. Comparing sample

A1 with B1, for example, sample A1 has stronger antibacterial ability than sample B1. The reason could be attributed to the larger surface area of CNTs with the coated Cu. Thus, the Cu-coated CNTs samples can provide more opportunities to make the Cu atom come in contact with the bacteria resulting in the death of the bacteria. The Cu coating on the surface of CNTs and pyrolytic carbon enables the Cu ions to be dissolved and to come in contact with the bacteria [9,10]. These copper ions can kill bacteria by penetrating the cell walls and cell membranes because copper ions can extract the free electrons from the bacteria cells, causing their cytoplasm to be run off and oxidize their cell nucleus [9,10]. A large amount of Cu coating on the sample corresponds to more copper ions being dissolved from the surface and shows better antibacterial ability. Thus, if the copper film on the pyrolytic carbon can provide sufficient copper ions, the antibacterial rate of the samples from B1 to B4 can reach 99% for all the Cu-coated CNTs samples. From Fig. 2, it can be seen that the antibacterial rate against S.aureus is lower than that against E.coli, because the antibacterial ability is also dependent on the thickness of the bacterial cell wall. Because the cell walls of E.coli and S.aureus are respectively about 10 and 100 nm in thickness, it is difficult for the copper ions to penetrate the cell walls to kill bacteria if the cell walls are too thick. Therefore, the antibacterial rate against S.aureus is lower than that of E.coli under the same condition.

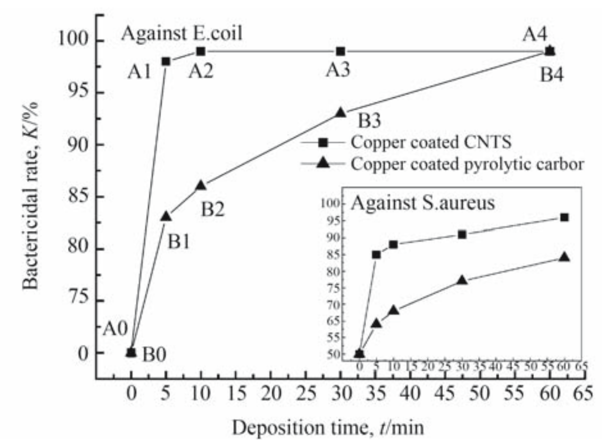

Fig. 2 The bactericidal rate of Cu coated CNTs samples and Cu coated pyrolytic carbon samples

3.2 Microanalysis results

Figure 3 shows the XPS spectra of the CNTs samples before and after Cu coating. The spectrum (a) corresponds to the sample (A0) before the Cu coating. It can be observed that a strong carbon peak of C1s at 275 eV shows the pyrolytic carbon substrate. The spectrum (b) corresponds to the sample (A1) after the Cu coating, which shows that there are strong Cu peaks Cu LMM at about 330.50 eV and Cu2p3 at about 929.46 eV and O1s at about 525.86 eV. The carbon peak of C1s becomes weak. Deposition of Cu onto the CNTs substrate results in a Cu-rich thin film, as well as some oxygen. The XPS spectra of Cu LMM on the right corner indicate that the Cu on the CNTs is in a state of pure Cu and its oxide. Cu and its oxide coated on CNTs and pyrolytic carbon may play a key role in killing bacteria.

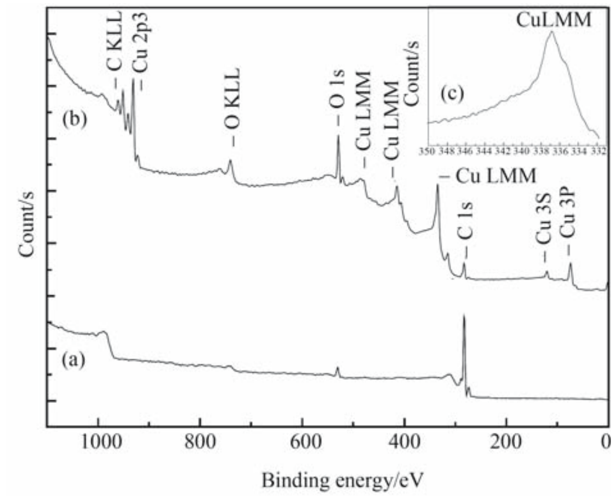

Fig. 3 (a) XPS spectrum of CNTs sample A0; (b) XPS spectrum of Cu coated CNTs sample A1; (c) Cu LMM XPS spectrum for Cu coated CNTs sample A1

It should be noted that the control of the Cu deposition rate is another vital factor in our studies. If the deposition rate is too high, the coated Cu may cover the CNTs in a clump, which results in the reduction of the surface area. In our experiments, the deposition rate is controlled within 1.67 nm/min. In this case, the Cu is only coated on individual CNTs. In order to examine if Cu was covered on single CNTs or covered on the CNT clump, SEM observation was performed. Figure 4 shows a typical image of the Cu-coated CNTs at a deposition rate of 1.67 nm/min. It is clear that the Cu is covered on a single CNT wall. Therefore, the huge surface area of the Cu coating plays a role in killing bacteria. Further, the advantage of the IBAD technique is to ensure an enhanced adhesion between the Cu coating and the substrate surface in comparison with general sputtering techniques.

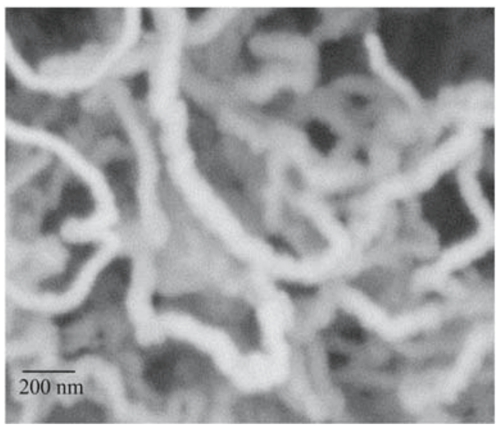

Fig. 4 SEM image of Cu coated CNTs sample (A1)

4 Conclusions

Based on experimental results, the following conclusion can be drawn.

Cu coating both on pyrolytic carbon and CNTs substrate shows antibacterial capability. The Cu-coated CNTs by IBAD show much stronger bactericidal property than that of Cu-coated pyrolytic carbon under the same condition, because of the huge surface of CNTs. XPS and SEM characterization indicates that Cu is coated on single CNT in the state of pure Cu and its oxide. Cu and its oxide play a key role in killing bacteria. The copper-coated CNTs may pave a new way for fabricating artificial heart valves and some other biomedical devices.

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