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ARTICLE

# Preparation of Silver-Epoxy Resin Paste with Ag/MWCNTs Composites Using Lodinated Multi-walled Carbon Nanotubes

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**Abstract:** A method was developed for preparing silver/multi-wall carbon nanotubes (Ag/MWCNTs) composites after iodination of the MWCNTs. The MWCNTs were functionalized by ball milling in the presence of iodine, and characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, and thermogravimetric analysis (TG). The results show that the silver-nanoparticles (Ag-NPs) adhere better to the surface of the MWCNTs after iodination, which can improve the connection between the Ag-NPs and the MWCNTs. The hydroxyl (-OH) group stretching vibration is clearly enhanced, which activates the surface of the MWCNTs and increases the number of $Ag^+$ nucleation sites on the surface of the MWCNTs. At temperatures lower than 260 °C, the mass loss of Ag/MWCNTs composite is less than that of MWCNTs. Finally, three silver-epoxy resin pastes were separately prepared, and the paste prepared using the Ag/MWCNTs composites has the lowest resistivity and the highest thermal conductivity.

**Key words:** MWCNTs; ball milling; iodination; Ag/MWCNTs composite; silver-epoxy resin paste

As information technology progresses, lightweight and miniaturized electronic devices continue to develop, which puts forward requirements on the thermal conductivity of thermal interface materials. At present, the working life of electronic devices is largely determined by the working temperature, so generated heat must be removed as soon as possible[1-3]. Low-temperature curing electronic pastes are widely used in thermal interface materials, but traditional low-temperature curing pastes have thermal conductivity bottlenecks. Thus, there is an urgent need to develop new thermal interface materials with improved properties. In recent years, composites combining silver nanoparticles (Ag-NPs) and multi-wall carbon nanotubes (MWCNTs) have attracted much interest as electronic pastes, because these composites have good catalytic, mechanical, thermal, and optical properties[4-9]. Due to the high thermal conductivity, electrical conductivity and oxidation resistance of Ag-NPs, the deposition of Ag-NPs on the surface of MWCNTs modifies and improves the performance of the MWCNTs. This may be due to the interactions and synergistic effects between the Ag-NPs and the MWCNT surface[9-15]. The performance of MWCNTs can be further improved by depositing Ag-NPs on its surface. On the one hand, the van der Waals force between MWCNTs is reduced, the dispersion of MWCNTs in solution is improved, and the high conductivity and thermal conductivity of MWCNTs are promoted. On the other hand, Ag-NPs are easy to grow and agglomerate. If the size of Ag-NPs is too large, its conductivity and thermal conductivity will be seriously reduced, which limits its application. However, the existence of MWCNTs limits the size of Ag-NPs, which makes them maintain good sintering activity.

Several studies[16-21] have shown that the iodination of carbon nanotubes increases their surface charge, charge density, and surface charge distribution. In addition, iodination produces more defect sites on the surface of the MWCNTs,

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thus improving the chemical activity, accelerating the electron transfer rate, and improving the electronic conductivity[22-24]. Chen et al[25] used ball milling to iodize the graphene anode of a lithium ion battery, and found that the carbon-carbon bonds at the edge of the graphene material were broken, forming carbocations and carbanions. The carbocations reduces $I_2$ to $I^-$, and then $I^-$ is converted to $I^{3-}$ and $I^{5-}$. Finally, $C^+$-$I^{3-}$ and $C^+$-$I^{5-}$ bonds form with the carbocations, which increases the electron transfer rate and improves the charge transfer conductivity.

In a previous study, our team examined the effect of ammonium bicarbonate ($NH_4HCO_3$) on the Ag/MWCNTs composites obtained after the functionalization of the surface of MWCNTs[26]. In this study, we used ball milling with iodine to modify the surface of MWCNTs and to obtain functionalized MWCNTs. Ag/MWCNTs composites made using the iodinated MWCNTs were studied. Finally, a silver-epoxy resin paste containing the Ag/MWCNTs composites was fabricated and characterized.

## 1 Experimental

### 1.1 Materials

MWCNTs (95%) and iodine ($I_2$, AR) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium dodecyl benzene sulfonate (SDBS, 95%, mixture) and ascorbic acid ($C_6H_8O_6$, AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. Silver nitrate ($AgNO_3$, AR) was purchased from Shanghai Fine Chemical Materials Research Institute. Flake silver powder (Ag, 4.3 μm) was purchased from Deli Chemical Research Institute.

### 1.2 Preparation of Ag/MWCNTs composites

First, iodine ($I_2$) was added to the MWCNTs and the mixture was ball milled to functionalize the MWCNTs. Then the Ag/MWCNTs composites were prepared using SDBS as the dispersant and ascorbic acid as the reducing agent. The chemical equation for the reduction of $Ag^+$ by $C_6H_8O_6$ is given in Eq.(1). Specifically, as shown in Table 1, $I_2$ and MWCNT with different mass ratios were added to the ball mill tank, an appropriate amount of ethanol was added, and the mixture was rotated at a speed of 250 r/min for 12 h. After ball milling, the product was washed with ethanol several times. Pristine MWCNTs without any ball milling or $I_2$ addition were also used for comparison. Next, the functionalized MWCNTs or pristine MWCNTs were added to SDBS solution and ultrasonically dispersed using an ultrasonic oscillator for 2 h. The obtained mixture was added to a solution of $AgNO_3$ (0.026 mol/L) and magnetically stirred at a constant rate at room temperature for 6 h. Then, a solution of the reducing agent $C_6H_8O_6$ (0.1 mol/L) was added to the mixture at a uniform rate with a rubber-tip dropper, and stirred with a magnetic stirrer for 1 h. After standing for a period of time, the Ag/MWCNTs composite was collected by centrifugation[27].

$$2AgNO_3+C_6H_8O_6 \rightarrow 2Ag+C_6H_6O_6+2HNO_3 \quad (1)$$

**Table 1 Different mass ratios of $I_2$ and MWCNTs used**

| $I_2$/MWCNTs | 0 | 1:1 | 5:1 | 10:1 | 20:1 |
|---|---|---|---|---|---|
| $I_2$/g | 0 | 0.1 | 0.5 | 1.0 | 2.0 |
| MWCNTs/g | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |

### 1.3 Preparation of silver-epoxy resin paste

A modified silver-epoxy resin paste was prepared, composed of silver powder, bisphenol A epoxy resin, and the Ag/MWCNTs composite prepared by iodinating the MWCNTs. The initial mass of the paste was 20 g, of which flake silver powder accounted for 60wt% and bisphenol A epoxy resin accounted for 40wt%. 1wt% of the Ag/MWCNTs composite was added to the paste and a three-roll mill was used to mix the paste uniformly to obtain a modified paste. For comparison, a sample of pristine paste without any MWCNTs and a sample of paste with 1wt% unmodified MWCNTs were prepared separately.

### 1.4 Characterization

The samples were characterized using transmission electron microscopy (TEM, JEM-2100, Japan), Fourier transform infrared (FT-IR, Bruker ALPHA, Germany) spectroscopy, X-ray diffraction (XRD, D8-Advance, Germany), Raman spectroscopy (LabRAM HR Evolution, France), thermogravimetric analysis (TG) and Brunauer-Emmett-Teller (BET) analysis. TEM was used to observe the adsorption and agglomeration of Ag on the MWCNTs. FT-IR spectroscopy was used to analyze the changes in the strength of the chemical bonds. XRD was used to analyze the crystal structure of the composites. Raman spectroscopy was used to analyze the degree of surface modification of the MWCNTs, and TG was used to observe the mass loss of the composite. Hot disk thermal conductivity meter (TPS 2500, Sweden) was used to measure the thermal conductivity. The surface, pore volume and pore diameter of the Ag/MWCNTs composites were measured using a specific surface area and pore size analysis instrument. In addition, by screen printing, the silver pastes were printed to a fold line with a length of 100 mm and a width of 1 mm. After curing, the thickness and resistance of the fold line were measured by a film thickness meter and a multimeter, and finally the resistivity of the fold line was calculated.

## 2 Results and Discussion

### 2.1 Morphology and microstructure

The morphologies of the composites of the pristine MWCNTs and the iodinated MWCNTs are shown in Fig.1. It can be seen that the Ag/MWCNTs composites prepared with the pristine MWCNTs contain large Ag-NPs that tend to aggregate together and cannot be uniformly deposited on the MWCNTs. After $I_2$ is used to functionalize the MWCNTs, the surface-modified MWCNTs contain more defect sites, and thus form more nucleation sites to more easily adsorb Ag-NPs. In addition, $C_6H_8O_6$ is a weak reductant, which leads to a slower reduction and deposition reaction during the reduction process. Adding $C_6H_8O_6$ drop-wise into the solution with

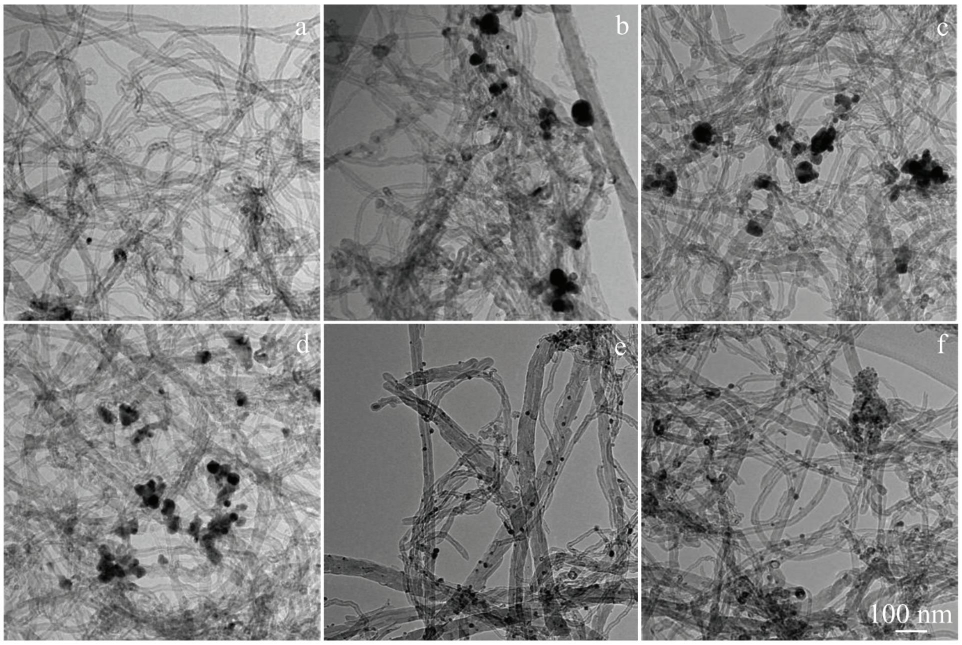

Fig.1 TEM images of pristine MWCNTs (a) and Ag/MWCNTs composites prepared with different mass ratios of $I_2$:MWCNTs: (b) 0, (c) 1:1, (d) 5:1, (e) 10:1, and (f) 20:1

magnetic stirring decreases the amount of aggregation and growth of the Ag-NPs on the surface of the MWCNTs. When the mass ratio of $I_2$: MWCNTs is 10: 1, the prepared Ag/MWCNTs composite has the best properties, with a high density of Ag-NPs uniformly distributed over the surface of the MWCNTs. Thus, the subsequent characterization was performed on the composite obtained with an $I_2$: MWCNTs mass ratio of 10:1.

XRD patterns of the three materials are shown in Fig. 2. Several clear diffraction peaks are observed for the Ag/MWCNTs composite that correspond to the crystal faces of crystalline Ag. The decreased intensity of the carbon peak indicates that iodine promotes the deposition of Ag-NPs on the surface of the MWCNTs. In addition, the results show that the ball milling cannot destroy the crystal structure of the MWCNTs[4].

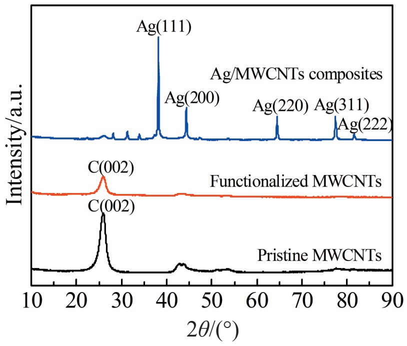

Fig.2 XRD patterns of pristine MWCNTs, functionalized MWCNTs and Ag/MWCNTs composites

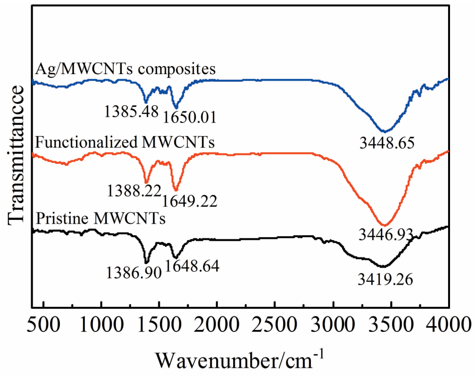

Fig.3 FT-IR spectra of pristine MWCNTs, functionalized MWCNTs, and Ag/MWCNTs composites

Fig. 3 shows the FT-IR spectra of the three different materials. The peak observed in the spectrum of the pristine MWCNTs at ~1386 $cm^{-1}$ is due to the OH bending vibration of the COOH functional group, while the vibration at 1650 $cm^{-1}$ is a C=C stretching vibration, and the broad peak at 3448 $cm^{-1}$ can be attributed to hydroxyl (-OH) group stretching vibration. The infrared spectra of the functionalized MWCNTs and the Ag/MWCNTs composite show similar peaks. The FT-IR results show that after treatment of the MWCNTs with iodine, the -OH stretching vibration is significantly enhanced. This suggests activation of the surface of the MWCNTs, which increases the number of nucleation sites on the surface of MWCNTs. It can reduce $Ag^+$ and increase the number of nucleation points for Ag-NPs. When $Ag^+$ nucleates and Ag-NPs form on the surface of the MWCNTs, the intensity of the -OH stretching vibration decreases[25].

Raman spectroscopy was used to analyze the degree of surface modification of the MWCNTs. Fig.4 shows the Raman

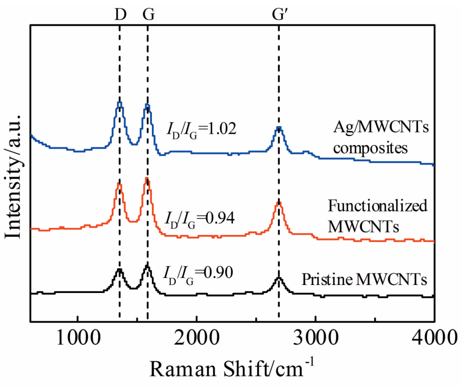

Fig.4 Raman spectra of pristine MWCNTs, functionalized MWCNTs, and Ag /MWCNTs composites

spectra of the pristine MWCNTs, the functionalized MWCNTs and the Ag/MWCNTs composites, and the peak positions and intensities can be compared. The interaction between the MWCNTs and $Ag^+$ can be analyzed based on shifts in the energy of different Raman bands. For convenience, the relevant bands are called the D-band, the G-band and the G′-band. The D-band is due to the vibration of $sp^3$ carbon atoms in a carbon-based material, and the G band is due to the vibration of $sp^2$ carbon atoms in a carbon-based material[17]. The intensity ratio of the D-band and the G-band ($I_D/I_G$) can be used to evaluate the degree of MWCNT functionalization. The $I_D/I_G$ ratio of the pristine MWCNTs is ~0.90, and the $I_D/I_G$ of the functionalized MWCNTs obtained after iodinating the MWCNTs is ~0.94. The higher ratio may be due to the presence of more defect sites on the surface after the surface modification of the MWCNTs. The $I_D/I_G$ ratio of the Ag/MWCNTs composite is ~1.02, indicating that the presence of the Ag-NPs disorders the surface structure of the MWCNTs, and that charge transfer occurs between the Ag-NPs and the MWCNTs.

The mass loss of the pristine MWCNTs, the functionalized MWCNTs, and the Ag/MWCNTs composites was analyzed at a heating rate of 10 °C/min. The results are shown in Fig. 5. The analysis shows that the pristine MWCNTs begin to degrade around 250 °C. When the temperature reaches 600 °C, a mass loss of 2.60% is observed, indicating the presence of moisture and a small amount of amorphous carbon on the surface of the MWCNTs. After functionalization of the MWCNTs with iodine, the mass loss increases significantly. When the temperature reaches 600 °C, a mass loss of 14.70% occurs. The Ag/MWCNTs composites begin to degrade at ~100 °C, with a mass loss of 5.53% at 600 °C, which is mainly due to the burning of the MWCNTs. In addition, the decomposition of silver oxide into pure silver and oxygen also causes some mass loss at high temperatures. The TG curve shows that the mass loss of Ag/MWCNTs composite is less than that of MWCNTs when the temperature is lower than 260 °C, which is due to the presence of Ag-NPs on the surface of MWCNTs. At high temperatures, the mass loss of Ag/MWCNTs composites increases, which is because the silver oxide from the Ag-NPs forms during heating, and then decomposes at high temperatures.

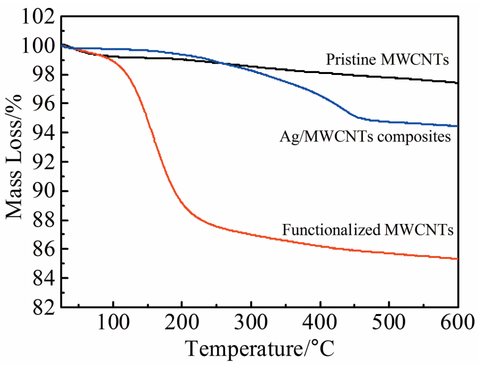

Fig.5 TG curves of pristine MWCNTs, functionalized MWCNTs, and Ag/MWCNTs composites

Table 2 lists the BET surface areas, pore volumes, and pore diameters of the three different materials. The specific surface area of the functionalized MWCNTs after treatment of the MWCNTs with iodine is 104.2726 $m^2/g$, which is higher than that of the Ag/MWCNTs composite, but lower than that of the pristine MWCNTs. The specific surface area of the Ag/MWCNTs composite is 53.0447 $m^2/g$, which is decreased by ~2/3 as compared to that of the pristine MWCNTs. This may be due to the increased density of the Ag/MWCNTs composite after addition of the Ag-NPs to the MWCNTs.

## 2.2 Resistivity and thermal conductivity of silver-epoxy resin paste

The resistivity of the three silver pastes is shown in Table 3. After the pristine MWCNTs are added to the epoxy paste, the resistivity of the paste increases. Even though MWCNTs are good conductors and can increase the number of carriers in the paste, more defect sites form during the oxidation process, generating more holes and increasing the resistance. In addition, MWCNTs tend to aggregate, which decreases the contact area between the flake silver powder and MWCNTs, and also decreases the contact area between the flake silver powder and the epoxy resin. As a result, good interface contact in charge transfer is inhibited, resulting in an increase in the resistivity of the paste.

**Table 2 BET surface area, pore volume, and pore diameter of different composites**

| Composite | BET surface area/$m^2 \cdot g^{-1}$ | Pore volume/$mL \cdot g^{-1}$ | Pore diameter/nm |
|---|---|---|---|
| Pristine MWCNTs | 148.8642 | 0.6425 | 17.26 |
| Functionalized MWCNTs | 104.2726 | 0.4959 | 19.02 |
| Ag/MWCNTs | 53.0447 | 0.3050 | 23.00 |

**Table 3 Resistivity of pristine paste, the paste made with MWCNTs, and the paste made with the Ag/MWCNTs composites**

| Samples | Pristine paste | Paste made with MWCNTs | Paste made with Ag/ MWCNTs |
|---|---|---|---|
| Resistivity/$\times10^{-6}$ Ω·m | 3.3318 | 4.3380 | 2.5710 |

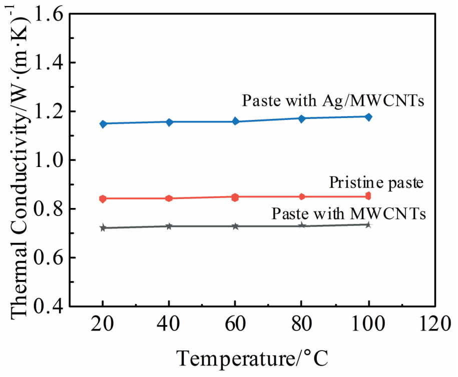

Fig.6 Thermal conductivity of the paste made with MWCNTs, the pristine paste and the paste made with the Ag/MWCNTs composites

After adding the Ag/MWCNTs composite to the paste system, the resistivity of the paste decreases. This is attributed to the Ag-NPs on the surface of the MWCNTs, which can be sintered at low temperature. The low-temperature sintering of the Ag-NPs on the surface of the MWCNTs forms good interface contacts with the flake silver powder, resulting in charge transfer and decreasing the contact resistance of the MWCNTs in the paste[23].

In the range of 20~100 °C, the thermal conductivity of different silver pastes was studied, as shown in Fig. 6. The thermal conductivity of paste with MWCNTs is about 0.72 W/mK, while that of the pristine paste is about 0.85 W/mK, which is about 0.13 W/mK higher than the former. It may be because in the paste with MWCNTs, there is a certain gap and transmission barrier between MWCNTs and flake silver powder, which reduces the thermal conductivity. The thermal conductivity of the paste with Ag/MWCNTs composite is about 1.16 W/mK, which is mainly due to the fact that Ag-NPs fill the contact gap between flake silver and MWCNTs, and promote the interface bonding. Phonon transport pathways are constructed between flake silver and MWCNTs, increasing the heat conduction paths and reducing the transmission barrier[28]. In this way, Ag-NPs act as a bridge between MWCNTs and flake silver powder, which can transfer heat in time and increase the thermal conductivity.

## 3 Conclusions

1) A series of Ag/MWCNTs composites can be prepared by ball milling with different amounts of iodine to functionalize MWCNTs, using SDBS as dispersant and ascorbic acid as reducing agent.

2) When the $I_2$ to MWCNTs mass ratio is 10:1, the prepared Ag/MWCNTs composites have the best properties, and the Ag-NPs are densely and uniformly distributed on the surface of the MWCNTs.

3) The surface of the MWCNTs is modified by the iodine treatment, which increases the number of nucleation sites for $Ag^+$ reduction on the surface of the MWCNTs and improves the connection between the Ag-NPs and the surface of the MWCNTs.

4) Compared with the pristine MWCNTs, the specific surface area of the Ag/MWCNTs composite decreases and the density increases. At temperatures lower than 260 °C, the mass loss of Ag/MWCNTs composite is less than that of MWCNTs.

5) Silver-epoxy resin paste with Ag/MWCNTs composite has the lowest resistivity and the highest thermal conductivity.

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# 碘化多壁碳纳米管制备含有Ag/MWCNTs复合材料的银-环氧树脂浆料

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**摘 要：**提出一种将多壁碳纳米管碘化后制备银/多壁碳纳米管（Ag/MWCNTs）复合材料的方法。通过球磨对碘化多壁碳纳米管进行了功能化，并通过透射电子显微镜（TEM）、X射线衍射（XRD）、傅里叶变换红外光谱（FT-IR）、拉曼光谱和热重分析（TG）对其进行了表征。结果表明，经碘化处理后，银纳米粒子（Ag-NPs）能更好地粘附在碳纳米管表面，改善了银纳米粒子与碳纳米管之间的连接。羟基（-OH）基团的伸缩振动明显增强，激活了碳纳米管的表面，增加了碳纳米管表面$Ag^+$形核的数量。在260 ℃以下，Ag/MWCNTs复合材料的质量损失小于MWCNTs的质量损失。最后，制备了银-环氧树脂浆料，发现使用Ag/MWCNTs复合物制备的浆料具有最低的电阻率和最高的热导率。

**关键词：**MWCNTs；球磨；碘化；Ag/MWCNTs复合材料；银-环氧树脂浆料

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