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Efficient strategy to Cu/Si catalyst into vertically aligned carbon nanotubes with bamboo shape by CVD technique

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Abstract. **Bamboo-shaped vertically aligned carbon nanotubes (bs-VACNTs) were fabricated on Cu/Si catalyst by chemical vapour deposition (CVD) technique under the atmospheric pressure. The catalytic material (Cu/Si) played a vital role in attaining bs-VACNTs, which is synthesized by drop cast method in a cost-effective manner. Using this catalytic support, we have achieved the tip growth bs-VACNTs at low temperature with well graphitization. The as-grown carbon material was then characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX) analyzer, high-resolution transmission electron microscope (HRTEM) and Raman spectroscopy. XRD technique confirms the formation of hexagonal graphitic carbon planes of carbon nanotubes (CNTs). The surface morphology of the material was characterized by SEM, which clearly infer vertically aligned CNTs. The nature, diameter and crystallinity were noticed by HRTEM and Raman spectroscopy, respectively. Further, we have also studied the electrochemical properties of the bs-VACNTs and it seems to be proved as highly electroconductive when compared to multi-walled carbon nanotubes (MWCNTs).**

Keywords. **Vertically aligned carbon nanotubes; drop cast method; electron microscopes; electrical properties.**

1. Introduction

Carbon nanotubes (CNTs) consist of cylindrical graphitic layers which have attracted mostly material science researchers due to their unique structure and their extraordinary properties. Particularly, vertically aligned carbon nanotubes (VACNTs) are proved for its high electron transport property due to the π electron density present on the sides of the walls [1] and high strength with flexibility [2]. Various shapes and structures such as straight [3], branched [4], bamboo [5,6] and helical [7,8] of CNTs also possess important characteristics for specific applications in diverse fields. Among them, bamboo-structured CNTs are considered to be significant for its better electron transport property, which have been found wider applications in sensors and solar cells [9–11]. Thus, the combination of bamboo shape with vertical alignment will enhance the electron transfer rate in CNTs and this superior performance is more useful in electrochemical applications like ultracapacitors [12,13], energy storage devices [14], solar cells [15], field emitters [16], batteries [17] and sensors [18]. Generally, CNTs have been synthesized by various methods such as arc discharge [19], laser vaporization [20], chemical vapour deposition (CVD) [21,22], HiPco [23] and fluidized bed [24]. Obviously, CVD technique is gaining attention due to its advantages such as ability to control the number of the walls in tube, alignment, high yield, tube diameter, length and the structure of CNTs by varying process parameters.

Mostly, aligned CNTs growth could be achieved by metal-coated substrate rather than powder catalyst. Several techniques, including electron beam evaporation, direct current sputtering, radiofrequency sputtering, magnetron sputtering and thermal evaporation are commonly used to coat the catalyst particles on substrate material. These deposition techniques are very expensive and hence reduce the large scale production of CNTs. However, aligned CNTs are less defective compared to erratically aligned CNTs. Furthermore, it is quite challenging to deposit metal particles on substrate material at an affordable cost.

In this work, we have performed a single step-drop casting method to prepare the catalytic material. This approach is simple and an economic way to deposit the catalyst particles on Si wafer material when compared to the other commercially available sputtering techniques. Copper particles on Si substrate could be attained at low temperature, which can be used for the synthesis of bamboo-shaped vertically aligned carbon nanotubes (bs-VACNTs) with tip growth model. We have also performed the electrochemical impedance spectroscopy (EIS) study on bs-VACNTs, which showed lesser internal resistivity of the tubes.

2. Experimental

2.1 *Catalyst preparation*

Si wafer (15 × 15 mm) was first cleaned with mixture of H_2SO_4: H_2O_2 (2 : 1), followed by washing it with deionized water and then etched in 40% HF for 5 min. By treating SiO_2

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(interfacial barrier layer) with HF increases the effective area of CNTs in contact with the metal which lead to the conclusion that for each metal, a finite contact length between the metal and the CNT. Thus, the removal of thin SiO_2 wafer leads to an increased CNT–metal contact and hence improves the performance of the CNTs [25,26]. The Si wafer was washed several times with deionized water to remove the acid impurities, which is then used to coat the copper metal source on the surface by drop cast method. Cleaned Si wafer was heated on hot plate at 80°C and then few drops of 20 mM $Cu(NO_3)_2{\cdot}3H_2O$ in ethanol were added on Si wafer, evaporated quickly and then dried at room temperature.

2.2 *Fabrication of bs-VACNTs*

According to our previous report [27], we have produced bs-VACNTs using Cu coated Si wafer which was inserted in the middle of the horizontal tubular furnace. The Cu/Si catalyst was heated gradually from room temperature to 650°C ramping under the mixture of N_2/H_2 atmosphere. Then, N_2/H_2 flow was stopped and immediately carbon source C_2H_2 flow was fed into the reactor with a flow rate of 40 sccm for 5 min at 650°C. Then, C_2H_2 gas flow was discontinued followed by purging the N_2 gas to cool down the furnace temperature.

2.3 *Fabrication of bs-VACNTs/GCE working electrode*

To examine the electrochemical properties of bs-VACNTs by EIS technique, glassy carbon (GC) working electrode, 3 mm in diameter was polished with 0.1 μm alumina slurry and then washed ultrasonically with ethanol and water for few minutes, respectively. As-synthesized bs-VACNTs were purified according to our previous report [6] by a simple HCl treatment to remove the catalyst particles. Purified bs-VACNTs about 2 mg were dispersed in 1 ml of dimethylformamide (DMF) followed by ultrasonication for 10 min. DMF dispersion of bs-VACNTs (5 μl) was evenly spread by a micropipette onto the GC electrode surface to obtain bs-VACNTs/GC electrode and allowed to dry for 12 h at room temperature.

2.4 *Physical characterization*

X-ray diffraction (XRD) pattern accumulated from G.E. Inspection Technologies, XRD 3003 TT model using CuKα radiation ($\lambda = 0.1541$ nm) operated at 40 kV accelerating voltage for phase identification. A JOEL JSM-6300, scanning electron microscope (SEM) analysis was performed to know the morphology and alignment of carbon product. INCA PentaFET-x3 (Oxford Instruments, UK) energy dispersive X-ray spectroscopy (EDX) analyzer was used for elemental analysis at the tip of the CNTs. The nature and tube diameter of CNTs were examined by high-resolution transmission electron microscope (HRTEM) JEOL 3010, 300 kV instrument with a UHR pole piece. Raman spectrum was obtained using a Lab RAM HR (Horiba JOBIN-YVON Raman spectrophotometer) visible single spectrometer equipped by a microscope and a Peltier-cooled CCD detector. The 633 nm He–Ne laser line was used for excitation.

2.5 *Electrochemical characterization*

Impedance measurements were carried out with a CHI660D electrochemical workstation with a conventional three-electrode single glass compartment system. A 3 mm surface area GC was used as working electrode and platinum wire, Ag/AgCl electrodes were the auxiliary and reference electrodes, respectively. All the electrochemical measurements were conducted at room temperature.

3. Results and discussion

3.1 *XRD analysis of carbon product*

Figure 1 depicts the XRD pattern of bs-VACNTs grown under acetylene atmosphere. Three prominent peaks were observed at 25.86, 42.43 and 44.65°, which are assigned to (002), (100) and (101) of hexagonal graphitic carbon planes of carbon nanotubes, respectively (JCPDS no. 41-1487). The intense and broad peak at 25.86° indicates the highly graphitic nature of the synthesized product. The other small intense peak appeared at 62° indicates the presence of a trace amount of CuO on the as-synthesized CNTs, which also coincides well with JCPDS no. 80-1917. Usually copper nitrate decomposes upon thermal annealling and then, CuO is formed due to the high oxygen affinity of copper [28]. The CuO particles are responsible for the nucleation and growth of VACNTs. The obtained result indicates the high degree of crystallinity in the as-synthesized material. In addition, CNTs consist of a trace amount of CuO, which has found applications in photoelectron devices, supercapacitors and fuel cells, due to lower electrical resistance and good corrosion resistance [6,29].

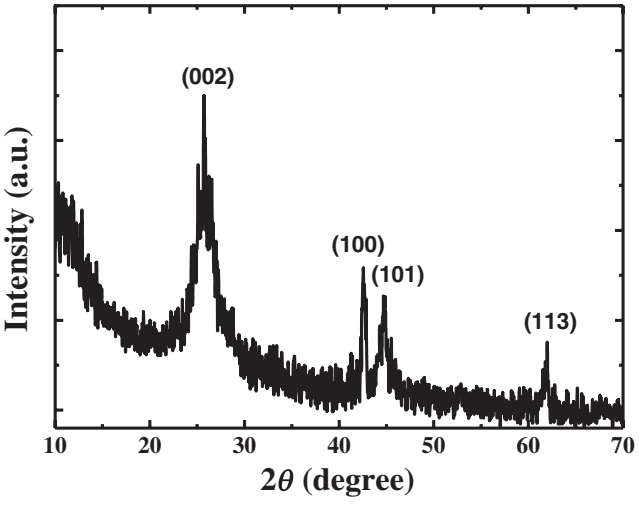

Figure 1. XRD pattern of as-grown carbon material.

3.2 *SEM analysis of carbon product*

SEM micrographs of the as-grown VACNTs using Cu-coated Si substrate at 650°C are shown in figure 2a and b. From SEM analysis, it is clearly observed that height of the CNTs is 20 ± 1 μm and also we infer that the catalyst particles are present on the tip of the VACNTs, which confirm the growth mechanism of VACNTs that represents to tip growth model [30–32] in figure 2c. Size of the Cu particles might be bigger than the CNTs nucleation when they are drop-casted. However, reaction temperature in horizontal furnace causes annealing of the Cu particles to form smaller particles. The as-formed smaller Cu or CuO particles are responsible for the growth of VACNTs.

To confirm the presence of metal particles at the tip of CNTs, we have performed elemental analysis by EDX

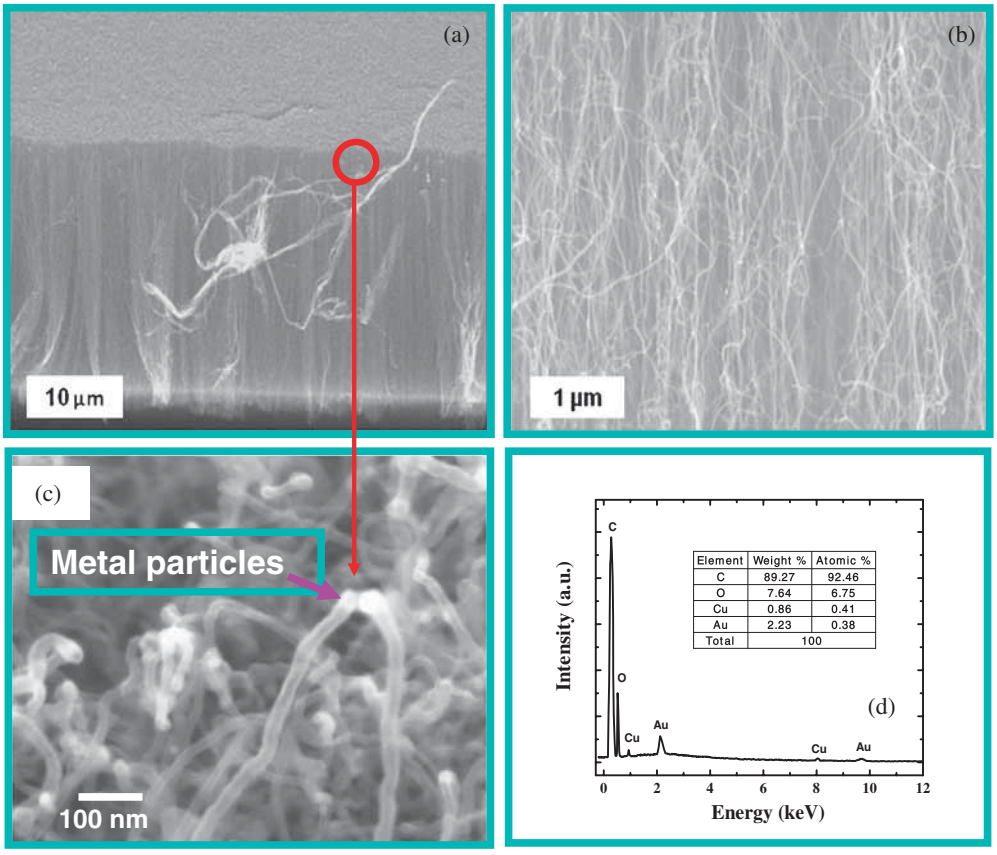

Figure 2. SEM images of (**a** and **b**) as-synthesized VACNTs, (**c**) metal particles at tip of the CNTs and (d) EDX spectrum.

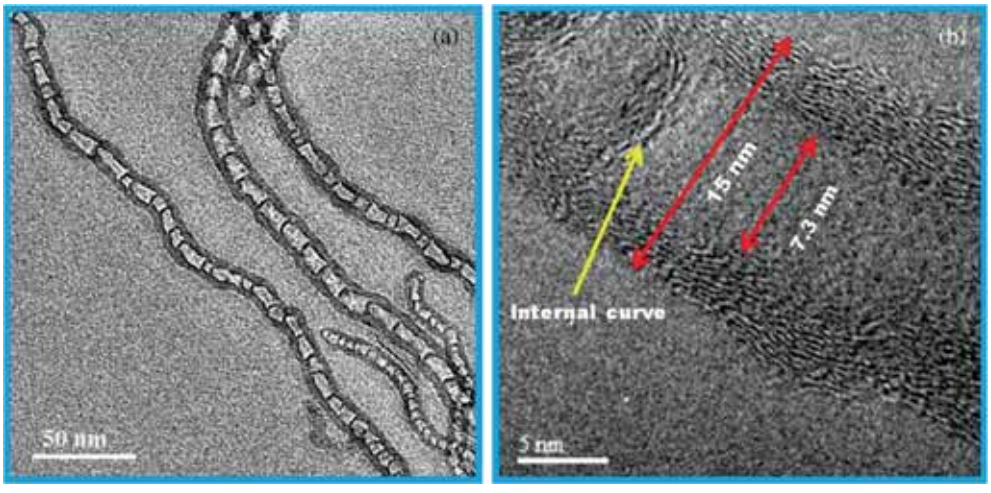

Figure 3. HRTEM images of (**a**) bs-VACNTs and (**b**) single bs-VACNT with higher resolution.

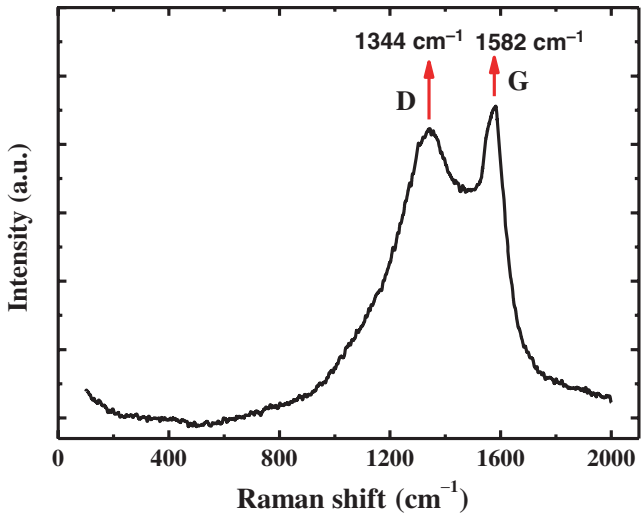

Figure 4. Raman spectrum of bs-VACNTs.

analyzer. The elemental composition of the obtained material VACNTs and the EDX spectrum are depicted in figure 2d. Two prominent peaks are observed for carbon (C), oxygen (O) and other four low intense peaks related to copper (Cu) and gold (Au). The atomic and weight percentages of C are very high, when compared to other elements in the material. This suggests that the vertical alignment gives less defective CNTs compared with randomly oriented CNTs. Low percentage of copper also observed at the tip of the CNTs, which confirms the CNTs, are grown by tip growth mechanism. The remaining Au peak is due to sputtered off Au at the top of the material during EDX analysis.

3.3 *HRTEM analysis of VACNTs*

Further, the sample was examined through HRTEM analysis to know the exact structure, nature and diameter of the carbon nanotubes. The curved with internal individual compartmental

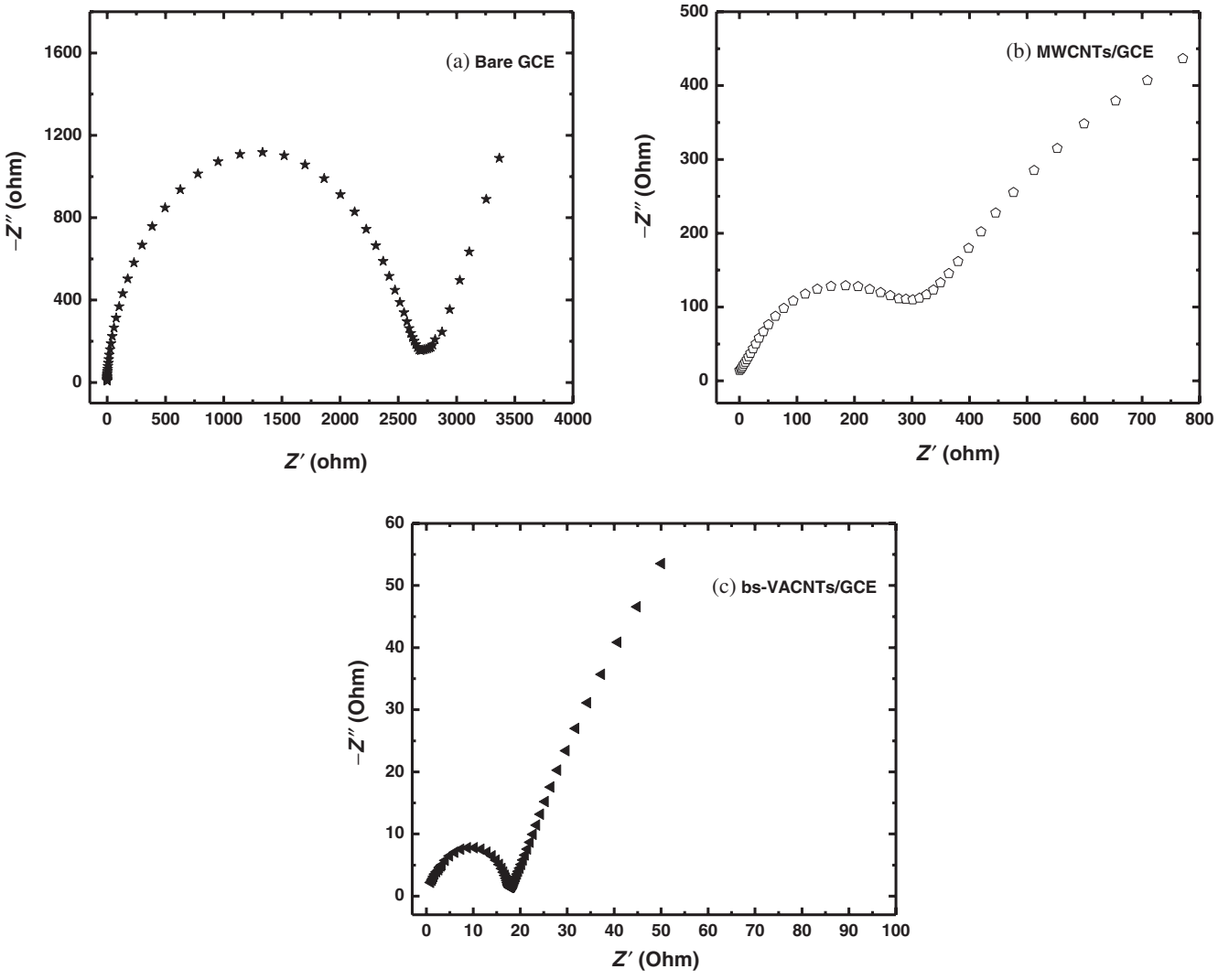

Figure 5. Nyquist plots of (**a**) bare GC electrode, (**b**) MWCNTs/GC electrode and (**c**) bs-VACNTs electrodes were recorded in 0.1 M KCl containing 5 mM $Fe(CN)_6^{3-/4-}$ solution by applying an a.c. voltage with 5 mV amplitude in a frequency range from 0.1 Hz to 100 kHz.

structures inside the tubes were observed in a TEM image which is depicted in figure 3a. It confirms that the structure of CNTs is bamboo-shaped and also well crystallized with highly graphitic in nature. The high resolution TEM image in figure 3b clearly shows the multi-layered graphitic carbon (10–15 layers) with bamboo shape. The inner and outer diameters of the tube were found to be 7.3 and 15 nm, respectively. Thus, the catalyst particles played a vital role in the growth of bs-VACNTs. In addition, the reaction parameters are also important to form essential size of catalyst particles to grow the CNTs in vertical direction with a particular shape.

3.4 *Raman spectroscopy of bs-VACNTs*

Raman spectroscopy can be used to identify the crystalline nature of CNTs. It provides the key information about the purity, defects and also differentiates the various types of carbonaceous materials. Raman spectrum described in figure 4 clearly shows a broad peak at 1344 cm^{-1} for the defects related to curved graphitic sheets and compartments inside the nanotubes. This result was confirmed by HRTEM analysis and also correlates with previous report [33]. Another peak at 1582 cm^{-1} represents the graphitic nature of CNTs due to the in-plane vibrations of sp^2 bonded carbon atoms in the graphitic layers. Absence of the peaks at radial breathing mode (RBM) region at 100–300 cm^{-1} is the evidence for the formation of nanotubes with multilayers. The intensity of I_G/I_D ratio was calculated and found to be 1.05 for the as-produced CNTs, which indicates that the nanotubes have good graphitization.

3.5 *EIS analysis*

Electrochemical Impedance Spectroscopy was employed to investigate electrical conductivity and internal resistance of the synthesized material. Figure 5 shows the Nyquist plots of bare GC, MWCNTs/GC and bs-VACNTs/GC electrodes. The plots were obtained in a.c. frequency range of 0.1 Hz–100 kHz in 5 mM $Fe(CN)_6^{3-/4-}$ containing 0.1 M KCl solution. The R_{ct} values of bare GC, MWCNTs/GC and bs-VACNTs/GC electrodes are 2695, 390 and 6.5 Ω, respectively. The R_{ct} value of the bare GC electrode at higher frequencies indicates the higher charge transfer resistance and interface impedance of the electrode. The impedance was decreased in the presence of MWCNTs, while comparing with bare GC electrode, suggesting the charge transfer resistance of the modified electrode is less. When GC electrode was coated with bs-VACNTs, the impedance has been diminished extremely due to better electron transfer kinetics provided by the large surface area of the bs-VACNTs. From obtained results, it can be concluded that the synthesized bs-VACNTs are more electroconductive, when compared to commercial MWCNTs. These superior electrochemical characteristics are attributed to the presence of larger number of electroactive sites, i.e., edge planes of graphene at regular intervals along the bamboo-shaped nanotubes [34] with vertical alignment. Thus, the bs-VACNTs have more advantages over the conventional MWCNTs for electroanalytical applications.

4. Conclusions

We have synthesized vertically aligned carbon nanotubes with bamboo-shape (bs-VACNTs) on Cu/Si catalyst by CVD technique under the atmospheric pressure. XRD, SEM, HRTEM and Raman spectroscopy were used to characterize the carbon product. The present work supports the catalyst preparation and bs-VACNTs formation at low temperature and is cost effective. Impedance spectroscopy results show that the bs-VACNTs modified GC electrodes have lesser resistivity when compared to the bare GC electrode and MWCNTs/GC electrodes, which confirm the improved electron transfer rate with good electrocunductivity of the synthesized material.

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