SHORT COMMUNICATION

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Electrophoretic deposition of nickel, iron and aluminum nanoparticles on carbon fibers

Abstract The electrophoretic deposition (EPD) of nickel (Ni), iron (Fe) and aluminum (Al) nanoparticles fabricated by an active hydrogen plasma evaporation method on the surface of carbon fibers was investigated, which will allow the obtained composites to be applied as practical catalysts or electrodes. SEM observations show that the Ni nanoparticles can build up a thick EPD coating with some cracks on the surface of carbon fibers, and the analyses of X-ray diffraction (XRD) and BET specific surface area indicate that fine particles from the as-received Ni powders were finally deposited after the EPD process without crystal growth. The surface oxidation of Fe and Al nanoparticles takes serious effect on the EPD process and the morphology of the as-prepared coatings.

Keywords Electrophoretic deposition · Nickel · Iron · Aluminum · Nanoparticle

Nanoscale metal particles hold promise for use as advanced materials with new electronic, magnetic, optic and thermal properties [1–4] as well as new catalytic properties [5, 6]. At present, it is uncomplicated to fabricate metal and alloy nanoparticles by physical methods, such as the active hydrogen plasma evaporation method [7]. Aluminum (Al) nanoparticles were reported to fabricate nanocomposite materials [8], and nickel (Ni), cobalt (Co) as well as iron (Fe) nanoparticles were regarded as catalysts for the synthesis of carbon nanotubes [9, 10]. It is known that metal nanoparticles are easily oxidized to some degree by air, especially for active metals such as Al and Fe, etc. However, recent

studies show that surface oxidation also makes sense: for instance, the redox of Fe/FeO_x can be employed as a source of pure hydrogen for polymer electrolyte fuel cell [11], and the slightly oxidized Al nanoparticles can form alloy with lithium ($LiAl_x$) to provide additional lithium storage capacity and additional channel to conduct lithium in lithium-ion batteries [12].

Metal nanoparticles generally cannot be directly used for engineering considerations. Metal microparticles were reported to form coatings on conductive substrates by low-cost and flexible electrophoretic deposition (EPD) method [13], which has been established as a versatile method to prepare platinum, gold, silver, alumina, Yttria-stabilized zirconia and fullerene EPD films [14–19]. Nonaqueous suspensions are generally employed since they can avoid the electrolysis of the solvent to achieve a bubble-free deposit [18, 20], and only a few articles discussed the aqueous systems [17, 21]. In this article, EPD method was employed to deposit Ni, Fe and Al nanoparticles fabricated by an active hydrogen plasma evaporation method on the surface of carbon fibers in mixing suspensions, which were comprised of acetone, a small amount of iodine and HCl aqueous solution as well as metal nanoparticles. It is meaningful for practical application as electrodes or catalysts [12, 22] if metal nanoparticles can combine with stable and conductive carbon fibers.

The conductivity of the above suspensions is derived from the acid-catalyzed iodination of acetone [23]. In the electrolyte, the protons, Cl^- and I^- ions as well as the charged metal nanoparticles can carry most of the electric current except for the excess solvent iodine. Considering the standard electrode potentials in a similar nonaqueous solution [24], the possible cathode reaction should be the reduction of iodine/iodide, and problems with hydrogen evolution are avoided, which leads to compact and bubble-free coatings of metal nanoparticles on the surface of carbon fibers.

The EPD process of the as-received Ni, Fe and Al nanoparticles is illustrated in Fig. 1. The EPD coating of Ni nanoparticles (nano-Ni coating) keeps almost

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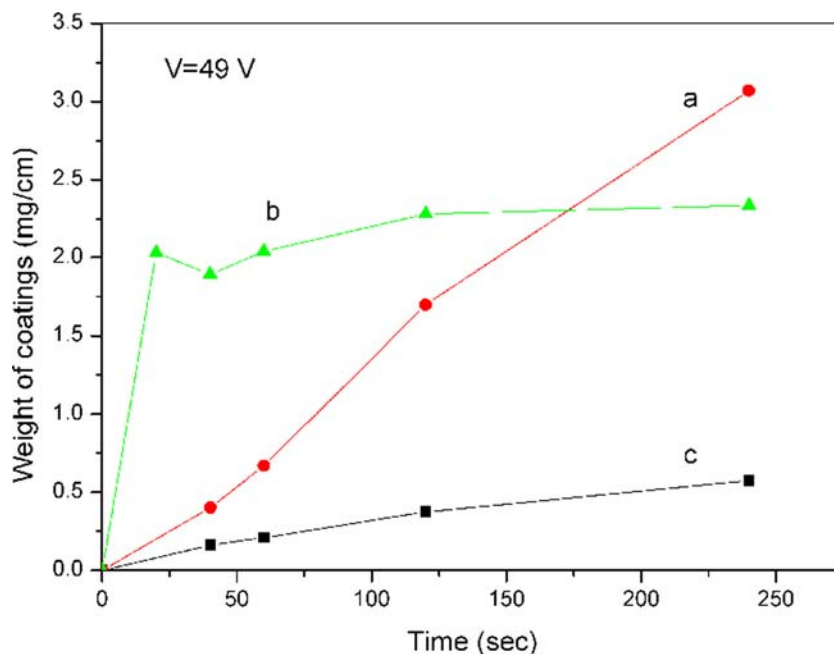
linearly increasing its weight with time (see curve a). The EPD coating of Fe nanoparticles (nano-Fe coating) mounts up so quickly that it nearly reaches its maximum within the first 20 s as shown in curve b, but afterwards the curve becomes a platform without obvious increment, which suggests that the EPD coating on the surface of carbon fibers should have compact structure and poor conductivity to baffle the charge exchange in the electrode/solution interface. However, the experiment showed that the EPD coating of Al nanoparticles (nano-Al coating) tended to form agglomerates on the outer surface of carbon fiber strands; after removing them by experimental operation, the weight increment of nano-Al coating (curve c) becomes rather small, which indicates that it is hard for the Al nanoparticles to distribute inside the strands of carbon fibers.

Figure 2 shows the SEM observations of the carbon fiber specimens with the nano-Ni, nano-Fe and nano-Al coatings. The EDP coating of Ni nanoparticles on carbon fibers is quite thick (shown in Fig. 2a), and the cracks after drying (see Fig. 2b) reveal that the interaction force among Ni nanoparticles is rather weak, which suggests that the nano-Ni coating is probably stacked by Ni nanoparticles. The nano-Fe coating is also rather thick and compact but displays a special morphology as shown in Fig. 2c, which is stacked by big shuttle-like particles. In the enlarged image (Fig. 2d), the shuttle-like particles consisted of many smaller particles, which means that the as-received Fe powders were likely oxidized to agglomerate together and were therein deposited on the surface of carbon fibers in the EPD process. Figure 2e shows that the Al nanoparticles actually cannot form a continuous EPD coating on the complicated surface inside the carbon fiber strands.

Figure 3 compares the XRD patterns of the as-received Ni, Fe and Al powders and the corresponding EPD-treated carbon fibers. The as-received Ni powders have three peaks of (1,1,1), (2,0,0) and (2,2,0), and only the (2,2,0) peak is not distinct on the XRD pattern of the treated carbon fiber specimen. The nano-Fe coating on carbon fibers is determined to be amorphous by XRD analysis due to surface oxidation of the as-received Fe powders. The as-received Al powders exhibit five peaks of (1,1,1), (2,0,0), (2,2,0), (3,1,1) and (2,2,2), and four of them appear on the XRD pattern of the treated carbon fibers except for the (2,2,2) peak. The average crystalline size of the nanoparticles can be calculated using the Debye–Scherrer equation from the (1,1,1) peak widths of the XRD patterns. The equation is $d = 0.89\lambda/B \cos \theta$, where λ is the wavelength of Cu K_{α} radiation (here $\lambda = 0.1542$ nm), B the calibrated half-width of the peak in radians and θ the half diffraction angle of the (1,1,1) peak in degrees. The calculated average crystalline size of the as-received Al powders is about 80 nm, and the nano-Al coating on carbon fibers has the same value. It is the same with the as-received Ni powders and the nano-Ni coating, both of which have the average crystalline size of nearly 40 nm. The calculations illuminate that the EPD process is so mild that it cannot cause any crystal growth for the as-received metal nanoparticles.

The specific surface area is important to the composites for application as catalysts or electrodes, which is related to the change in particle diameter during the EPD process. Considering the effect of oxidation on the specific surface area for the active Al and Fe nanoparticles, the as-received Ni powders and nano-Ni coating were selected to carry out the measurement. The BET (Brunauer Emmett Teller Procedure) specific surface area of the as-received Ni nanoparticles is determined as 6.68 m^2 g^{-1} and that of the nano-Ni coating is 13.68 m^2 g^{-1}. The equation to evaluate the average particle diameter is $d = 6/\rho \ S_w$ (suppose the nickel

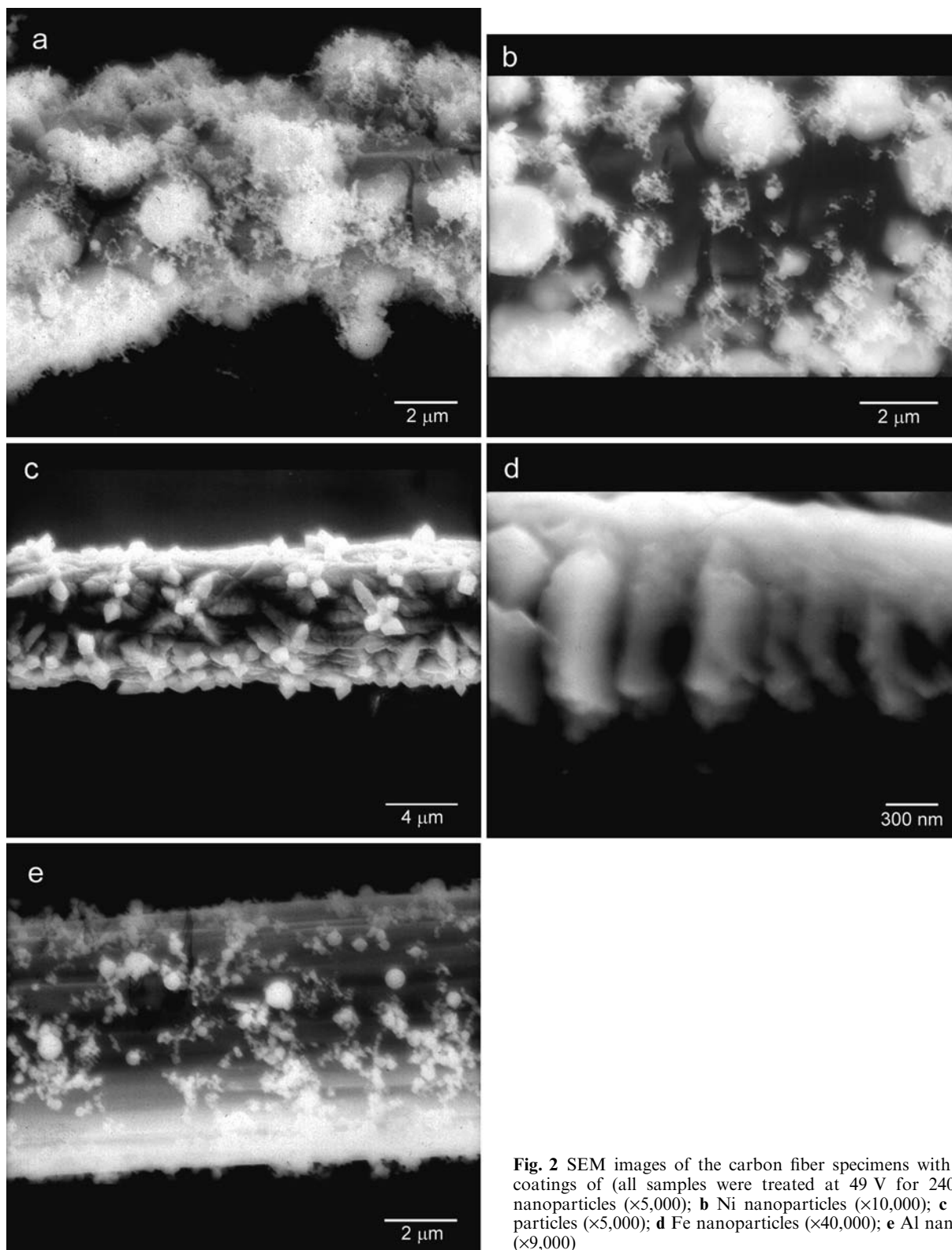**Fig. 2** SEM images of the carbon fiber specimens with the EPD coatings of (all samples were treated at 49 V for 240 s): **a** Ni nanoparticles (×5,000); **b** Ni nanoparticles (×10,000); **c** Fe nanoparticles (×5,000); **d** Fe nanoparticles (×40,000); **e** Al nanoparticles (×9,000)

nanoparticles are spherical) [25], where S_w is the BET specific surface area measured by nitrogen absorption and ρ the density of nickel. The calculated average diameter of the as-received Ni powders is 102 nm and that of the nano-Ni coating is 50 nm. The results show that fine particles from the as-received Ni powders were finally deposited on the surface of carbon fibers, which lead to the increase of specific surface area.

In summary, the investigation demonstrates that the as-received nickel nanoparticles by an active hydrogen

Fig. 3 X-ray diffractograms of the as-received Ni, Fe and Al nanoparticles and the corresponding EPD-treated carbon fiber (carbon fiber specimens were treated at 49 V for 20 s)
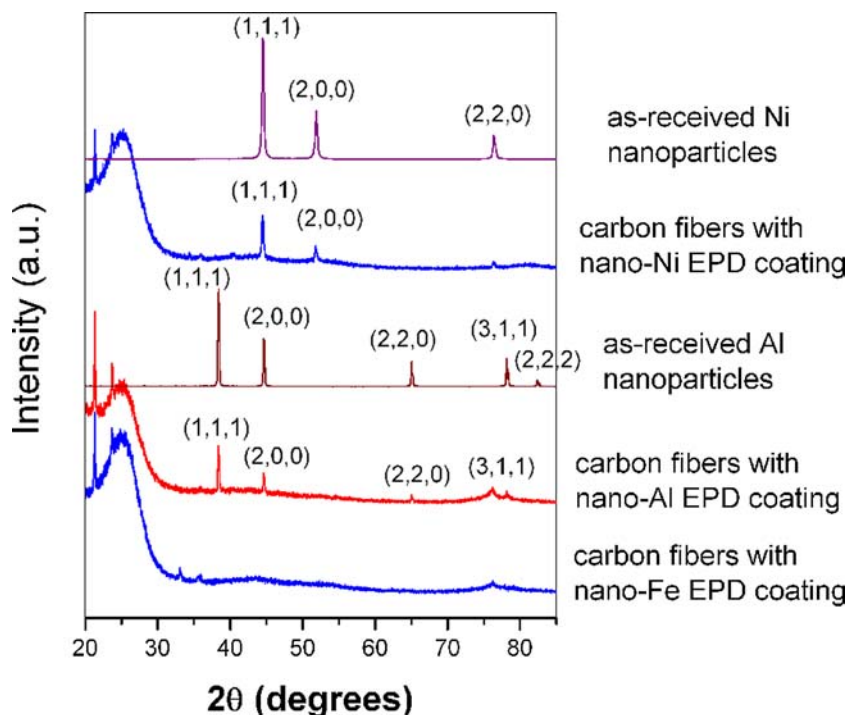
plasma evaporation method can form a thick and compact EPD coating on the surface of carbon fibers without crystal growth, and fine particles from the as-received powders were finally deposited due to the experimental operation. The composite fibers with nano-Ni coating allow to be applied as practical catalysts or electrodes, and the EPD method should be extended to other metal nanoparticles. However, the surface oxidation takes serious effect on the EPD process and the morphology of the as-prepared coatings from the study of Fe and Al nanoparticles.

Experimental section

Polyacrylonitrile (PAN)-based carbon fiber strands T300 (TORAY, brand name TORYCA) were employed as cathode, which were sonicated in acetone bath and dried at 70 °C in an oven prior to use. The anode was a cylindrical stainless steel sheet that kept a distance of 30 mm from the cathode. The as-received metal powders (Ni, Fe and Al) were fabricated by an active hydrogen plasma evaporation method in Shenyang National Laboratory for Materials Science with an average particle size of less than 100 nm. A direct current supply (WYJ-50, Liaoning Precision Instrument Manufacturer) offered a constant voltage of 49 V during the EPD process. In each experiment, 0.15 g of iodine was dissolved in a mixed solution containing 50 ml of acetone and 2 ml of 0.2 mol L^{-1} HCl solution as electrolyte. Under ultrasonic stirring, 0.2 g each of the as-received Ni, Fe and Al powders was dispersed into the above solution separately, and the upper suspensions were employed. During the EPD process, some agglomerates of the metal nanoparticles were deposited on the outer surface of carbon fibers which were easy to break off, so the treated fiber strands were slightly shaken before taking out in order to remove them. The carbon fibers were weighed before and after the EPD process, and the weight increment of EPD coatings can reflect the EPD distribution of metal nanoparticles inside the substrate carbon fibers to some degree. Then the specimens were rinsed with acetone and dried at 70 °C for 4 h. The morphology of the treated carbon fibers was observed by scanning electronic microscope (SEM, JSM-6301F), and the as-received Ni, Fe and Al powders and their EPD coatings were characterized by X-ray diffraction (XRD, Rigaku D/max-2500TC, Cu K_α $\lambda = 0.1542$ nm). The BET specific surface area was measured by Micromeritics ASAP 2010.

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