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Silver nanoparticles supported on graphitization micro-diamond as an electrocatalyst in alkaline medium

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ABSTRACT

Graphitization micro-diamond composites are prepared by spark plasma sintering and which was modified by Ag nanoparticles subsequently. The samples are characterized via X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller analysis and Raman spectroscopy. Results show that the 1400-15 min diamond/graphite composite with core/shell structure has a more suitable thickness of graphite layer than other sintered samples. The silver nanoparticles are dispersed on the surface of graphitization micro-diamond in the form of elemental silver, with a size of approximately 15 nm. Electrocatalyst activities are investigated by cyclic voltammetry, linear sweep voltammetry, chronoamperometry and electrochemical impedance spectroscopy techniques. The test of the rotating disk electrode reveals the electrons transfer number of Ag/1400-15 min is about 3.90. Compared with pure micro diamond and 1400-15 min diamond/graphite composite, Ag/1400-15 min composites shows superior electrocatalytic activity and durability because of Ag particles facilitating charge transfer, and the core/shell structure of diamond/graphite can provide more active sites during the electrochemical reaction. The present results highly promise the silver-modified graphitization micro-diamond composite as a potential electrocatalyst.

1. Introduction

Diamond as a remarkable material are arousing great interests in many applications due to its particularly attractive properties combining chemical resistance, ultrahigh hardness, thermal conductivity, high biological inertness and electrochemical properties [1–5]. Many attempts have been carried out to extend the application of diamond in industry, like surface modification with precious metals (Au, Pt) [6,7], composite with other materials [8], dope with nitrogen and boron to generate semiconductor materials [9,10]. All the studies showed that diamond is a potential material for further development.

However, most of studies are focused on the diamonds with nanoscale (ND). Whereas it is also notable that micron diamond powders also possess the good performances, like ultrahigh hardness, high thermal conductivity, excellent chemical stability in both acid and basic media [11–15]. In addition, the micron diamond powders have a weaker trend to form agglomerates and easier to fabricated with a relatively concentrated size distributions. In the past, micro diamond is generally recognized as an insulating material and widely used in cutting tool areas [5,16]. Furthermore, compared to NDS, the specific surface area of micro diamond is small, which is profitless to the chemical reactions on its surface, so there are also some facts severely restrict the applications of micro diamonds. It is well known that the specific surface area of diamond particles become larger and the conductive activity is superior after graphitization, which is caused by the different modes of carbon atoms stacking and the generated defects along with formation of graphite [17,18].

More recently, noble metal such as gold, silver and palladium have become as emerging catalyst due to their potential performance. Among these, silver nanoparticles are widely investigated for its comparable electrochemical properties with Pt and Au, a relative low cost and the remarkable ability of antimicrobial [19,20]. It has also been reported that Ag nanoparticles (AgNPS) was one of the most effective substrates for surface-enhanced Raman scattering substrates (SERS) [21]. In this study, AgNPS as an ideal conductor is used to improve the performance of electrochemical. Because of the outstanding conductivity, AgNPS has proven to have the excellent ability to facilitate the four electrons ($4e^-$) reaction [22].

To date, some investigations on NDS and graphitization NDS modified by silver have studied. Saeed Shahrokhian et al. [23] reported that nanodiamond decorated with silver nanoparticles as a sensitive film modifier in a jeweled electrochemical sensor. The results indicate that

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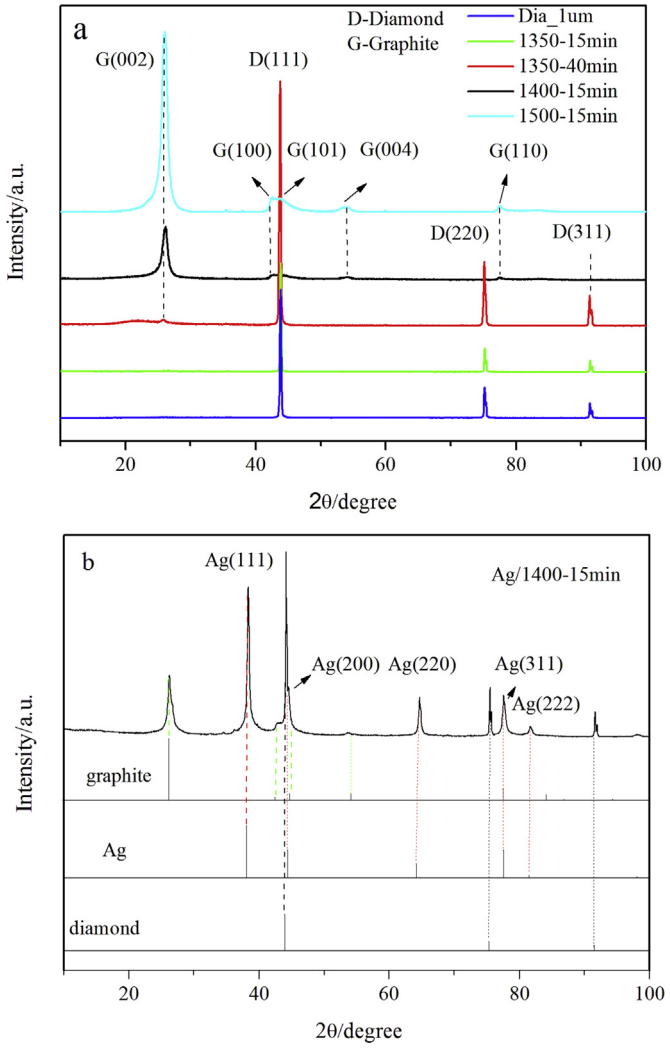

Fig. 1. XRD patterns of (a) pure Dia, 1350-15min, 1350-40min, 1400-15min and 1500-15min; (b) Ag/1400-15min, Ag, graphite and Dia.

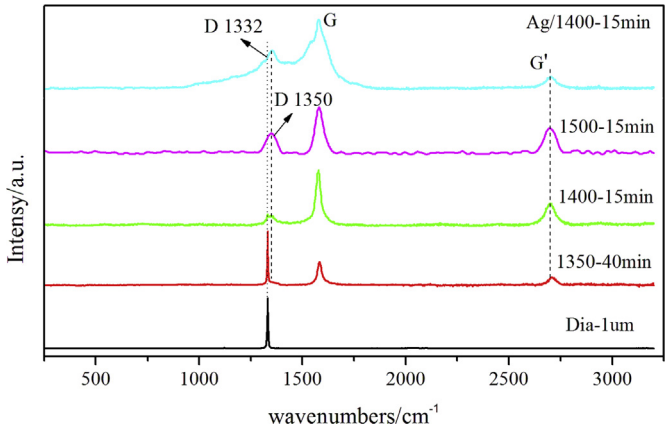

Fig. 2. Raman spectra of pure Dia, 1350-40min, 1400-15min, 1500-15min and Ag/1400-15min.

the prepared modified electrode showed several advantages: simple preparation method, high stability and uniformity in the composite film, high sensitivity, long-term stability and remarkable voltammetric reproducibility in response to TR. Zhenliang Yang et al. [24] researched microstructure and graphitization behavior of diamond/SiC composites fabricated by vacuum vapor reactive infiltration and they found that for the graphitized samples, the thermal conductivity decreases significantly. Nano diamond has high synthesis cost, low yield and poor affinity with the load, which makes the load easy to migrate and reunite, so it is still limited in application. Micro diamond has higher output, cheaper price and relatively uniform size. So in this paper, a core/shell structure micro diamond/graphite composite was prepared by spark plasma sintering and the graphitization of micro diamond in the temperature range of 1300–1500 °C was studied. The sample sintered at 1400 °C for 15min was used as a support material for silver (Ag) nanoparticles, which owns a suitable thickness of graphite layer than other sintered samples. The catalytic activity and stability of pristine diamond, sintered at 1400 °C for 15min and silver modified samples were evaluated. As a result, the silver modified graphitization micro diamond composites have a better bi-functional performance and electrocatalytic activity. The defects and pours generated with the formation of graphite as well as the high conductivity AgNPS, which increase the active site of the catalyst and the three-phase reaction interface. So, the composite is a good potential electrocatalyst, which may expand the application range of micro diamond.

2. Results and discussions

2.1. XRD analysis

The XRD patterns of diamond and composites which were spark plasma sintered at different temperatures are shown in Fig. 1a. The main peaks (2θ = 43.9°, 75.3° and 91.4°) are correspond to the diamond (111), (220) and (311) (PDF reference code 06–0675), respectively. The thermal treatment process is according with the phase transformation temperature of diamond and graphite, which is about 1400 °C [24]. It can be seen that no graphite peaks are observed for 1350-15min, implying the graphitization of diamond does not take place or the graphitization extent is too slight to be detected for the sample. However, when the temperature at 1350 °C for 40min, the graphite peak (002) appeared, it showed that the sp^3 hybridization diamond began to translate to sp^2 hybridization carbon, which indicates that a longer holding time at the same temperature has slight effect for the graphitization process. When the temperature of thermal treatment is above 1400 °C, the obvious graphite peaks (002) are observed, which means a higher graphitization degree. The main peaks in 1500-15min sample at 2θ = 26.3°, 42.6°, 44.8°, 54.2° and 77.5° are correspond to the graphite phase (002), (100), (101), (004) and (110) (PDF 01–0640), respectively. It shows that the thermal treatment temperature is a more important factor than holding time for the phase transformation of diamond to graphite. In Fig. 1b, the XRD pattern of Ag/1400-15min composites and the standard PDF cards of silver, graphite and diamond are given. For the Ag/1400-15min composites, the main peaks at 2θ = 38.1°, 44.2°, 64.4°, 77.5° and 81.5° are correspond to the metal silver (111), (200), (220), (311) and (222) planes, which is according to the PDF card of the face centered cubic (fcc) silver (04–0783). Because the graphitization process is proceeded from the surface to the inner for the diamond particle [25], it can be inferred that the structure of Ag/1400-15min particles have a core of diamond, an outer layer of graphite and the silver nanoparticles are deposit on the surface of graphite, which is further proved by SEM and TEM. The average crystallite size of Ag in the composites is approximately 15 nm, which is calculated in terms of the Scherrer's formula based on the diffraction peak of Ag (111).