Thin Film of Zn/rGO Nanocomposites Fabricated by Electrodeposition

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***Abstract*—Thin film of Zn/rGO nanocomposites were prepared by electrodeposition in zinc chloride solution with graphene oxide (GO) sheets. The crystal structure of zinc growth was investigated by X-ray diffraction and the results show that the prefer orientation of zinc growth was changed from (100) to (002). The micro morphologies of film were captured by scanning electron microscopy which dramatically changed from compact bulged crystal to nanocrystal sheets owing to the addition of GO. The GO was reduced after electrodeposition process which was demonstrated by Raman and the reduced GO (rGO) sheets were uniformly distributed in the film, forming Zn/rGO nanocomposites thin film.**

***Index Terms*—Zn/rGO composites, electrodeposition, crystal orientation, nanocrystal sheets**

I. Introduction

There is a significant interest in the production and development of nanocrystalline materials because of their unique properties and applications in science and technologies [1]. Zinc deposits are employed to provide good protection to iron and steel components due to its sacrificial nature, low cost and ease of application [2]. Nanocrystalline zinc shows improved properties such as hardness, ductility, corrosion and wear resistance [3]. These are a number of methods to fabricate nanocrystalline zinc, such as electrodeposition, arc discharge, laser ablations, CVD (chemical vapor deposition), PVD (physical vapor deposition), VLS (vapor liquid solid), and SLS (solid liquid solid) [4]. However, electrodeposition can lead to easy control of thickness and low cost of production compared with the other processes. Recently years, Nanocrystalline zinc was obtained by changing the plating conditions. Previous works have reported that pulse-current electrodeposition and organic additives were utilized to produce homogeneous and ultrafine deposits and the additives had a significant effect on the size and shape of nanocrystalline zinc [5].

Since graphene was discovered by Geim in 2004, it has been widely investigated in a number of fields due to its excellent properties, such as high electronic conductivity and chemical stability [6]. The graphene based metal materials have been widely reported that the graphene as a support material for metal nanoparticles to obtain catalytic, optoelectronic and magnetic properties, etc [7]. To the best of our knowledge, no effort was paid on using GO sheets as an additive to obtain nanocrystalline zinc consisting of rGO sheets. And the composites are expected to exhibit more excellent nano properties.

In this work, GO was added to the zinc chloride solution. Thin film of Zn/rGO nanocomposites were produced on the cathode. The orientation of zinc growth was changed and GO was reduced as rGO. The most interesting thing was that zinc grew into nano sheets and rGO sheets uniformly mixed among the nano zinc sheets which looked like flower petals.

II. Experimental Methods

A. Synthesis of GO

Graphite oxide was synthesized from purified natural graphite by the modified Hummers method, which has been reported in our previous work [8]. The GO can be obtained by dispersing graphite oxide in deionized water and sonicated for 2 h at room temperature.

B. Preparation of Zn/rGO Nanocomposites

A zinc chloride solution, consisting of 70 g/L $ZnCl_2$, 200g/L KCl, 25g/L H_3BO_3 and 1g/L GO, were prepared to fabricate Zn/rGO nanocomposites. A two-electrode cell system was used for the deposition with matrix NdFeB as working electrode and a piece of pure zinc as counter electrode. The solution was stirred by magnetic stirring, which could prevent the GO nanosheets descending. The electrodeposition process was carried out at a constant current density of 1 A/dm^2 at room temperature. At the end of the growth duration, the film was rinsed by flowing distilled water to eliminate any remaining reactant from its surface. Pure Zn film was also prepared under the same condition for comparison.

C. Characterization

X-ray diffraction (XRD) analysis was conducted with Rigaku D/MAX–RB using Cu Kα radiation (Kα=0.15406 nm). The patterns of Zn and Zn/rGO were analyzed by JADE version 6.0 software. Raman spectra were recorded on a RM1000 microscopic laser Raman spectrometer in the range of 1000-3500 cm^{-1}. The morphology of samples

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was studied by a tungsten scanning electron microscopy (SEM, CS3400) with an EDAX Genesis detector. The thickness of the film was detected by coating thickness gauge (UTD 20A).

III. Results and Discussions

The crystal structure of Zn and Zn/rGO films was investigated by XRD, and the results are shown in Fig. 1. These peaks are in good agreement with those of the reference patterns for the PDF card 04-0831. In the pattern of Zn film, there is a weak peak at 36.42° and an intense peak at 38.98° corresponding to the (002) and (100) crystal plane of zinc, respectively. However, in the pattern of Zn/rGO film, the intensity of the peak at 36.42° decreased and that of the peak at 38.98° increased. The relative intensity of the two peaks was almost equivalent. Moreover, the intense peak at 70.62° divided into two weak peaks at 70.15° and 70.79°, respectively. Compared with the XRD pattern of pure Zn, the preferred orientation of Zn/rGO was changed after adding GO into the plating bath. Whereas, these was no peak found to associate with rGO in the pattern of Zn/rGO. The reason should be that GO sheets were reduced during electrodeposition process and the XRD pattern of graphene was a weak and broadening peak [9]. What's more, GO can be reduced using Zn/acid in aqueous solution at room temperature [10]. Therefore, the weak and broadening peak cannot be easily detected in the pattern of Zn/rGO.

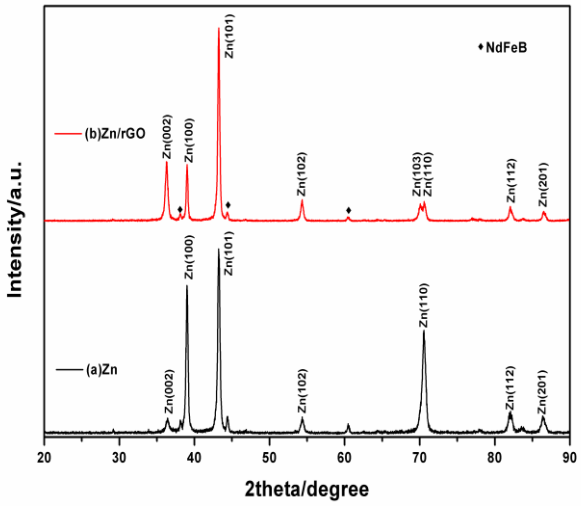

Figure 1. XRD patterns of electrodeposited (a) Zn film and (b) Zn/rGO film

Raman spectroscopy was also utilized to analyze Zn/rGO nanocomposites, as shown in Fig. 2. Since pure electrodeposited Zn is not Raman activity, these no peak in the Raman spectrum of electrodeposited Zn (Fig. 2 (a)). The spectrum of graphite oxide (Fig. 2 (b)) shows a broadening D-band around 1361 cm^{-1} and a G-band around 1606 cm^{-1}, which are corresponding to the ordered sp^2 bond and the defects or edges [11]. Compared with GO, in the spectrum of Zn/rGO film (Fig. 2 (c)), D-band is almost unchanged while G-band is shifted to lower wave numbers. And the I(D)/I(G) ratio (the relative intensity ratio of D peak to G peak) is calculated as 1.345. In other words, the intensity of the D and G bands is reversed in comparison with that of that of GO. It has been demonstrated that if GO is reduced, the intensity of the D and G bands will reverse for the reason that the ordered sp^2 C atoms network structure is repaired [12]. Therefore, the result of Raman further illustrate that the GO sheets are reduced to rGO during electrodeposition process.

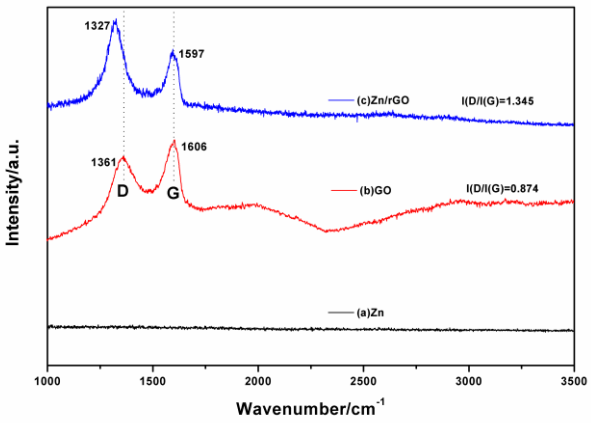

Figure 2. Raman spectra of electrodeposited (a) Zn film, (b) GO and (c) Zn/rGO film.

Fig. 3 shows the representative SEM images of Zn film and Zn/rGO film. Fig. 3A is the morphology of the pure Zn film, showing closely stacked grains which looks like steamed buns. It is normal growth pattern of zinc under the DC plating condition in the zinc chloride solution [13]. However, in Fig. 3B, the morphology of Zn/rGO composites film changes significantly with high roughness. It is readily observed that the zinc crystal is flaky which look like clusters of petals and the rGO sheets intersperse among them and link them together. In Fig. 4A, some clearly visible rGO sheets are marked by black rectangles. The bright wrinkles indicate the scattering rGO sheets throughout the zinc flakes. This dramatic change in morphology is certainly caused by the introduction of GO. It has been demonstrated that the reduced rGO layers tend to interact with each other to form aggregated structure and generate an open pore structure, which provides an easy path for the insertion and extraction of electrolyte ions through the rGO surfaces [14]. And considering that large specific surface area of rGO sheets, Zn ions are proposed to adsorb on the surface of them. Therefore, nucleation sites will easily form on the surface of rGO sheets. And, the GO sheets will migrate towards to and adsorb on matrix owing to the effect of adsorption and mixing. Moreover, there must be nucleation sites on the surface of matrix due to the applied electric field. Combining the two nucleation factors, the introduction of GO sheets leads to a rising in nucleation sites number which will accelerate the growth of zinc and changes the preferred orientation of the electrodeposited Zn. Furthermore, the thickness of pure zinc film and Zn/rGO film are 8 μm and 17μm, respectively. The distinction in thickness between the two films further demonstrates that the addition of GO sheets

accelerate the growth of zinc. Fig. 4B, Fig. 4C and Table I show the EDS spectra and the quantitative elementary analysis of Zn/rGO film at different area, respectively. Accordingly, the EDS spectrum 1 is pure zinc which further indicates that the petal-like nanosheets are zinc. However, these are not only C but also Zn in the EDS spectrum 2. The EDS analysis also gives a proof to the existence of rGO in the composites. And the presence of Zn in the EDS spectrum 2 may indicate that Zn^{2+} ions are reduced on the conductive rGO surface.

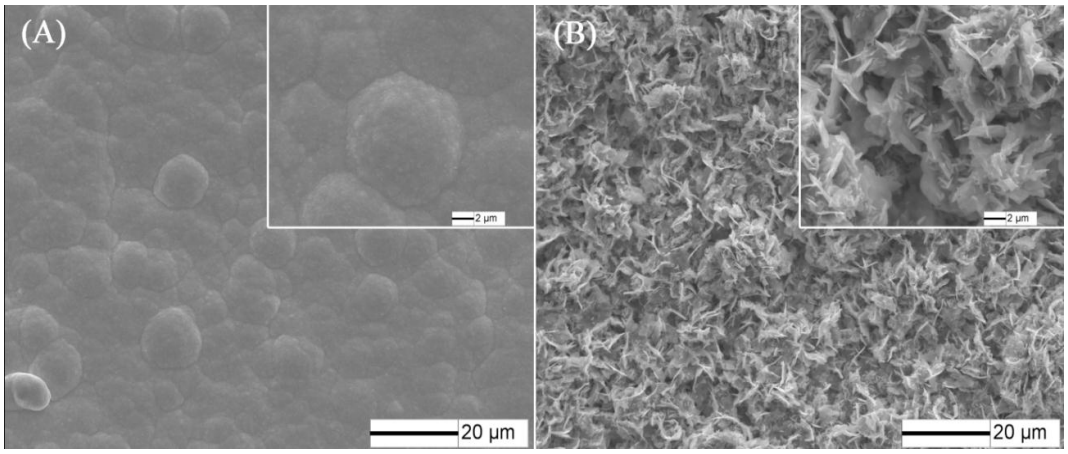

Figure 3. Representative SEM images of (A) Zn film and (B) Zn/rGO film. The insets are the corresponding high-resolution images.

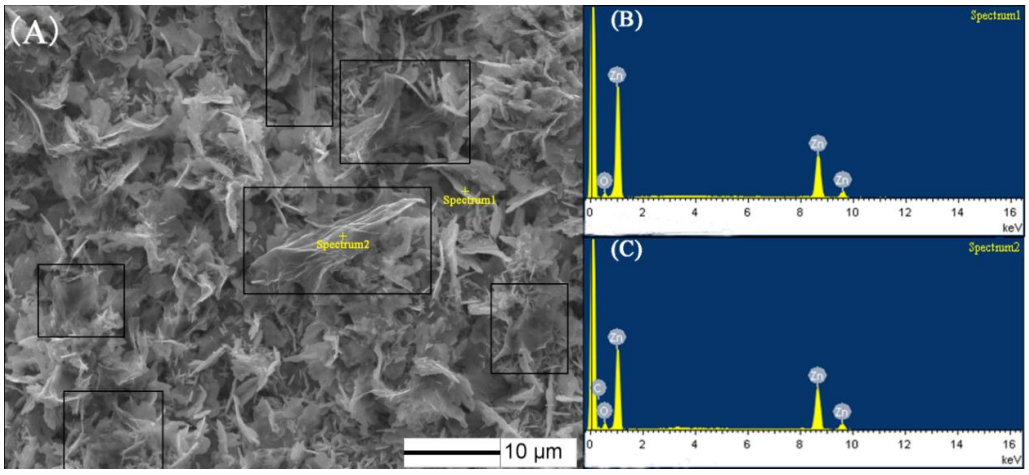

Figure 4. (A) SEM images of Zn/rGO film with clearly visible rGO sheets on the surface and the corresponding EDS spectra: (B) spectrum 1 and (C) spectrum 2

TABLE I. QUANTITATIVE ELEMENTARY ANALYSIS

Element	Weight%		Atomic%	
	Spectrum 1	Spectrum 2	Spectrum 1	Spectrum 2
C K	0	9.73	0	32.32
O K	4.51	6.68	16.16	16.65
Zn K	95.49	83.59	83.84	51.03
Totals	100.00		100.00	

IV. CONCLUSIONS

Zn/rGO film was successfully fabricated by electrodeposition from zinc chloride solution. Compared with pure Zn film, the preferred orientation of Zn/rGO film was changed from (100) to (002) with dramatic change in micromorphology. At the concentration of GO is approximately 1mg/mL, the morphology of Zn/rGO film was controllable to be petal-like zinc nanosheets and rGO sheets situate among them. The GO sheets were reduced to be rGO sheets after electrodeposition process while Zn^{2+} also reduced on the surface of rGO sheets. Besides, due to the greatly increasing in the specific surface area, the Zn/rGO film may be used as efficient catalyst for the reaction of methanol generated by carbon dioxide and hydrogen.

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