Boron Nitride Nanosheets for Metal Protection

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Although the high impermeability of graphene makes it an excellent barrier to inhibit metal oxidation and corrosion, graphene can form a galvanic cell with the underlying metal that promotes corrosion of the metal in the long term. Boron nitride (BN) nanosheets which have a similar impermeability could be a better choice as protective barrier, because they are more thermally and chemically stable than graphene and, more importantly, do not cause galvanic corrosion due to their electrical insulation. In this study, the performance of commercially available BN nanosheets grown by chemical vapor deposition as a protective coating on metal has been investigated. The heating of the copper foil covered with the BN nanosheet at 250 °C in air over 100 h results in dramatically less oxidation than the bare copper foil heated for 2 h under the same conditions. The electrochemical analyses reveal that the BN nanosheet coating can increase open circuit potential and possibly reduce oxidation of the underlying copper foil in sodium chloride solution. These results indicate that BN nanosheets are a good candidate for oxidation and corrosion protection, although conductive atomic force microscopy analyses show that the effectiveness of the protection relies on the quality of BN nanosheets.

1. Introduction

The deterioration of metal by oxidation and corrosion affects all aspects of industry, costing the United States around $300 billion each year.1 Surface coatings using metals (including alloys), ceramics and organics to slow ion movement and hence corrosion rate is a common corrosion-control strategy.2 Recently, graphene, a two-dimensional (2D) nanomaterial, has also been proposed as an oxidation and corrosion barrier on metals.3,4 Graphene has many desirable properties, including a high impermeability to gases (including helium) and moisture,5 high thermal conductivity6 and low reactivity to most chemicals. Graphene coatings are also very thin, which minimizes geometric and morphological changes in the protected surface. Furthermore, it is almost transparent to visible light,8 and hence causes little color change to the coated metal. A fatal problem with graphene, however, is that it can form a galvanic cell with the underlying metal and even accelerate oxidation and corrosion in the long term.9,10

Boron nitride (BN) nanosheets, sometimes called “white graphene”, may provide a better alternative to graphene: one with the desirable properties of 2D nanomaterials, but without causing galvanic corrosion. BN nanosheets have comparable impermeability, mechanical properties and thermal conductivity to graphene.11–17 In addition, BN nanosheets are more transparent to visible light due to their wide bandgap and have greater chemical and thermal stability.18 Most importantly, BN nanosheets are electrically insulating19 and do not enhance galvanic corrosion of the underlying metal. BN nanosheets of relatively large sizes can be produced by chemical vapor deposition (CVD).11,20–27 As is the case for graphene, these can be used directly on the metal substrate or transferred to arbitrary substrates as an anti-corrosion coating. Recently, it was reported that a ~5 nm thick BN nanosheet could protect copper from oxidation at 500 °C for 0.5 h.27 In fact, many practical applications require anti-oxidation protection of metals at relatively low temperatures over a long period of time. In this work, the performance of a commercially available CVD-grown BN nanosheet in inhibiting metal oxidation at 250 °C for up to 100 h and corrosion in sodium chloride (NaCl) solution has been examined by using electrochemical tests and analysing the effects of heating on coated and uncoated copper foils.

2. Results and Discussion

A bare Cu foil and one coated with CVD-grown BN nanosheets (BN+Cu) were used as received. The thickness of the BN nanosheet was determined to be 7–8 nm (~20 layers) by atomic force microscopy (AFM) after a transfer to a silicon substrate with a 90 nm oxide layer (SiO2/Si) (see Supporting Information, Figure S1).28 Thanks to BN’s low absorption of visible light, the BN-covered Cu foil has a very similar metallic color to the bare Cu foil, as shown by the optical microscopy and digital camera photos in Figure 1a and 1e. The heating treatments were conducted at 250 °C in open air for up to 100 h, because oxidation resistance at a low to moderate temperature range for an extended period of time can mimic more the practical
The heating of the two foils produced contrasting color changes, indicating differences in their oxidation levels. The bare Cu foil turned dark-brown after just 2 h of heating (Figure 1b), as a result of the formation of large amounts of black cupric oxide (CuO) and red cuprous oxide (Cu$_2$O) on its surface. Under the same conditions, the BN+Cu foil retained much of its metallic luster, indicating a much lesser degree of surface oxidation, although some black oxidized areas were observed under an optical microscope (Figure 1f). After heating from 20 to 100 h in air, the BN+Cu foil became light orange (Figure 1g and 1h), while the bare Cu foil became completely black (Figure 1c and 1d). The black regions observed on the BN+Cu foil under optical microscopy increased only slightly in size, from about 30% from 2 h heating to about 37% as the heating time increased to 100 h.

The surface morphology of the two foils after heating was examined by scanning electron microscopy (SEM). The bare Cu foil was completely covered with oxide particles after 2 h heating, with the size of these particles increasing as the heating time increased to 100 h (Figure 2b and c). In contrast, most of the surface of the BN+Cu foil was unchanged after heating for 2 h (Figure 2e) and decorated with only a small amount of oxide particles after 100 h (Figure 2f). Furthermore, the oxide particles on the BN+Cu foil after oxidation for 100 h (Figure 2f) are much smaller than those on the corresponding bare Cu foil (Figure 2b), indicating that the degree of oxidation is substantially reduced. This is confirmed by energy-dispersive X-ray (EDX) spectroscopy, which shows a strong intensity increase in the O signal of the bare Cu foil after 2 h heating, in contrast to the relatively low level for the BN+Cu foil even after the 100 h (Figure 3a and 3b). The atomic ratios between O and Cu from standardless quantitative analyses are plotted in Figure 3c. The O:Cu ratios for the unheated bare Cu and BN+Cu foils are similar (0.021 ± 0.005 and 0.024 ± 0.004, respectively), whereas the
O:Cu ratio for the BN+Cu foil heated for 100 h (0.088 ± 0.020) is substantially smaller than that of the bare foil heated for only 2 h (0.554 ± 0.095).

As the EDX technique is not sufficiently surface sensitive to probe the BN nanosheet, chemical changes to the BN nanosheet before and after the 100 h heating treatment were investigated using X-ray photoelectron spectroscopy (XPS). The B 1s spectrum of the BN nanosheet on the copper foil prior to heating appears to comprise two components (Figure 4a): a dominant peak centered at 190.4 eV which is characteristic of B–N bonds \(^{29}\) and a shoulder at 189.0 eV assigned to hydrogenated boron atoms (B–H) \(^{30}\) which are intermediate products during the CVD growth process. \(^{25}\) The N 1s spectrum of the BN nanosheet prior to heating is also dominated by the B-N bonds with the binding energy of 398.0 eV, along with a shoulder at 396.8 eV which is possibly associated with nitrogen atoms bonded to the hydrogenated boron atoms (Figure 4b). \(^{30}\)

After heating for 100 h, the shoulders at the lower binding energies in both the B 1s and N 1s spectra disappear. The N 1s spectrum reduces to a single peak corresponding to B–N; the B 1s spectrum, on the other hand, contains a new shoulder at 191.7 eV, which is attributed to the formation of B–O bonds. \(^{29,31}\) The XPS results suggest that the BN nanosheet on the copper foil is not affected much by the heating. So it can be summarized that the BN nanosheet has an excellent protection of the underlying metal from oxidation at an elevated temperature for relatively long time.

Although the BN nanosheet shows remarkable performance in inhibiting oxidation of the Cu foil, its protection depends on the quality. As shown in the optical microscope images (Figure 1f-h), heating still resulted in the oxidation of about 30% of the surface of the BN+Cu foil. The SEM images in Figure 5 also show patches of oxide particles on the BN+Cu foil after heating for 2 h (white patches and white particles). The quality and homogeneity of the BN nanosheet was investigated using Raman spectroscopy. Most of the BN nanosheet produced a very weak Raman G band at around 1370 cm\(^{-1}\), corresponding to the \(E_{2g}\) vibration mode in hBN; however, for some areas this band was absent (see Supporting Information, Figure S4). Although BN has a much lower Raman yield than graphite, high-quality BN monolayers can still produce a sharp G band. \(^{18,32}\) So the Raman results imply that the BN nanosheet is not of high quality. To gain a better understanding on the spatial variation in the quality of the BN nanosheet, we turned to conductive atomic force microscopy (AFM). BN nanosheets are a wide bandgap semiconductor and electrical insulating; however impurities as well as low crystallinity can increase its conductivity. \(^{33}\) Consequently, the variation in crystal quality can be determined from the local electrical conductivity by conductive AFM. Both the height image (Figure 5c) and the deflection image (Figure 5d) of the pristine BN+Cu foil (without heating) show some disk-like protrusions (arrows) and ripples (rectangle) on the surface of the BN nanosheet. Raman spectroscopy shows that the disk-like protrusions are BN of greater thickness (see Supporting Information, Figure S5). The conductivity map (Figure 5e) shows that the middle area of the BN nanosheet is insulating (dark red area representing currents of 0 nA) and that the
upper-right and lower-left regions are much more electrically conducting (yellow area representing currents ≥8 nA). The overlay of the deflection and conductive AFM images reveals that the area around the disk-like protrusions is more conductive and hence of lower crystal quality (Figure 5f). This is very different from high-quality CVD-grown graphene, in which defects are mainly located at grain boundaries and edges.[3] It can be seen from the SEM image of the BN+Cu foil heated for 2 h (Figure 5b) that the oxide particles appear around the disk-like BN protrusions (arrows), whereas the area containing ripples of BN nanosheet is free of oxide particles. The excellent match between the conductive AFM image and the SEM image shows that the oxidation of the underlying Cu foil mainly happens at places where the BN nanosheet is of low quality, allowing oxygen to penetrate and react with the underlying Cu during heating. In addition, thicker BN tends to have better protection. The formation of B–O bonds shown in the XPS (Figure 4a) is likely to have occurred at these low-quality regions where the BN nanosheet could be torn up by the growth of the copper oxide particles and then oxidized, because BN nanosheets are found to be resistant to oxidation below 850 °C[18] and the heating of the transferred BN nanosheet on SiO₂/Si causes no morphology change (see Supporting Information, Figure S6). In contrast, the part covered by the BN nanosheet of a relatively good quality effectively blocks oxygen diffusion so that the underlying Cu is only slightly oxidized after heating for 100 h. These results suggest that the protection provided by BN nanosheets can depend on crystal quality.

The corrosion passivation of the BN nanosheet in aqueous environment was tested in 0.1 M NaCl solution by electrochemical methods. The open circuit potentials (OCPs) of the two foils show that the BN+Cu foil is nobler than the bare Cu foil. The BN+Cu foil reaches equilibrium very quickly, and the corrosion potential is about -152 mV (BN+Cu in Figure 6). In contrast, the OCP of the bare Cu foil initially drops off from −130 to −180 mV, probably due to the desolution of copper oxide on its surface,[34] and then gradually stabilizes at about −165 mV (Cu in Figure 6).

Figure 5. (a), (b) SEM images of the BN nanosheet covered Cu foil (BN+Cu) after the heating at 250 °C in air for 2 h; (b) magnified view of the rectangular area in (a); conductive AFM images of the BN+Cu foil without heating: (c) height image; (d) deflection image; (e) conductive AFM image under a bias voltage of 1 V and (f) overlay of the deflection and conductive AFM images. All the AFM images have the same scale bar.

Figure 6. OCPs of the bare Cu foil (Cu) and BN covered Cu foil (BN+Cu) in 0.1 M NaCl solution.
Tafel analyses have also been carried out to illustrate the corrosion kinetics of the Cu foil with and without the BN nanosheet. In aerated NaCl solution, the BN+Cu foil shows a lower anodic current, but a higher cathodic current, than the bare Cu foil (Figure 7a), suggesting that the BN nanosheet deactivates copper oxidation but enhances oxygen reduction.\cite{35} To confirm this, similar cyclic voltammetry (CV) tests were conducted in nitrogen-saturated NaCl solution. According to the Tafel plots, the BN+Cu foil has lower anodic and cathodic currents, and a decreased corrosion current density (Figure 7b). The corrosion currents ($i_{corr}$) of the bare Cu and the BN+Cu foils are 0.93 and 0.27 $\mu$A/cm$^2$, respectively. In addition, the corrosion potential shift for the BN+Cu foil from $-0.20$ V to about $-0.17$ V indicates a passivation of the underlying Cu by the nanosheet. The comparison between the Tafel plots from the aerated and nitrogen-saturated solution confirms that the higher cathodic current from the BN+Cu foil is due to the enhanced reduction of oxygen which may be due to pure BN impurities or defective BN nanosheets. Carbon and oxygen impurities are often present in BN crystals\cite{36,37} and carbon doping can form boron carbide nitride which has been found to be efficient in oxygen reduction.\cite{38,39} Nevertheless, the lower anodic current from the BN+Cu foil in aerated solution and the excellent anti-oxidation performance in air suggests that the oxygen reduction by the BN nanosheet does not enhance the formation of Cu$_2$O on the underlying Cu surface.

4. Experimental Section

Both the Cu foil coated with CVD-grown BN nanosheet and the bare Cu foil (20 $\mu$m thick) were purchased from Graphene Supermarket and used as received. The BN nanosheets grown from borazine cover both sides of the copper foil. Oxidation of the foils was conducted in open air using a tube furnace (Tetlow). An Olympus BX51 optical microscope equipped with a DP71 camera and a Carl Zeiss Supra 55VP SEM equipped with an Oxford INCA EDX system were used to examine the foils before and after heating. X-ray photoelectron spectra were acquired using a Kratos AXIS Nova spectrometer (Kratos Analytical Ltd, U.K.) equipped with a monochromated Al Kα X-ray source ($h\nu = 1486.6$ eV) operating at 150 W. The spectra were recorded at 0.1 eV/step and a pass energy of 20 eV. The pressure in the analysis chamber was below 4×10$^{-9}$ torr. The conductive AFM images were taken in contact mode under a bias voltage of 1 V using an Asylum Research Cypher scanning probe microscope (SPM) with a cantilever of conductive titanium and platinum (Ti/Pt) coating (Olympus AC240TM). All the electrochemical experiments were performed on an Ivium-n-Stat electrochemical analyser using a 3-electrode system, which had Ag|AgCl (3M KCl) as a reference electrode and Pt wire as a counter electrode. The electrolyte was prepared with NaCl (purity 99.9%, Univar) in deionised water at a concentration of 0.1 M. All the foils were cut to stripes with a width of 10 mm. During the electrochemical measurements, the foil strips of 4 mm were immersed in 40 mL electrolyte (with an immersed area of 40 mm$^2$). The nitrogen-saturated NaCl solution was prepared by bubbling with nitrogen gas (purity 99.99%, Coregas) for 20 mins before the measurements. The Tafel plots were acquired from CV tests with a scan rate of 1 mV/s from 0 to -0.4 V. The $i_{corr}$ were determined from the intersection of the linearly fitted anodic and cathodic currents.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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