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Intercalation and coordination of copper (II) 2,2'-bipyridine complexes into graphite oxide

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Abstract

Copper-intercalated graphite oxides (GO) were prepared by adding complex solutions of cupric ions and 2,2'-bipyridine (L) ligands to exfoliated GO suspension at pH = 7. High adsorption capacity (>140 mg Cu/g GO) was found for adsorption from equimolar solution of Cu^{2+} and L, while the excess of ligand results in progressively decreasing adsorbed amounts. Electron spin resonance spectra revealed two principal adsorption mechanisms: the $[CuL_3]^{2+}$ complex undergoes ion exchange adsorption, while $[CuL]^{2+}$ and $[CuL_2]^{2+}$ bind to graphene oxide by coordination.

Graphene-based nanocomposites of transition metals, metal oxides or metal-organic frameworks have stimulated intense research over the past few years because of promising applications as high-surface-area supported catalysts, supercapacitors or biosensors [1,2]. The solution-based construction methods of these composites are very versatile but, in general, they rely on the same principle: adsorption of metal precursors on exfoliated graphite oxide (GO) in aqueous dispersion followed by transformation to graphene-supported metal/metal oxide nanoparticles. Crucial to the improvement of this synthetic route, together with potential use for removal of toxic inorganic contaminants from water, is the understanding of the adsorption mechanism of transitional metal ions and their complexes on GO. Quantitative characterization has first been performed for the

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adsorption of Cu^{2+} by Yang et al. [3]. They found a high adsorption capacity of ca. 47 mg/g at pH = 5. In line with other reports [1,4,5], this strongly suggested for the coordination of GO's oxygen functionalities to the cupric ions, although ion exchange could not be ruled out [6]. In order to obtain direct molecular-level information on the binding mode of copper, we studied the adsorption of Cu(II) 2,2'-bipyridyl complexes of different compositions on GO by electron paramagnetic resonance (EPR) spectroscopy, supplementing the adsorption and X-ray diffraction (XRD) data.

Adsorption of copper species was studied in neutral saline solution (pH=7, 20 mM $NaNO_3$), where GO has sufficiently high surface charge to undergo exfoliation and produce single- and few-layer graphene oxide [7] (experimental details are found as Supplementary Information). Neutral 2,2'-bipyridine molecule was chosen as ligand (L) and added to the $Cu(NO_3)_2$ solution in order to avoid precipitation of copper at pH = 7. Isotherms were constructed at different total analytical concentrations of Cu (T_{Cu}) and the ligand (T_L) to examine adsorption from solution in which one of the three homoleptic complex species CuL_n^{2+} (n=1,2,3: monocomplex, biscomplex or triscomplex, respectively) is dominant. To this aim, the distribution diagrams of copper(II)/L systems of various T_{Cu} at pH = 7 (displayed in Fig. 1 along with the chemical structures of the complex species) were calculated by an EPR software [8] using experimentally determined complex stability constants [9].

Dominant species ($\geq$ 90%) in the starting complex solutions are CuL^{2+} for equimolar mixtures of Cu^{2+}/L, CuL_2^{2+} for double ligand excess, and CuL_3^{2+} for T_{Cu}:T_L = 1:5.[†] Fig. 2 shows the adsorption isotherms of copper complexes on GO at the above three metal-to-ligand ratios. They are H-type isotherms characterized by quantitative adsorption up to a certain loading. The steeply increasing adsorbed amounts in this region indicate strong interaction between the solute and adsorbent surface. Rapid coagulation of the suspension upon addition of the complex solutions also inferred high affinity of copper species to GO. At T_{Cu}:T_L = 1:5, quantitative adsorption roughly coincided with the maximum amount of adsorbed Cu (0.41 mmol/g = 26 mg/g). At a lower ligand excess of T_{Cu}:T_L = 1:2, greater initial concentrations yielded a non-linear increase of adsorbed

[†] It is noted, though, that the contribution of $[Cu_2L_2(OH)_2]^{2+}$ in concentrated solutions at T_{Cu}:T_L = 1:1, and CuL_2^{2+} in dilute solutions at T_{Cu}:T_L = 1:5 becomes more pronounced at the expense of CuL^{2+} and CuL_3^{2+}; see Fig 1.

amount, tending towards an adsorption capacity of 1.55 mmol/g (99 mg/g). Finally, in equimolar solutions of $Cu(NO_3)_2$ and L, a continuous increase in the amount of adsorbed copper was found without reaching a plateau in the studied range; the highest loading was 2.18 mmol/g or 139 mg/g. These high capacities considerably exceed those obtained for Cu^{2+} adsorption on GO at pH=5 (47 mg/g, [3]) or on activated carbon based sorbents (typically 5-20 mg/g), and they are also higher than the maximum amount of exchangeable divalent cations on GO (CEC/2 = 0.175 mmol Me^{2+}/g GO at pH = 7 and 20 mM ionic strength, [7]). Therefore, it is clear that mechanisms other than ion-exchange (most likely surface complexation) must operate upon the sorption of CuL_n complexes. Since all of these species have the same charge of +2, a purely ion-exchange based binding mechanism would give rise to the same adsorption capacity (i.e. CEC/2) because the surface charge of GO is constant at constant pH and ionic strength.

The Cu-loaded GO samples used in the adsorption experiments exhibited broad, blurred EPR spectra, which are difficult to analyze. To reduce linewidth, adsorption at lower T_{Cu} (≤0.04 mM) and T_L was carried out. The low g values and resolved superhyperfine pattern by the ligand N donors for the spectra of the latter samples (Fig. 3) support that L is coordinated to Cu^{2+} adsorbed on GO. At low concentration of the complex solutions, the EPR spectra of the samples obtained at $T_{Cu} < T_L$ (where CuL_2^{2+} and CuL_3^{2+} predominate in the solution) are closely similar to those gained at $T_{Cu} = T_L$, when only CuL^{2+} can be adsorbed. This shows that the adsorption of the monocomplex, which has two strong equatorial and two weak axial coordination sites for the O donor groups of GO (carboxylate, phenolate and tertiary OH), is particularly favoured. CuL_2^{2+} has merely two weak axial sites for GO (if it is flattened between the adjacent graphene layers), while CuL_3^{2+} can be adsorbed only by ion-exchange mechanism. At $T_{Cu} = T_L$, the dominating monocomplex is readily chemisorbed, while at excess L, GO either has to replace one or two molecules of L from the complexes present in the solution, or they can only be bound electrostatically at ion exchange sites (carboxylate and phenolate but not to uncharged tertiary OH). This explains why the maximum adsorbed amount of Cu^{2+} decreases with increasing excess of L (Fig. 2). The experimental spectra

are the superpositions of two component curves, suggesting two different coordination environments around Cu^{2+} bound to GO. For both of them, the g values are lower than for the monocomplex in the solution, indicating stronger ligand field formed by the coordination to GO.

X-ray diffractograms of air-dry Cu-modified graphite oxides prepared at different metal-to-ligand ratios containing low and high amounts of complexes are compared in Fig.4. At low loadings (ca. 0.4 mmol/g), two peaks appear near diffraction angles of ~ 10° and ~ 20°, characteristic of (001) and (002) lattice planes. Basal spacings show subtle changes from 0.84 to 0.88 nm with decreasing T_{Cu}:T_L. These distances are larger than the d-spacing of air-dry GO (typically 0.7 nm), which suggests that the complexes intercalated into graphite oxide. For T_{Cu}:T_L of 1:1 and 1:2 at high loadings, the reflections are shifted towards lower angles, which implies that larger amounts of complexes are accommodated between graphene oxide sheets due to random interstratification. At 1:5 metal-to-ligand ratio, markedly different diffractograms appear at the same loading of ca. 0.4 mmol/g. Besides the aforementioned double-peak pattern of the sample prepared from a complex solution of T_{Cu} = 0.8 mM, a higher total Cu concentration of 4 mM gave rise to a peak, together with its second order reflection, which relate to a 1.24 nm basal spacing. This can be explained by the presence of two different phases in this sample: one that contains nearly planar CuL^{2+} or CuL_2^{2+} (ligands aligning parallel to the GO sheet), and the other stuffed with much larger CuL_3^{2+}. At low initial concentration, copper is present in the starting solution as CuL_2^{2+} and CuL_3^{2+}. From this solution, the planar biscomplex is preferentially adsorbed, leading to a lower interlayer expansion. However, at T_{Cu} =4 mM, the triscomplex is dominant in the starting solution, and this is adsorbed at the expense of CuL_2^{2+}, while the total adsorbed amount remains similar to that at T_{Cu} = 0.8 mM.

Overall, high quantities of Cu(II)-bipyridine complexes intercalate into graphite oxide without hydrolysis and concomitant precipitation of copper at pH = 7. The dominant binding modes (ion-exchange or coordination) as well as the structure and composition of the intercalation complexes highly depend on the metal-to-ligand ratio. Since the adsorbed metal ions constitute different

nucleation sites for nanoparticle growth, these results are of especial importance for controlled synthesis methods of chemically derived metal/graphene composite materials.

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Appendix A. Supplementary data

Supplementary data associated with this Letter can be found in the online version, at doi:XXXX

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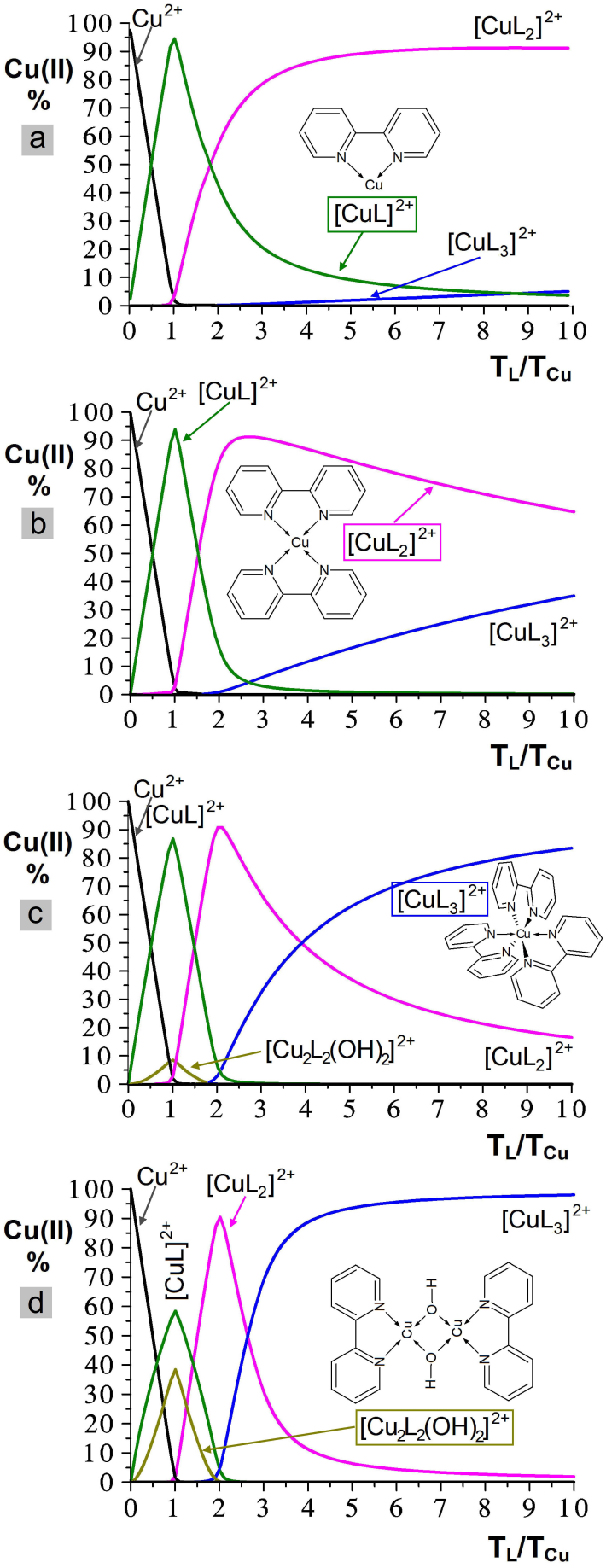

Fig. 1 – Distribution curves of Cu(II)-2,2'-bipyridine complexes at T_{Cu} = 0.004 mM (a), 0.04 mM (b), 0.4 mM (c), and 4 mM (d), pH = 7, including chemical structures of enframed complex species.

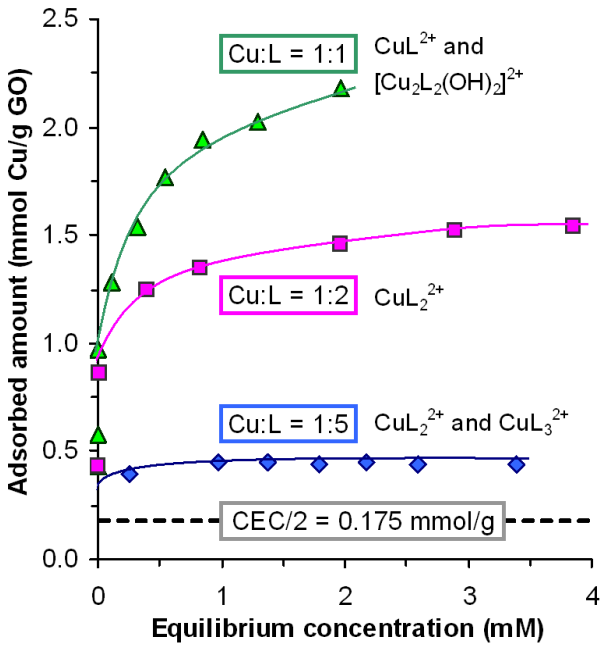

Fig. 2 – Adsorption isotherms of copper(II)-bipyridine complexes on graphite oxide at different metal-to-ligand ratios (pH = 7, I = 20 mM).

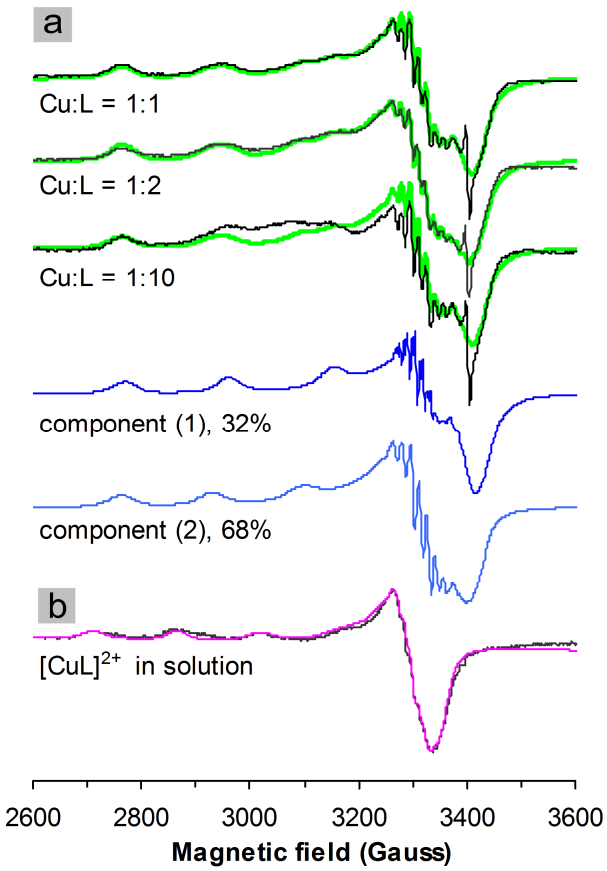

Fig. 3 – EPR spectra of CuL_n^{2+} complexes (a) adsorbed on GO at $T_{Cu}=T_L=0.016$ mM; $T_{Cu}=0.02$ mM, $T_L=0.04$ mM; $T_{Cu}=0.04$ mM, $T_L=0.4$ mM from top to bottom. Black: experimental, light green: calculated as superpositions of two component curves, blue: the component spectra with $g_{xx}=2.050$, $g_{yy}=2.034$, $g_{zz}=2.225$, $A_{xx}=14.3$ G, $A_{yy}=17$ G, $A_{zz}=187$ G for the minor, while with $g_{xx}=2.069$, $g_{yy}=2.030$, $g_{zz}=2.258$, $A_{xx}=34$ G, $A_{yy}=23$ G, $A_{zz}=169$ G for the major species. (b) in solution at $T_{Cu}=T_L=1$ mM, pH=7; black: experimental, magenta: calculated with $g_{xx}=g_{yy}=2.060$, $g_{zz}=2.310$, $A_{xx}=A_{yy}=9$ G, $A_{zz}=150.5$ G.

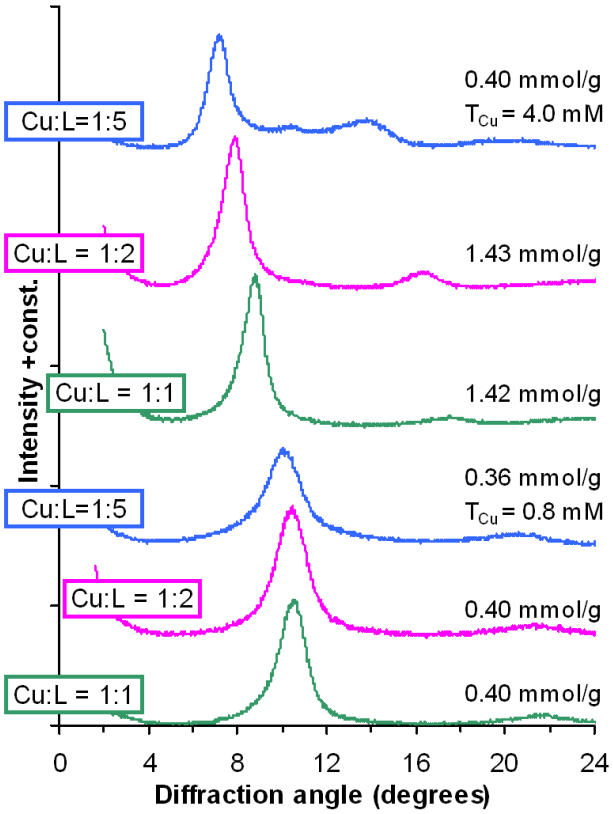

Fig. 4 – XRD patterns of CuL_n-loaded graphite oxides at different metal-to-ligand ratios at lower (on the bottom) and higher (on the top) adsorbed amounts.