



Materials Chemistry

Polyol Solvation Effect on Tuning the Universal Growth of Binary Metal Oxide Nanodots@Graphene Oxide Heterostructures for Electrochemical Applications

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Abstract: Tuning the uniformity and size of binary metal oxide nanodots on graphene oxide (BMO NDs@GO) is significant but full of challenges in wet-chemistry, owing to the difficulties of controlling the complicated cation/anion co-adsorption, heterogeneous nucleation, and overgrowth processes. Herein, the aim is to tune these processes by understanding the functions of various alcohol solvents for NDs growth on GO. It is found that the polyol solvation effect is beneficial for obtaining highly uniform BMO NDs@GO. Polyol shell capped metal ions exhibit stronger hydrogen-bond interactions with the GO surface, leading to a uniform cation/

anion co-adsorption and followed heterogeneous nucleation. The polyol-solvated ions with large diffusion energy barrier drastically limit the ion diffusion kinetics in liquids and at the solid/liquid interface, resulting in a slow and controllable growth. Moreover, the synthesis in polyol systems is highly controllable and universal, thus eleven BMO and polynary metal oxide NDs@GO are obtained by this method. The synthetic strategy provides improved prospects for the manufacture of inorganic NDs and their expanding electrochemical applications.

Introduction

Binary traditional metal oxide nanodots (BMO NDs, diameter: 2-20 nm) show merits for catalysis, supercapacitors, lithium-ion batteries (LIBs) in terms of the more active sites, superior conductivity, shortened ion diffusion distance and high surface area.^[1] However, the high surface area of BMO NDs aggravates self-aggregation, leading to the loss of active sites and the increase in interface charge transfer resistance.^[2] Graphene oxide (GO), as a two-dimensional (2D) substrate, is employed to anchor zero-dimensional (0D) BMO NDs to prevent the self-aggregation and increase electron conduction, largely improving their electrochemical performance.^[3] Depending on the electrostatic adsorption between metal cations and the surface functional groups (hydroxyl and carboxyl) of GO,^[4] and subsequent nucleation and growth processes,^[5] various wet-chemistry methods, including immersion-annealing, water bath, hydrothermal/solvothermal, were used to synthesize the monometallic oxide NDs@GO (e.g., CoO,^[6] SnO₂,^[3b] Fe₂O₃,^[7] TiO₂/ SnO₂,^[8] FeOOH,^[9] and so forth) and cation-type BMO NDs@GO,

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(e.g., $MnFe_2O_4$,^[10] $ZnCo_2O_4$,^[11] $CoFe_2O_4$,^[12] and so forth). However, for the synthesis of some BMO NDs@GO aggregated by metal cations and anions (such as Co^{2+} and VO_3^{-} , Fe^{3+} and MoO₄²⁻), the co-absorption of cations and anions on GO in one solution system still remains a huge challenge, owing to the easy precipitation reaction between cations and anions with high reaction activity instead of them interacting with the GO template.^[13] This undesired reaction leads to an unsatisfactory distribution of BMO NDs on GO. In the following nucleation and growth processes, the sizes of the BMO NDs are mainly determined by the ion diffusion kinetics and surface energy of BMO.^[14] In the aqueous-phase methods, the hydrated ions show fast diffusion kinetics,^[15] which leads to an ultrafast growth rate of BMO. This goes against the capture of BMO NDs@GO in the early reaction stage. In addition, the high surface energy of seeds easily renders the self-aggregation or rapid orientation growth of BMO NDs.^[4b] Therefore, inducing the strong co-absorption of cations and anions on GO accompanied with decreasing the ion diffusion rate and surface energy of BMO are suggested to effectively obtain the uniformly ultrafine BMO NDs@GO, but this approach remains largely unexplored.

Compared with the water bath and hydrothermal method, the solvothermal method shows more functions including solvent molecules as surfactants, soft-template agents, reducing agents, and so forth.^[16] In the solvothermal method, solvation effects between ions and the polar solvent play an important role in the above-mentioned three processes.^[17] Solvation shells can affect the adsorption strength between the solvated



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ions and the GO surface through hydrogen-bond and/or van der Waals forces. Meanwhile, the desolvation energy and diffusion kinetics of the solvated ions in liquids and at the liquid/ solid interface could significantly affect the nucleation and growth rates.^[18] By tuning the solvation shell of molecules, the uniformity of cation/anion co-absorption and the nucleation and growth rates of BMO NDs are suggested to be effectively controlled. However, the solvent effect for the interaction between the solvated cation/anion and GO and the rules related to various alcohol systems, growth size, and distribution of BMO NDs have lacked investigation and remain largely unexplored.

Herein, the solvent effects of a series of alcohols with varying amounts of hydroxyl groups and carbon chains and the ratios of alcohol/water for the ion adsorption, nucleation, and growth processes of BMO NDs@GO were systematically investigated. The designed polyol solvothermal systems are universal for synthesizing lots of BMO and even polynary metal oxide (PMO) NDs@GO. Selectively combining the re-crystallization process, we obtained thirteen kinds of uniform metal oxide NDs@GO. The as-synthesized Co₂VO₄ and VN/Co NDs@GO possess abundant activity sites, shortened ion diffusion distance, and excellent conductivity, which give highly active catalysts for the oxygen reduced reaction (ORR) process and as highperformance electrode materials for LIBs with high cycling stability and rate performance.

water content is discussed below), including methanol, alcohol, n-propanol, butanol, octanol, glycol, 1,2-propanediol, 1,3-butanediol, and glycerol were first performed to explore the effects of carbon chain length (n) and hydroxyl number (m) on the uniformity and size of BMO NDs. Binary metal oxide, cobalt vanadate (noted as Co-V-O) is used as the research object in followed experiments. The related morphologies are shown with transmission electron microscopy (TEM) images (Figure 1 and Figure S1 in the Supporting Information) and scanning electron microscopy (SEM) images (Figure S2 in the Supporting Information). Given that various alcohol solvents have different boiling points, the low-temperature controlled experiments (under boiling points) were also designed in two cases; one is n=3, $1 \le m \le 3$ at 90°C, the other is m = 1, $1 \le n \le 3$ at 60°C (Figures S3, S4 in the Supporting Information). Briefly, there are the same two trends in the size and uniformity of NDs with the changes in the *n* and *m* values at low or high temperature conditions. Among the monohydric alcohols (Figure 1 i-v), there is more non-uniformity/agglomeration and larger-sized NDs with the increase of n. Another trend is that the smaller NDs' sizes and more uniform distribution accompany the increase in m (Figure 1 iii, vii, ix). In addition, the increase in solvothermal temperature in the same alcohol solvent is beneficial for enlarging the size of NDs. These results suggest the following points: (1) the increase in n is adverse to the small size and uniformity of Co-V-O NDs; (2) the increase in m is beneficial to obtain smaller and more uniform Co-V-O NDs on GO; (3) the change in solvothermal temperature hardly affects the above rules (1) and (2); (4) glycol and glycerol with less nand more *m* are ideal candidates for the universal solvent sys-

Results and Discussion

The effects of various alcohol solvents on size and uniformity of BMO NDs@GO

A series of control experiments at $180\,^\circ$ C using different alcohol solvents (water content of 7.7%, the detailed effect of



tems.

Figure 1. The effects of various alcohol solvents on the size and uniformity of Co-V-O NDs@GO. TEM images of Co-V-O NDs@GO prepared at 180 °C in different alcohol solvents (alcohols/H₂O = 12:1): methanol (i), alcohol (ii), *n*-propanol (iii), butanol (iv), octanol (v), glycol (vi), 1,2-propanediol (vii), 1,3-butanediol (viii), glycerol (ix).

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Cation/anion co-adsorption, nucleation, and growth mechanisms

To obtain deep insight into the effects of alcohol solvents on the uniformity and size of Co-V-O NDs@GO, the detailed analyses of three steps, including ion adsorption, nucleation, and growth processes are separately discussed, as illustrated in Figure 2. The solvated cations absorb on the GO surface by the coulombic and hydrogen-bond interactions. The coulombic force is dominated by the charge quantity and the distance between ion and GO surface based on Coulomb's law.^[19] The coulombic adsorption strength is affected by the valence of the metal ion and the radius of the solvated ions (a), implying that the long-chain solvent molecules decrease the coulombic force. In addition, hydrogen bonds between the peripheral groups of the solvated ion and the surface functional groups of GO also contribute to the ion adsorption process. First, the surface oxidation state of GO was revealed by Raman spectrum (Figure 3 a). The two signatures located at approximately 1340 and 1590 cm⁻¹ correspond to the disorder-induced phonon mode (D-band) and graphite band (G-band), respectively.^[20] The intensity ratio of D-band to G-band (I_D/I_G) was calculated as 1.54, indicating abundant defects and surface groups of GO.^[21] Ultraviolet/visible (UV/Vis) absorption spectra were further used to evaluate the hydrogen-bond interactions between GO and different alcohol solvents (Figure 3b-e). The UV/Vis spectrum recorded from GO aqueous solution exhibits two characteristic peaks. A main peak located at approximately 231 nm refers to the $\pi{\rightarrow}\pi^*$ transitions of C–C bonds, and a shoulder peak located at approximately 300 nm is attributed to the $n \rightarrow \pi^*$ transitions of C=O bonds.^[22] When GO nanosheets were dispersed in different polar alcohols, the hydrogen bonds between the hydroxyl groups of alcohols and functional groups of GO enhance the absorbed light energy, compared with GO dispersed in non-polar solvent. The absorbed light energy is partly consumed with the $n \rightarrow \pi^*$ transitions, and the other part is used to break the hydrogen bond. Therefore, the decrease of hydrogen-bond strength leads to a redshift of the shoulder peak.^[23] The UV/Vis spectra of the different monohydric alcohols (Figure 3 b) show a gradual redshift of the shoulder peaks along with the increase of carbon chain (*n*), indicating a reduction of the hydrogen-bond strength. On the contrary, with the increase of hydroxyls (*m*), the shoulder peaks tend to blueshift, indicating the gradual enhancement of the hydrogen-bond strength (Figure 3 c).

Further, the systems with the addition of Co^{2+} and VO_{3^-} in the GO dispersed alcohol solvents were investigated (Figure 3d and e). Glycol and butanol systems were selected to represent polyol and monohydric alcohols to elucidate the interaction mechanism between the solvated ion and GO. In the GO and Co²⁺ butanol system, a clear redshift of the shoulder peaks is observed, indicating a reduced interaction between the solvent and GO after the formation of the solvated Co(bu $tanol)_{x}^{2+}$ cations. However, in the GO and Co^{2+} glycol system, the shoulder peak at approximately 300 nm shows almost no redshift, indicating the unaltered hydrogen-bond interaction between glycol and GO after the formation of the solvated $Co(glycol)_{x}^{2+}$. Owing to the central symmetric configuration and larger dipole moment of glycol^[24] (inset of Figure 3 d and Table S1 in the Supporting Information), the hydroxyls of glycol are exposed on the periphery of $Co(glycol)_x^{2+}$, leading to the uniform and tight adsorption of the solvated Co²⁺ ions on the GO surface through strong hydrogen bonds (Figure 2a). As a contrast, the solvated $Co(butanol)_x^{2+}$ ion with the exposed alkyl group dramatically decreases the interaction of the hydrogen bonds (Figure 3e), resulting in weak cation absorption on GO.^[25] Meanwhile, the strong steric effect between the long alkyl chains of butanol further impedes the absorption on the GO surface. After further introducing VO_3^- , the shoulder peak at approximately 300 nm in glycol is only slightly redshifted (Figure 3 d). However, in the butanol system, this shoulder peak has almost disappeared (Figure 3e). These results reveal that the sequential adsorption of $VO_3(glycol)_x^-$ onto the Co(gly $col)_x^{2+}/GO$ surface could be accomplished by the coulombic force and hydrogen-bond interaction (Figure 2a). However, VO_3 (butanol)_x⁻ mainly combines with the dissociative Co(buta- $\operatorname{nol}_{x}^{2+}$ by coulombic force, rendering a possible formation of Co-V-O nucleus on the near-surface of GO (Figure 2b).^[13]



Figure 2. Growth mechanisms of BMO NDs@GO. Schematic of the detailed ion absorption, nucleation, and growth processes of BMO NDs@GO in glycol (a) and butanol (b) solvents.

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Figure 3. Spectroscopy measurements, size statistics, and solvated ion diffusion mechanism. (a) Raman spectrum of GO prepared by the Hummers method. UV/Vis of GO dispersed in different solvents (alcohols/H₂O = 12:1): (b) methanol, alcohol, *n*-propanol, and butanol; (c) *n*-propanol, 1,2-propanediol, and glycerol; (d) glycol, 0.45 mM Co^{2+} in glycol, 0.45 mM Co^{2+} and VO_3^{-} in glycol; (e) butanol, 0.45 mM Co^{2+} in butanol. Insets are the configurations of the solvated $Co(glycol)_x^{2+}$ and $Co(butanol)_x^{2+}$ ions. (f) The size distribution curves of Co-V-O NDs@GO prepared in various alcohol solvents at 180 °C for 24 h. Optimized geometries of the most stable $Co(glycol)^{2+}$ (g) and $Co(butanol)^{2+}$ (h) on the $Co_2VO_4(001)$ surface. (j) Potential energy profiles for $Co(glycol)^{2+}$ and $Co(butanol)^{2+}$ diffusion along different adsorption sites on the $Co_2VO_4(001)$ surface.

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Under solvothermal reaction, the nucleation and growth processes occur sequentially. The above co-absorption process of the solvated cations/anions can further affect the nucleation and growth of BMO NDs on GO. The strong absorption of Co- $(glycol)_x^{2+}/VO_3(glycol)_x^{-}/GO$ is beneficial for the further uniform heterogeneous nucleation and growth of BMO NDs on GO. Inversely, non-uniformly weak absorption leads to a scattered distribution, which is in accord with the SEM and TEM observations (Figure 1 vi, iv and Figures S1, S2 in the Supporting Information). The final sizes of BMO NDs are dominated by the growth processes, which are discussed as follows.

To evaluate the growth step, the morphology evolution of Co-V-O NDs@GO in glycol were observed by SEM (Figure S5 in the Supporting Information). With the increase of solvothermal time from 3 to 48 h, the size of the Co-V-O NDs gradually increase and no significant aggregation or larger nanoparticles occur. This suggests that the glycol solvent effectively confines the overgrowth of Co-V-O NDs and the average growth rates of Co-V-O NDs at different time intervals are consistent. The diameter distributions of Co-V-O NDs@GO samples in various alcohol solvents were counted and summarized in Figure 3 f, based on the observation of high-resolution (HR)TEM images (Figures S6 and S7 in the Supporting Information). Among the monohydric and dihydric alcohols, the average particle diameters gradually increase with the increase of the carbon chain, whereas they rapidly decrease with the increase of hydroxyl

groups (*m*). The Co-V-O NDs prepared in glycol (n=2, m=2) solvent have an average diameter of approximately 4.34 nm, but a large size of about 12.1 nm is obtained in alcohol (n=2, m=1) solvent. In an attempt to build more a direct relationship between average growth rate (k) and the carbon chains and hydroxyls, k is expressed as Equation (1),^[26]

$$k = \frac{8\gamma D V_{\rm m}^2 c_{r=\infty}}{9RT} \tag{1}$$

where *D* is the ion diffusion coefficient in solvent, γ is the surface energy of BMO, V_m is the molar volume, $c_{r=\infty}$ is the bulk solubility, and *T* is the temperature. The *D* is obtained from the Stokes–Einstein equation (Eq. (2)),^[27]

$$D = \frac{k_{\rm B}T}{6\pi\eta a} \tag{2}$$

where $k_{\rm B}$ is the Boltzmann constant, η is the solvent viscosity, and *a* is the radius of the solvated ion. Substituting Eq. (2) into Eq. (1), Eq. (3) is thus obtained,

$$k = \frac{8\gamma V_{\rm m}^2 c_{r=\infty}}{54\pi\eta a N_{\rm A}} \tag{3}$$

where $V_{\rm m}$ could be considered as a constant for Co-V-O. Therefore, k is a function of γ , η , $c_{r=\infty}$, and a. The carbon chain

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length and hydroxyl number of the solvent could significantly affect these factors, thereby affecting the growth rate of metal oxides. Among the monohydric alcohols, a and η gradually increase with the increasing chain length at room temperature. The bulk solubility $c_{r=\infty}$ is proportional to the permittivity (ε) of the solvents, because the ε determines the dissolution mechanism of ionic solids in alcohols.^[28] Thus, the $c_{r=\infty}$ of BMO in monohydric alcohols decreases with the increase of chain length (Table S1 in the Supporting Information). According to Eq. (3), the k seemingly decreases with the increase of chain length. However, the actual growth rates of BMO increase (Figure 3 f). This abnormal phenomenon is possibly determined by the increasing surface energy (γ) of BMO along with the increased surface tension of monohydric alcohols (Table S1 in the Supporting Information), when the alcohol molecules cap the BMO seeds (Figure 2b).^[29] Moreover, the η of low-boiling monohydric alcohols in the solvothermal reaction is sharply reduced, which has a small influence on the growth rate. With the increase of hydroxyl groups, the viscosities η of high-boiling polyols would dramatically increase by one or even two orders of magnitude (Table S1 in the Supporting Information). The $c_{r=\infty}$ and γ of polyols just have a small increase. Thus, the growth kinetics of BMO are mainly limited by the drastically increased viscosity. The high viscosity significantly reduces the solvated ion diffusion rate D in liquid, thereby decreasing the growth kinetics of BMO (Figure 2a). When the viscosity further increases by three orders of magnitude, such as with glycerol, the size of Co-V-O NDs were well confined (Figure S6 in the Supporting Information), but the crystallinity dramatically reduces, demonstrated by the selected area electron diffraction (SAED) images of Co-V-O NDs observed with the same contrast (Figure S8 in the Supporting Information).

The diffusion rate of the solvated ions on the solid surface of BMO NDs significantly affects the growth rate of nanodots. During the diffusion process, the binding energy between the exposed hydroxyl or alkyl groups of the solvated ions and metal atoms of BMO NDs determines the diffusion barrier. The optimized geometries of the $Co(glycol)^{2+}$ and $Co(butanol)^{2+}$ on Co₂VO₄(001) surface were examined to investigate their diffusion mechanisms by using density functional theory (DFT) calculations (Figure 3 g, h). Along the *a* axis on the $Co_2VO_4(001)$ surface, the Co(butanol)²⁺ diffusion exhibits a low energy barrier of 0.08 eV, whereas that of Co(glycol)²⁺ is 1.03 eV (Figure 3 i, j). This indicates the peripheral hydroxyl groups will increase the diffusion energy barrier of the solvated ion, thereby decreasing its diffusion kinetics, reducing the growth rate of BMO NDs. However, the weak interaction between the alkyl groups and BMO surface only slightly confines the solvated ion diffusion and allowed growth of BMO. These results are consistent with the TEM observations and size statistics. On the other hand, the reaction concentrations may affect the growth kinetics and morphology of BMO NDs. The Co-V-O NDs@GO prepared with different molar numbers in glycol solvent were observed by SEM (Figure S9 in the Supporting Information). With the increase of reaction concentration, the loading of Co-V-O NDs on the GO surface gradually increases, whereas the sizes are almost unchanged. This suggests that the glycol has high solubility and its confining effect may be suitable for mass production of BMO NDs@GO.

Universal synthesis of BMO and PMO NDs@GO in polyol system

According to the above results and discussions, it is found that polyol solvents are favorable for uniform distribution of ultrafine NDs on GO nanosheets. It ensures uniform and tight cation/anion co-absorption on the GO surface by hydrogenbond and coulombic interactions, while confining the growth rate by decreasing the ion diffusion kinetics. The above-mentioned samples were prepared by using GO aqueous solution, and the solvent to water ratio is adjusted to 12:1 by volume. Deionized water with high permittivity but low viscosity could decrease the viscosity of the mixed solvents and increase the surface energy and bulk solubility of BMO (Table S1 in the Supporting Information), thus increasing the growth rate (detailed discussions in Figure S10 in the Supporting Information). This result indicates that the glycol/H₂O solvent system may exhibit a highly tunable and universality for many metal oxide NDs by adjusting the ratio of glycol/H₂O. To confirm its versatility, BMO NDs@GO, such as Co₂VO₄, FeMoO₄, Co₂SnO₄, and CoFe₂O₄ and so forth (Figure 4A-D and Figure S11 in the Supporting Information), PMO (Na-Fe-Mn-O), and phosphate (Na₃V₂(PO₄)₃) precursor NDs@GO, and monometallic oxide NDs@GO, such as SnO₂ and Fe₂O₃ (Figure S12 in the Supporting Information), were all obtained by using the glycol/H $_2O$ solvothermal method, selectively combined with a subsequent annealing processes. These NDs all exhibit a uniform size distribution and loading on the GO surface. The corresponding SAED patterns also reveal their polycrystalline natures. The XRD are well indexed to pure metal oxides phases. Further, the broad diffraction peaks indicate the metal oxide NDs have a small size according to the Scherrer equation. This is consistent with the observations from HRTEM images. When the metal oxide ND precursors were moderately annealed in NH₃ atmosphere, metal nitride NDs@GO, such as VN/Co, FeN/MoN, were also obtained (Figure 4E, F). This implies that the metal oxide NDs@GO are promising to be transformed into various nitrides, sulfides, and phosphides NDs on GO, expanding their functional applications.

Electrochemical applications of BMO NDs@GO

For electrochemical catalysis applications, the BMO NDs@GO with abundant surface-active sites, high surface area, and good electron conduction are considered as highly efficient catalysts. Linear sweep voltammetry (LSV) using a rotating disk electrode in O₂-saturated 0.1 \times KOH solution was carried out to evaluate the catalytic activities of various BMO NDs@GO for ORR application (Figure 5a). Among the vanadate NDs@GO, the Co₂VO₄ clearly exhibits a higher onset potential (E_{onsetr} 0.88 V vs. RHE) and half-wave potential ($E_{1/2r}$ 0.76 V). Meanwhile, among the cobalt-based BMO NDs@GO, it displays a similar activity but higher diffusion-limited current density than those of spinel CoFe₂O₄ NDs@GO. These results indicate cubic Co₂VO₄

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Figure 4. The universality of the polyol system for BMO NDs@GO. SEM, TEM, HRTEM (insets: SAED patterns) images and XRD patterns of various NDs@GO: Co₂VO₄ NDs@GO (A,i–v), FeMoO₄ NDs @GO (B,i–v), Co₂SnO₄ NDs@GO (C,i–v), CoFe₃O₄ NDs@GO (D,i–v), VN/Co NDs@GO (E,i–v), FeN/MoN NDs@GO (F,i–v).

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NDs@GO is a promising non-noble metal catalyst. To obtain higher catalytic activity and expand the catalytic applications of BMO NDs@GO, various nitride/metal-composited NDs@GO were prepared by ammonia nitridation/reduction at 550°C for 2 h. Under these conditions, the V-O, Mo-O, and Fe-O bands tend to transform to the V-N, Mo-N, and Fe-N bands, but the Co-O and Cu-O bands are preferably reduced to metallic Co and Cu atoms (Figure 4E, F and Figures S13, S14 in the Supporting Information), which agrees well with the previous reports.^[30] The comparisons of LSV curves, E_{1/2}, and kinetic current density at 0.8 V (J_{kr} calculated from the Koutechy–Levich equation) of various nitrides or metals NDs@GO are shown in Figure 5 b and c, respectively. The Co/VN NDs@GO exhibits the highest E_{onset} (0.92 V), $E_{1/2}$ (0.80 V), and J_k than those of other nitride/metal-composited NDs@GO, indicating the best catalytic activity. In addition, these values are closer to those of commercial Pt/C (0.99 V and 0.83 V), and significantly surpass those of Co₂VO₄ NDs@GO (0.88 V and 0.76 V) and Co/VN NPs@GO (0.9 V and 0.77 V; Figure 5 d and Figure S15 in the Supporting Information). These results indicate that Co/VN NDs provide more exposed active sites and offer a favorable access of the electrolyte to the reactive sites compared with the large-sized Co/VN NPs@GO, facilitating mass transfer of the O2 and ion conduction on the catalyst surface.^[31] Moreover, the good contact between the high-activity metallic Co and conductive VN substrate renders a faster charge transfer compared with other nitride/metal-composited NDs@GO and Co₂VO₄ NDs@GO.^[30a] At different rotation speeds, LSV curves of Co/VN NDs@GO (Figure 5e), Co/VN NPs@GO (Figure S16a in the Supporting Information), and Co₂VO₄ NDs@GO (Figure S16b in the Supporting Information) exhibit similar ORR polarization. The electron transfer number per oxygen molecule of the Co/VN NDs@GO electrode was calculated to be approximately 4.2 at 0.45–0.60 V, suggesting a 4e⁻ oxygen reduction process (inset of Figure 5e). The current-time (*i*-*t*) chronoamperometric responses (Figure 5 f) were further tested in 0.1 \times KOH solution at 1600 rpm. When methanol was added into the solution during the chronoamperometric tests, the current for Co/VN NDs@GO stays constant whereas that for commercial Pt/C suffers a sharp decrease, indicating Co/VN NDs@GO exhibit better tolerance for the methanol crossover effect and better long-term durability than commercial Pt/C.

The BMO NDs@GO with abundant oxidation and reduction states can be also regarded as very promising electrode materials for high capacity LIBs.^[32] Co₂VO₄ NDs@GO as the research object with high surface area, shorten the ion diffusion distance and high electron conduction is beneficial for overcoming poor rate performance and unsatisfactory capacity fading. The thermogravimetric (TG) analysis indicates the GO content is 18.8 wt%^[33] (Figure S17 in the Supporting Information). The charge/discharge cycling test was first performed at 0.1 Ag⁻¹ (Figure S18a, b in the Supporting Information). The Co₂VO₄ NDs@GO anode delivers a high discharge capacity of 820 mAh g⁻¹ after 150 cycles at 0.1 Ag⁻¹ with a superior cy-



Figure 5. Electrochemical performances for the ORR process. (a) LSV curves of various BMO NDs@GO, including Co₂VO₄, CoFe₂O₄, Co₂SnO₄, Fe-Mo-O, Fe-V-O, Cu-V-O, and Cu-Mo-O NDs@GO. (b) LSV curves of various nitrides or metal NDs@GO, including Co/VN, Cu/VN, Co/Fe₃N, Cu/MoN, FeN/MoN, and FeN/VN NDs@GO. (c) Comparison of $E_{1/2}$ and J_k for different nitrides or metal NDs@GO. (d) LSV curves of Co/VN NDs@GO, Co/VN NPs@GO, Co₂VO₄ NDs@GO, and Pt/C, the inset is the comparison of $E_{1/2}$ and J_k . (e) LSVs with different scanning rates of Co/VN NDs@GO. The inset shows the corresponding Koutecky–Levich plots at different potentials. (f) Chronoamperometric response of Co/VN NDs@GO and Pt/C. The methanol (3 M) was introduced into the electrolyte at 500 s.

cling stability. The slight capacity increase is due to the gradual activation process and reversible reaction between metal particles and electrolytes.^[34] Moreover, it also exhibits a good cycling retention of 80% after 500 cycles at a high current density of 1 Ag^{-1} (Figure S18c in the Supporting Information). The rate capability of the Co₂VO₄ NDs@GO anode was investigated at different current densities (Figure S18d in the Supporting Information). At 1 and 2 Ag^{-1} , it also exhibits a high specific capacity of 414 and 297 mAhg⁻¹, respectively. The favorable cycling stability and rate performance indicate the BMO NDs@GO structure has lots of merits for the storage of large and fast Li⁺ ions.

Conclusion

We present a facile and universal glycol/water solvothermal system to prepare various BMO and PMO NDs on GO. It is found that the solvation effect and functional groups of alcohol solvents significantly affect the cation and anion co-adsorption, nucleation, and growth of BMO NDs on GO. The hydrogen-bonding interactions among the polyol-solvated cation, anion, and GO surface dominate to give an ordered and tight co-assembly, inducing a uniformly heterogeneous nucleation. It also dramatically confines the ion diffusion kinetics in liquids and at the solid/liquid interface, leading to controllable growth. Therefore, the BMO NDs@GO with both high uniformity and controllable size were obtained and exhibited good oxygen reduction activity and Li⁺ ion storage performance. The present rules provide fundamental theoretical support for the manufacture of various nanodots and GO-composited 2D heterostructures on the laboratory- or even the industrial scale. These metal oxide NDs@GO heterostructures are also promising to be transformed into various nitrides, sulfides, and phosphides NDs on GO, expanding the potential applications in electrical energy storage and conversion.

Experimental Section

Materials and methods

Synthesis of Co-V-O NDs@GO, Fe-Mo-O NDs@GO, Co₂VO₄ NDs@GO, FeMoO₄ NDs@GO: First, Co(CH₃COO)₂·4H₂O (0.35 mmol, 87.2 mg) was added into ethylene glycol (30 mL) and stirred for 30 min to obtain a clear solution (A). GO (20 mg) and deionized water (5 mL, or 5 mL, 4.0 mg mL⁻¹ GO aqueous dispersion) were then added directly into the Co(CH₃COO)₂ solution (A) and stirred for 1 h. NH₄VO₃ (0.35 mmol, 40.9 mg) was dissolved in ethylene glycol (30 mL) with stirring at 80 °C for 15 min. The obtained transparent NH₄VO₃ solution (B) was added into the solution (A) and stirred for 1 h. The obtained brown suspension was transferred into a 100 mL Teflonlined autoclave and hydrothermally treated at 180°C for 24 h. Then, Co-V-O NDs@GO was collected, washed with deionized water and ethanol, and freeze-dried for 48 h. Fe-Mo-O NDs@GO was prepared by the same steps except adding Fe(NO₃)₃·9H₂O (0.35 mmol) and (NH₄)₆Mo₇O₂₄·4H₂O (0.05 mmol) as the original materials. Co2VO4 NDs@GO and FeMoO4 NDs@GO were obtained by annealing Co-V-O NDs@GO and Fe-Mo-O NDs@GO at 500°C for 2 h in Ar gas, respectively.

Synthesis of SnO₂ NDs@GO, Fe₂O₃ NDs@GO, Co₂SnO₄ NDs@GO, and CoFe₂O₄ NDs@GO: First, SnCl₂ (0.35 mmol, 66.4 mg) was added into ethylene glycol (60 mL) and stirred for 30 min to obtain a clear solution. GO (20 mg) and deionized water (5 mL, or 5 mL, 4.0 mg mL⁻¹ GO aqueous dispersion) were then added directly into the SnCl₂ solution and stirred for 1 h. The brown suspension obtained was transferred into a 100 mL Teflon-lined autoclave and hydrothermally treated at 180 °C for 24 h. Then, the SnO₂ NDs@GO product was collected, washed with deionized water and ethanol, and freeze-dried for 48 h. Fe₂O₃ NDs@GO was prepared by the same steps except adding Fe(NO₃)₃·9H₂O (0.35 mmol). Co₂SnO₄ NDs@GO was prepared by the same steps except adding Co(CH₃COO)₂·4H₂O (0.35 mmol) and SnCl₂ (0.35 mmol) as the original materials. CoFe₂O₄ NDs@GO was prepared by the same steps except adding Co(CH₃COO)₂·4H₂O (0.35 mmol) and Fe(NO₃)₃·9H₂O (0.35 mmol) as the original materials.

Synthesis of Co/VN NDs@GO, FeN/MoN NDs@GO and other nitrides/metals-composited NDs@GO. These were all prepared by annealing BMO NDs@GO at 550 $^\circ$ C for 2 h in NH₃.

Synthesis of Co/VN NPs@GO. Co(CH₃COO)₂·4H₂O (0.5 mmol) was added into H₂O (30 mL) and stirred for 30 min. GO solution (5 mL, 2 mg mL⁻¹) was then added directly into the Co(CH₃COO)₂ solution and stirred for 1 h. NH₄VO₃ (0.5 mmol) was dissolved in ethylene glycol (30 mL) with stirring at 80 °C for 15 min. The obtained transparent NH₄VO₃ solution was added into the GO and Co(CH₃COO)₂ solution and stirred for 1 h. The brown suspension was added into ethylene glycol (1 mL) and ethane diamine (1 mL) and stirred for

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1 h. Then, the solution was transferred into a 100 mL Teflon-lined autoclave and hydrothermally treated at 180 °C for 24 h. Then, the resulting product was collected, washed with deionized water and ethanol, and freeze-dried for 48 h. Finally, the obtained product was sintered at 550 °C for 2 h in NH₃ to get Co/VN NPs@GO.

Material characterization

X-ray diffraction (XRD) data of the samples were collected with a D8 Advance X-ray diffractometer with an area detector using $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å) in a 2θ range from 5° to 70°. Raman spectra were obtained by using a Renishaw INVIA micro-Raman spectroscopy system. The microstructures were observed by using FESEM (JEOL-7100F), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM; JEM-2100F). The UV/Vis spectra were collected by using an ultraviolet visible spectrometer (Lambda 750 S).

Electrochemical measurements

The electrochemical properties of Co₂VO₄ NDs@GO were characterized in 2016-type coin cells with Li metal foil as the anode. The anode electrodes were composed of 70% active material, 20% acetylene black, and 10% carboxymethyl cellulose (CMC) binder. The slurry was cast onto Cu foil and dried in a vacuum oven at 120 °C for 12 h. The electrode loading was 1–1.5 mg cm⁻². LiPF₆ (1 M) in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (volumetric ratio = 1:1:1) was used as the electrolyte. The cells were assembled in an argon-filled glovebox. Galvanostatic charge/discharge measurements were performed with a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry was conducted with a CHI 1000C electrochemical workstation. For the ORR catalytic performance, working electrodes were prepared by dispersing catalyst (5 mg) and Vulcan XC-72R carbon (5 mg) in deionized water (150 µL), isopropanol (800 µL), and 5% Nafion solution (50 $\mu L).$ An aliquot (12 $\mu L)$ of the obtained slurry was pipetted out onto a glassy carbon electrode (0.196 cm²). The ORR tests were carried out in a rotating disk electrode in O²saturated 0.1 M KOH solution. The saturated calomel electrode (SCE) and a Pt plate were used as the reference and counter electrodes, respectively. In this paper, all the potentials were referenced to the reversible hydrogen electrode (RHE). The CV tests were performed in the range 0.2-1.1 V at a scan rate of 25 mVs⁻¹. The LSV measurements were carried out at the potential range 1.1-0.2 V with a scan rate of 5 mV s⁻¹. During LSV measurements, the working electrode was rotated from 400 rpm to 1600 rpm. All measurements were carried out at room temperature.

DFT calculations

The present calculations were carried out by using the projector augmented wave (PAW) method within DFT, as implemented in the Vienna ab initio simulation package (VASP). The generalized gradient approximation (GGA) in the form of the Perdew–Burke– Ernzerhof (PBE) was used to treat the exchange-correlation energy. A kinetic energy cutoff of 500 eV was used for wave functions expanded in the plane wave basis. All atoms were allowed to relax until the forces were less than 0.05 eV Å⁻¹. The (001) surfaces were created based on the corresponding Co₂VO₄ bulk unit cell, which were in good agreement with the experimental values. For the Brillouin-zone sampling, a $3 \times 3 \times 3$ Monkhorst–Pack k-point mesh was adopted to ensure convergence of the total energy. A vacuum slab of about 10 Å was inserted between the surface slabs for all the metal oxide models. The cell parameter was $17.78 \times 17.78 \times 17.09$ Å for $Co_2VO_4(001)$. Ultrasoft pseudopotentials were used to describe the interactions of the ionic core and valence electrons.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: 0D/2D graphene heterostructures • binary metal oxides • nanodots • oxygen reduction reaction • polyol solvation effect

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FULL PAPER

Materials Chemistry

S. Tan, Y. Pan, Q. Wei, Y. Jiang, F. Xiong, X. Yao, Z. Cai, Q. An, L. Zhou, L. Mai*

Polyol Solvation Effect on Tuning the Universal Growth of Binary Metal Oxide Nanodots@Graphene Oxide Heterostructures for Electrochemical Applications



Binary metal oxide nanodots@graphene oxide: Polyol solvent systems with high controllability and universality are designed to synthesize eleven uniform binary and polynary metal oxide nanodots@graphene oxide heterostructures by solvation-effect-induced cation/ anion co-absorption, nucleation, and diffusion-confined growth processes. This strategy shows the huge prospects for manufacture and applications of inorganic nanodots and zero/two-dimensional heterostructures in energy storage and conversion fields.

