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Controlled nanostructures of atomically thin 2D oxides for next generation functional materials

**Sehirlioglu, Alp**  
**CASE WESTERN RESERVE UNIV CLEVELAND OH**  
**10900 EUCLID AVE**  
**CLEVELAND, OH,**  
**US**

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## FA9550-18-1-0030 Final Report

### Controlled nanostructures of atomically thin 2D oxides for next generation functional materials

#### I. Accomplishments:

*Research Objectives:* The main goal of this work was to develop a better understanding of the processing-structure and morphology-property relationships in 2D oxide nanosheets. The objective is beyond just obtaining the nanosheets but to understand how the processing parameters affected the nanosheets size and thickness, its composition, ionic structure and the distribution of point defects, and its electronic structure.

*Big picture accomplishments:*

- Developed controlled processing of CoO<sub>2</sub> nanosheets and elucidated its effects on the electronic and crystal structure of the 2D flakes as well as their morphology.
- Developed structure-property relationships in 2D oxides including CoO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub> and MO<sub>3</sub>.
- Developed methods to apply the 2D oxides including as armored particles, catalysts and gate dielectrics.
- Initial objective of finding a simpler characterization tool to quantify the statistics of size distributions was not successful. Attempt was made to relate UV-vis spectra to AFM images, since UV-vis is easier and measures in statistically representative quantities unlike AFM which is the direct measurement technique of size.

*Dissemination:* The results were published in 13 journal articles and led to numerous presentations. A 14<sup>th</sup> paper is in preparation at the time of this report and will be submitted during spring of 2022. There were four Ph.D. theses and 1 M.S. thesis as a result. In addition, four other Ph.D. students were partially supported to complete the work. One of the publications was an invited perspective paper by Journal of Applied Physics. Students were active both in international conference and local conferences. In addition, some of the X-Ray Diffraction work on the nanosheets were accepted to the ICDD database.

#### II. Impact

*Development of the principal discipline(s) of the project:* Traditional way of exfoliating two dimensional sheets of CoO<sub>2</sub> from LiCoO<sub>2</sub> was previously shown in the literature but was limited in its scope related to the underlying science. We have discussed the effects of processing parameters on the morphology, processing yield, defect structure and electronic structure of the nanosheets. Such structure is critical in controlling the properties of the material, especially electrical properties. We were able to tune this relationship by additional processing steps such as annealing in vacuum. When processed in the traditional way, the solution is very basic (pH =13), which damages many surfaces it is introduced. Since these nanosheets are also targeted to be used in electronics they need to be compatible with the surfaces they will be integrated with. To help this, we have also developed new exfoliation techniques that allow stabilization in

different solutions including pH neutral water. The physical foundation we built in describing such materials and the processing techniques we developed to make them in real life will open the path for incorporation of new oxide nano-materials in applications as well as expand the library of oxide nanosheets.

*Other disciplines:* We used the nanosheets, the byproducts of the exfoliation (i.e., ready to exfoliate powders) and armored nano-particles we have built using nano-sheets in emulsions to investigate their effectiveness in catalysis that is specifically related to environmental engineering. We were able to show that these materials were effective in degradation of bisphenol A (also known as BPA), and methylene blue and oxidation of carbon monoxide. Converting nanosheets into armored particles allowed recovery of the catalyst from the solution.

*The impact on the development of human resources:* This project led to 4 Ph.D.s and 1 M.S. in Materials Science and Engineering, Chemistry and Physics. These students are now working in both federal government (i.e., NASA Glenn Research Center) and industry (Agnostic Inc., SVKroma LLC). It also led to international collaborations with Paris-Tech, France (who were a part of the proposal), and University of North South Wales, Australia. In addition, it supported numerous projects for undergraduate researchers in all the departments involved.

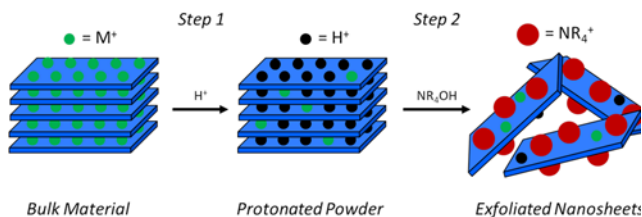
*Impact on teaching and educational experiences:* The project did not lead to new approaches in course design or new pedagogical tools. It provided research experiences (as a part of the undergraduate curricula) to undergraduate students.

*The impact on physical, institutional, and information resources that form infrastructure:* A new chemistry lab was built in Materials Science and Engineering Department at Case Western Reserve University for the purpose of chemical exfoliation.

*Impact on society beyond science and technology:* The project is likely to have two big impacts, one in its catalytic application that can help with environmental conditions and the other in increasing interest and research in processing of a new library of oxide nanosheets which can enable many future applications.

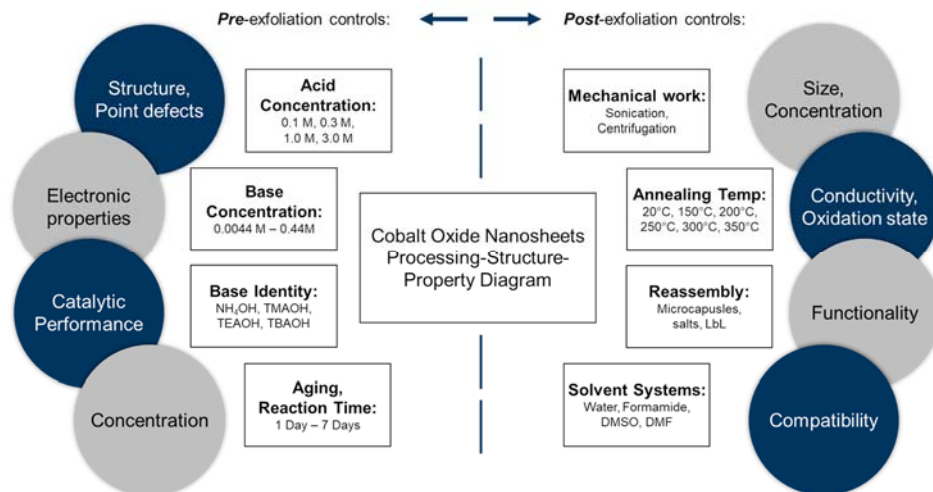
## Technical Updates

*Processing:* Exfoliation of  $\text{LiCoO}_2$  (LCO) was achieved by a two-step processing route which includes (i) protonation and (ii) intercalation of bulky organic molecules. The first step removes  $\text{Li}^+$  and replaces it with  $\text{H}^+$  via etching in HCl solution. Then in the second step, tetramethylammonium with hydroxide groups (TMAOH) was used where the OH from TMAOH and H in the protonated LCO interacts to form water that swells up the structure and allows bulky TMA in to pull apart the layers into nanosheets (Fig. 1). This is the traditional way of processing that was discovered before this project. In this project we focused on more detailed analysis of the technique including the



**Fig. 1:** Sketch of the chemical exfoliation process.

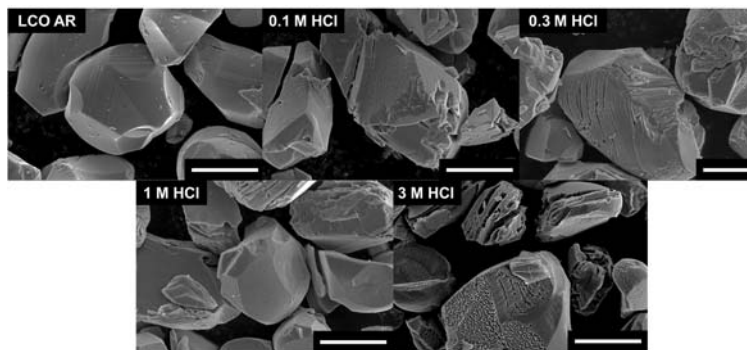
effects of molarity of HCl, molarity of TMAOH, treatment time, aging time, acid type, base type and mechanical work. This project identified changes to composition and structure at every step of the processing as a function of processing parameters. Other post-processing



**Figure 2:** A diagram of the processing-property relationships created through pre-exfoliation and post-exfoliation chemical treatments of LCO.

(Fig. 2) By a combination of UV-Vis, ICP-OES, XRD, SEM and XPS characterization we were able to show that HCl treatment led to both partial dissolution of the LCO powder and leaching of Co ions into the solution. Control of the molarity of the HCl showed low molarities led to inefficient exfoliation and high molarities led to dissolution of the powder. A good range exists near 1-3M HCl. It was also shown that HCl was the most effective acid to use. The morphology of the acid treated powders also changed with the HCl molarity leading to more surface area with increasing molarity (Fig. 3). This became critical later on as we also showed that these powders were useful for catalytic applications that depend on the surface area per volume. Overall it was also shown that complete delithiation did not occur. In addition all the Li lost was not necessarily replaced by H<sup>+</sup>, thus also there was only partial protonation. Combined with Co leaching and charge balance obtained by a change in the ionicity of the bonds (i.e., decreasing ionicity of oxygen ions from 2- to 1.97-) a complicated composition was proposed.[1]

By using UV-vis, effect of variety of processing parameters were investigated including acid type, concentration, base type and concentration (Fig. 4). Different base types provided different NR<sub>4</sub><sup>+</sup> sizes of which TMA<sup>+</sup> was shown to be the best in exfoliation of LCO. The focus was the efficiency of exfoliation. Standards were developed to relate the UV-vis intensity to concentration. Efficiency maps



**Fig. 3:** Morphology of the powders as a function of molarity of the HCl.

were created (Fig. 5). In addition, this analysis was used to determine the stability of the solution (i.e., aging effects in concentration). The higher concentration of HCl in the ideal range (3M in 1-3M HCl) resulted in attainment of higher yield after the second step of exfoliation. A critical ions size to the interlayer spacing ratio (1.3:1) was determined. It was also shown that the aqueous environment was critical to the exfoliation. Even under same acid and base conditions, for example in methanol, exfoliation was not achieved. We also found evidence against a previously suggested  $[NR_4^+]/[H^+]$  ratio by investigating multiple  $[H^+]$  ratios. Aging studies showed that these solutions had lower concentration of nanosheets (e.g., loss of 75% after 150 days). Poor aging can be a limiting factor in scaling of the process. [2] Band gap prediction from the UV-vis data was not successful in providing changes that are beyond statistical variations.

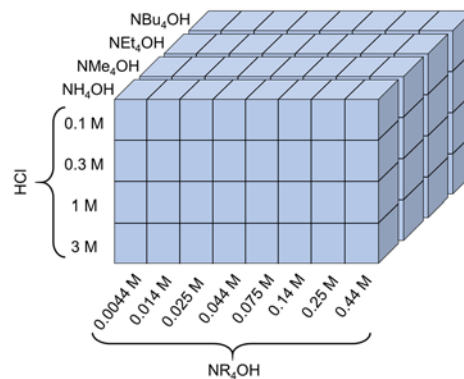


Fig. 4: Example processing study space

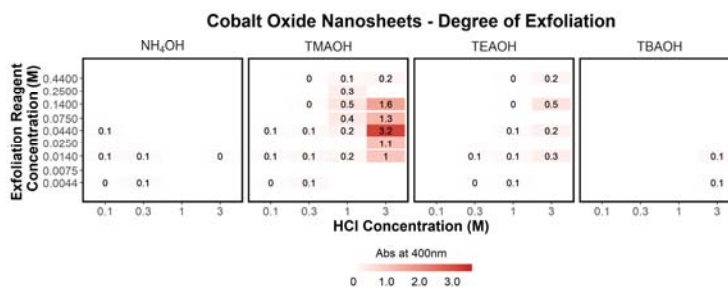


Fig. 5: An example of exfoliation efficiency maps.

Additional processing methods, other than the traditional method, have also been developed. In Method 1, the powder that were not fully exfoliated were washed with copious amounts of DI-water followed by centrifugation. The not fully exfoliated powders show plate like morphology (Fig. 6) that is ready to exfoliate. Typically the lateral size of the nanosheets are at maximum  $0.4 \times 0.4 \mu\text{m}^2$ . Using this technique we were able to obtain largest flakes ever reported where the lateral sizes were up to 10 $\mu\text{m}$ . This step was repeated couple of times after removing the solution with exfoliated nanosheet in each step. This removal step while gets rid of sought after nanosheets, it also results in removal of excess TMA that is highly basic and etches many surfaces and limits use of photolithography since it is a developer for photoresist. Thus repeating this step couple of times, leads to a solution of nanosheets in pH-neutral (=7) solution that is useful for a larger number of applications, especially those are electronic in nature, where the nanosheets may be drop-cast on surfaces of interest (i.e., Si, SiO<sub>2</sub>, Nb:STO etc.). It was also shown that in these nanosheets neither Li-extraction nor proton replacement was complete. The nanosheets obtain this

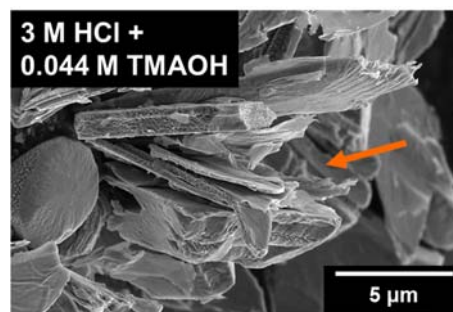


Fig. 6: Morphology of ready to exfoliate powders.

way were shown to be at variety of thicknesses in <10 unit cell size but were not monolayers.[3]

These nanosheets can also be reprecipitated from the solution by introduction of other salts. This allows both a method to remove them out of the caustic TMA solution and a way of making new powders where the cation between nanosheets can be exchanged, essentially restacking the nanosheets with different cations such as K, Ca, Al etc. [4] Additional methods included use of the nanosheet solution that is the product of the traditional method (Method 2). Here, the nanosheet solution were centrifuged at very high spin rates which led them to cake at the bottom of the tube. This cake of nanosheets were then dispersed again in variety of solutions (17 of them) with varying properties such as dielectric constant, boiling point, surface tension, being H-bond donor/acceptor of which the dielectric constant of the solvent was found to have the greatest impact in solubility and stability even after one month.

As nanosheets are processed, their stability becomes a topic of interest. As was discussed even in the nanosheets that are few-layer thin some Li remains. This affected the response of the nanosheets to elevated temperature annealing (or exposure). The evaporation of Li resulted in changes to the structure, disordering of Li and Co cations in the lattice and related distortions. The structure changed from R-3m to C2/m to P2/m to Fd3m to Fm-3m upon heating up to 350°C. All these changes were shown by TEM. The initial change to C2/m was due to Li loss followed by the Li-vacancy ordering leading to P2/m. The disordering leads to a lowering of the band gap related to the change in the valence for Co cation. When Li is removed at high quantities, rock salt (Fm-3m) structure formed. This was shown to be heterogeneous within the nanosheet with the losses maximizing at the edges.[4,5]

*Physics:* The main goal of this project was to evaluate how ultrathin and eventually monolayer forms of LiCoO<sub>2</sub> and/or isolated CoO<sub>2</sub> layers obtained by exfoliation differ from the bulk properties and to assist in the interpretation and understanding of the experimental studies performed. The broad goal of the project is to study 2D oxides and focuses on LiCoO<sub>2</sub> but also includes work on V<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub>. We performed first-principles calculations of LiCoO<sub>2</sub> and related nanostructures. A first important finding was that in LiCoO<sub>2</sub> Li-covered surfaces sustain a spin-polarized two-dimensional electron gas while the CoO terminated surface sustains a corresponding hole gas. This was first found for a monolayer with both terminations but subsequently confirmed for thicker layers indicating that it is a surface rather than a confinement effect. This result is surprising because it indicates that the Li-2s states normally empty in bulk LiCoO<sub>2</sub> are lowered in energy sufficiently for the Li states to become partially occupied. We eventually were able to demonstrate that there is a topological origin to this effect. A model involving Li-spz orbitals and CoO<sub>2</sub> representing orbitals was established and mapped onto the 1D Su-Schrieffer-Heeger SSH4 model with four orbitals, which is known to have non-trivial topology when obeying particle hole symmetry and under certain conditions on the interatomic hopping integrals. An extension of this model which is non-chiral (breaking the particle-hole symmetry) and includes lateral interactions broadening the bands shows that the surface states on the Li side can become partially occupied explaining the electron gas formation. The results were published in SciPost 10, 057 (2021).[6]

A second important finding on  $\text{LiCoO}_2$  is that the VIS-UV optical absorption is strongly affected by excitonic effects. The fundamental quasiparticle gap obtained from quasiparticle self-consistent GW (QSGW) calculations (3.76 eV) even with a screened Coulomb interaction  $W$  that includes electron-hole effects in the screening, is significantly larger than the optical gap ( $\sim 1.5$ ) obtained via the Bethe-Salpeter-Equations which includes electron-hole interactions. The lowest peaks in optical absorption are thus found to be excitonic rather than pure band-to-band transitions. These extremely high exciton binding energies exceeding 2 eV have not been appreciated before and are ascribed to the flatness of the valence and conduction bands. They are Frenkel type excitons. This was published in *Phys. Rev. B* 104, 115120 (2021).[7]

We also performed calculations for  $\text{LiCoO}_2$  in other structures than the  $R\bar{3}m$  layered structure in support of the experimental TEM-EELS investigation in our group on the changes of  $\text{LiCoO}_2$  as function of temperature. In particular, we calculated EELS spectra for this project and our calculations helped to establish that not only does Li become gradually more disordered, leading eventually to a disordered rocksalt structure, but also Li is lost from the nanoflakes at the edges of the sample. This followed from an analysis of the O-K edge EELS spectra which showed spectral changes which could only be reconciled with a significant loss of Li. This work was reported in *Phys. Rev. Mater.* 5, 015401 (2021).[5]

Earlier in the project, we studied how  $\text{ACoO}_2$  evolves with changing the alkali component  $A$  from Li to Na to K, Rb and Cs, thereby increasing the distance between the  $\text{CoO}_2$  layers. Some findings of this work were included in our invited perspective paper.[4] We found that beyond Na, the alkali atom is too large to support the  $R\bar{3}m$  structure. We also found that upon gradually increasing the layer distance between  $\text{CoO}_2$  layers, at some critical distance the Li or Na attach only to one of the layers instead of staying symmetrically located between the two adjacent layers. This symmetry breaking then leads to essentially decoupled  $\text{LiCoO}_2$  layers similar to the monolayer situation which then have the spin-polarized 2DEG associated with them. This critical distance is smaller in  $\text{NaCoO}_2$  owing to the larger lateral Na-Na interactions. We speculate that this 2DEG may play a role in the as yet not fully understood superconducting transition in  $\text{Na}_x\text{CoO}_2\cdot\text{H}_2\text{O}$  where  $\text{H}_2\text{O}$  intercalation contributes to the increase in the interlayer distances. As part of this work we also studied the exchange of Li by H which relates to the hydrogenation step of the chemical exfoliation procedure.

We studied the electronic structure of isolated  $\text{CoO}_2$  layers at the QSGW level starting from different LDA and LDA+U starting points. Depending on the initial density matrix describing which Co orbitals contain the hole left by the removal of Li, either metallic or gapped band structures were found. It was concluded that to resolve this problem, dynamic mean field theory (DMFT) may be required but, while attempts were made, this problem was not yet satisfactorily resolved with the impurity solvers we tried out.

Overall, our work contributed to the understanding of the exfoliation experiments carried out in the group, the changes in the resulting nanoflakes as function of temperature and the transport measurements carried out on those samples.

Finally, we performed a study of the phonons in layered MoO<sub>3</sub> in both the orthorhombic structure and a monolayer form, published in J. Appl. Phys. 130, 104302 (2021).[8] We were able to provide a detailed analysis of Raman spectra using these calculations and establish that large shifts occur in some of the phonon mode frequencies when the layers are isolated. This work was related to corresponding studies in V<sub>2</sub>O<sub>5</sub> carried out in an earlier AFOSR funding period and reviewed in the perspective paper mentioned earlier. We also found that the anisotropy in MoO<sub>3</sub> leads to hyperbolic behavior in the polaritons in the mid-IR.

We have also initiated research on Li-doped V<sub>2</sub>O<sub>5</sub>, but this work is unfinished. The goal here is to understand the relation between different crystal structures, the role of polarons in cathodoluminescence and other optical properties.

*Properties:* One key component of this project was to understand the electrical conductivity of ultrathin 2D layers of LiCoO<sub>2</sub> and van der Waals (vdW) oxides V<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub>. In the case of LCO, chemical exfoliated nanosheets were used to fabricate devices with metal contacts for transport measurement while for the case of vdW oxides, mechanically exfoliation of bulk crystals was used to obtain nanosheets. With our previous work during the earlier stage of the project establishing the proper contact method to these ultrathin nanosheets, the main focus of electrical studies during the last two years of the project was on the effects of different interlayer doping/intercalation levels, i.e. Li<sub>x</sub>CoO<sub>2</sub> and Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub>. The early study of contact development also revealed a phase transformation at near 150K related to Li ordering.[9] In Li<sub>x</sub>CoO<sub>2</sub> nanosheets, we found that annealing the sample above 200°C during the device fabrication and contact formation induces a gradual drop in conductivity. This loss in conductivity is attributed to the formation of more Li-Co interdiffused phases, in which a low-spin electronic structure is no longer valid and stronger correlation effects are expected.[5] In gated Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub> nanosheets, we demonstrated clear p-type conduction behavior, in striking contrast to the n-type behavior in pure undoped V<sub>2</sub>O<sub>5</sub> nanosheets in field-effect transistor devices, showing the versatile electrical control of electronic properties of V<sub>2</sub>O<sub>5</sub> nanosheets. The result was reported in our perspective paper.[4]

In conjunction with electrical conductivity measurements of doped 2D oxide nanoflakes, we investigated the dielectric property of intrinsic 2D van der Waals (vdW) oxide MoO<sub>3</sub> without doping. Such investigation is motivated by the imperative need to find high-k dielectrics that are compatible with 2D semiconductor materials to enable high gate coupling efficiency and seamless integration with these 2D materials, similar to the development of high-κ dielectrics HfO<sub>2</sub> and ZrO<sub>2</sub> in conventional semiconductor devices. Our dielectric constant measurements demonstrate that as-grown MoO<sub>3</sub> has a high dielectric constant, κ, of ≈35 at room temperature at low frequencies by fabricating parallel plate capacitors from these thin flakes. Moreover, mechanically exfoliated MoO<sub>3</sub> nanoflakes are used to create heterostructures with WSe<sub>2</sub> and a top-gate WSe<sub>2</sub>/MoO<sub>3</sub> heterostructure FET is demonstrated, showing the potential of MoO<sub>3</sub> as a promising high-κ 2D vdW gate dielectric for the integration with 2D vdW semiconductors.[9]

In addition to electrical device and property studies, we collaborated with Prof. Pablo Alonso-González's group from Universidad de Oviedo, Oviedo, Spain on the tuning of Phonon polaritons—light coupled to lattice vibrations— which are promising quasi-particles for

controlling the flow of energy in materials. By studying nanoflakes of  $\text{Na}_x\text{V}_2\text{O}_5$  with different Na doping/intercalation levels, we demonstrate that intercalation of Na atoms in the van der Waals semiconductor  $\alpha\text{-V}_2\text{O}_5$  enables a broad spectral shift of the phonon polaritons' frequency band, and that the phonon polaritons remain ultra-low loss (lifetime of  $4 \pm 1$  ps), similar to phonon polaritons in a non-intercalated crystal (lifetime of  $6 \pm 1$  ps). This result shows intercalated 2D oxide crystals bears potential for generating tunable and low loss phonon polaritons in broad spectral bands (in the mid-infrared domain).[10]

*Armored particles and catalysis:* Cobalt oxide nanosheets (CONs) were developed as sole particle surfactants in Pickering emulsions and used to produce CONs-armored polymer particles by dispersion polymerization. Advances we achieved in the conditions for the chemical exfoliation of CONs from  $\text{LiCoO}_2$  gave nanosheets that were stable as colloidal dispersions in water.[3] Indeed, the electrostatic repulsion between the nanosheets that led to their stable dispersion prevented their assembly at interfaces. The CONs could be flocculated with simple inorganic salts (e.g., NaCl) which shielded the negative charges of the nanosheets, and enabled them to reside at the oil-water interface in Pickering type emulsions.[4] Further, use of hydrophobic monomer followed by thermally induced free radical polymerization led to the formation of a solid polymer particle coated (or "armored") with the CONs.[12] We demonstrated that six different monomers could be used for this purpose and that the CONs-armored particles could be used as catalyst for the oxidation of bisphenol A (BPA) in water.[13] The armored particles could also be incorporated onto a graphite sheet and used repeatedly, with no significant decrease in BPA removal efficiency after the second cycle (i.e., they were conditioned after one cycle). The ability to control the dispersibility and interfacial assembly of transition metal oxide nanosheets opens new opportunities and possibilities in the fabrication of composite hybrid structures that incorporate the unique properties of the 2D structures. We are currently finalizing another manuscript related to the catalytic activity in degradation of methylene blue and oxidation of carbon monoxide.

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