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One-Pot Synthesis of Interpenetrating Inorganic/Organic Networks of CuO/Resorcinol-Formaldehyde Aerogels: Nanostructured Energetic Materials

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Mesoporous3D assemblies of nanoparticles are classified as aerogels.[1] Mixed aerogels, therefore, can be perceived as designer interpenetrating networks of nanoparticles with synergistic chemical and physical properties. Such chemical synergism is typically encountered in energetic materials (e.g., explosives, propellants, and pyrotechnics). Those consist of an oxidizer and a fuel and decompose into heat and gases.[2] Low-order explosives, LEs, are simple mixtures of the two components (e.g., black powder). High explosives, HEs, are compounds with both the oxidizing agent and the fuel within their molecule (e.g., TNT, RDX). The tradeoff is high energy content with slow rates of energy release (LEs) versus lower energy content with high reaction rates (HEs). To improve the reaction rates of LEs, the oxidizer and the fuel need to be mixed as intimately as possible, ideally at the nanoscopic level. A recent approach, along the lines of the general procedures of doping aerogels,[3] utilizes sol−gel chemistry to produce 3D assemblies of Fe_2O_3, NiO, or WO_3 nanoparticles (the oxidant), whereas Al (the fuel) is added to the sol and is trapped in the porous network of the gel.[4] These energetic materials are classified as thermites, and their reaction (e.g., $Fe_2O_3 + 2Al \rightarrow 2Fe + Al_2O_3$) generates heat, but not gases. Here, we report interpenetrating nanoparticle networks of a typical inorganic oxidant (CuO)[5] and an organic fuel (resorcinol-formaldehyde polymer: RF) made in one-pot by two sol−gel processes running concurrently, whereas the precursor of the one catalyzes the other. Upon pyrolysis in Ar, composite CuO/RF aerogels undergo smelting to metallic Cu. Pure RF aerogels do not burn easily in air, but CuO/RF composites sustain combustion, burning completely leaving only CuO (generated continuously by air-oxidation of Cu) as a solid residue.

Under acid catalysis (HCl) gelation of resorcinol (R) with formaldehyde (F) in CH_3CN takes place in ∼2 h at 23 °C as opposed to 7 days at 80 °C under base catalysis.[6] Meanwhile, CuO gels have been reported in isopropanol by dehydration of $CuCl_2 \cdot xH_2O$ with an epoxide.[7] Our process design uses the acidity of a gelling $CuCl_2 \cdot xH_2O$/epichlorohydrine sol (see Supporting Information) to catalyze cogelation of the RF system. However, the issue initially was that the R/F system does not gel in alcohols, and $CuCl_2 \cdot 2H_2O$ does not dissolve in CH_3CN. A common solvent is DMF, in which the R/F system does gel, but the $CuCl_2 \cdot xH_2O$/ epichlorohydrine sol does not gel under *any* conditions. It was noted though that DMF sols of the $CuCl_2 \cdot xH_2O$/epichlorohydrine system become viscous upon heating. Thus, a solution (A) made of 0.565 g (0.0033 mol) of $CuCl_2 \cdot 2H_2O$ (Aldrich), 0.240 mL (0.013 mol) of H_2O, 2.75 mL (0.03 mol) of epichlorohydrine, and 5 mL of DMF was heated at 80 °C for 30 min. Spin coating of the resulting viscous solution on a 5 cm × 5 cm glass slide and drying either under ambient conditions or by using supercritical fluid (SCF) CO_2 in an autoclave gave films that by FE-SEM/EDS (Energy Dispersive Spectroscopy) consist of CuO nanoparticles (Figure 1A). Subsequently, solution A was mixed with a solution B made of 0.337 g (0.00306 mol) of R, 0.455 mL of a 37% w/w commercial solution of F (0.0061 mol), and 5 mL of DMF, and it was left at 80 °C to gel (4 h). Gels were aged in their molds (48 h, 23 °C), washed with DMF and acetone (3 × with each solvent, 8 h each time, using 4 × the volume of the gel for each wash), and dried with SCF CO_2 yielding aerogel monoliths with bulk density $\rho_b = 0.083 \pm 0.009$ g cm^{-3}, skeletal density $\rho_s = 2.65 \pm 0.14$ g cm^{-3}, and a calculated porosity ($= [(1/\rho_b) - (1/\rho_s)]/(1/\rho_b)$) of 98.2 ± 0.3% v/v of empty space. All DMF and acetone wash solutions were combined and analyzed for Cu,[8] showing that only 2.3 mol % of the original metal in the sol was lost during processing. Clearly, the oxide remains trapped in the mesoporous voids of the RF network. Figure 1B shows that the composite aerogels consist of a network of nanoparticles as designed. N_2 adsorption isotherms indicate the presence of mesoporosity (BET surface area $A = 108$ m^2 g^{-1}, average pore size = 11.8 nm by the $4V_T/A$ method; V_T: total pore volume); EDS analysis shows no chlorine and an isotropic distribution of C, O, and Cu (Supporting Information); XRD shows no diffraction pattern and therefore absence of crystallinity. The absence of chlorine and crystallinity from our composites signifies that our inorganic component is distinctly different from the material reported from isopropanol sols ($Cu_2(OH)_3Cl$).[7] (The difference is attributed to the low solubility of $CuCl_2 \cdot 2H_2O$ in that solvent.)

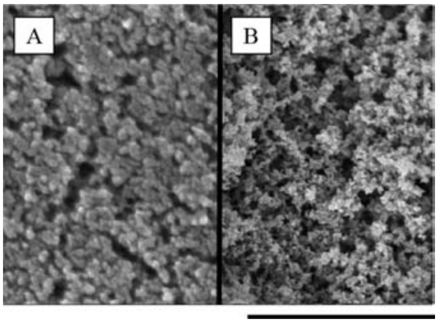

Figure 1. (A) SEM of a CuO xerogel film spin-coated on glass. Scale bar, 500 nm. (B) SEM of a CuO/RF aerogel composite. Scale bar, 5 μm.

By thermogravimetric analysis (TGA) in air, CuO/RF aerogels (Figure 2) give a sharp mass loss at ∼200 °C and a residual mass of 78%, equal to the weight percent of CuO in the composite. Also, considering the early (<100 °C) ∼2% w/w mass loss of adsorbed solvents (H_2O) leads to ∼20% w/w RF. Thus, the mol ratio of the CuO/RF repeat unit in the composite is ∼6.3. Based on the composition of the sol, our CuO/RF composites should contain ∼60% w/w RF. Therefore, ∼67% of resorcinol was lost during processing, presumably due to incomplete gelation.

By TGA under N_2, CuO/RF aerogels give three distinct steps, one below 100 °C, one at ∼200 °C, and one above 500 °C (Figure 2). The mass remaining at 700 °C is 85% of the original. In contrast, TGA of pure RF aerogels under the same conditions gives the initial mass loss of adsorbed solvents at <100 °C and only one additional

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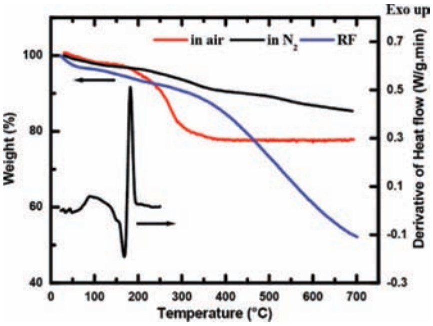

Figure 2. TGA (10 °C min^{-1}) and DSC (5 °C min^{-1}) of CuO/RF composite aerogels under the conditions shown. The TGA trace of a pure RF aerogel prepared by HCl-induced gelation of solution B has also been included for comparison (blue line).

step above 400 °C, yielding at 700 °C a carbon aerogel with a mass of ~50% of the original. However, the mass remaining at 700 °C from the CuO/RF composite is not a superposition of the thermal evolution of the two components. To begin with, the mass loss from CuO/RF at ~200 °C is accompanied by a sharp exotherm in the DSC (Figure 2), indicating a chemical reaction between the two components. Subsequently, different CuO/RF samples were pyrolyzed in a tube furnace under flowing Ar at different temperatures from 200 to 1000 °C. EDS analysis shows that the amount of Cu increases and the amounts of C and O decrease. XRD analysis of the resulting materials (Figure 3) shows that the dominant crystalline phase is cubic metallic Cu even for pyrolysis at as low as 400 °C. A similar smelting reaction has been observed recently in analogous Fe_2O_3/RF composite aerogels at ≥800 °C.[9] At those temperatures, however, the RF framework is first converted to a porous carbon network.[10] The much lower reaction temperature observed in the CuO/RF composites suggests direct oxidation of RF by CuO.

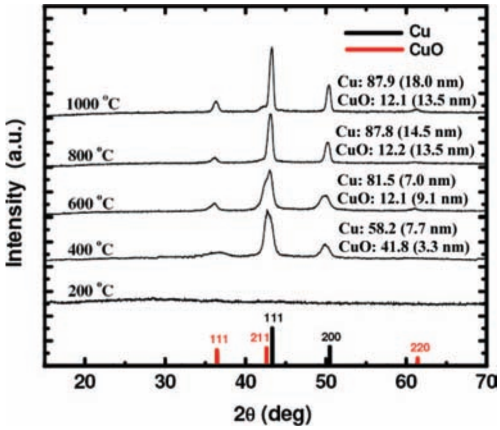

Figure 3. Powder XRD of CuO/RF composite aerogels pyrolyzed in Ar at the temperatures indicated. Insets: Percent weight of the two components; crystallite sizes by peak-width analysis via the Scherrer equation.

The RF framework contains 7−8 carbon atoms per repeat unit (depending on the degree of cross-linking) and thus requires at least 15 mol equiv of CuO for complete oxidation to CO_2 and H_2O. Hence, the substoichiometric mole ratio of CuO to RF (~6.3:1, identified by TGA in air above) precludes complete conversion of RF to gaseous products. Nevertheless, upon ignition with a flame in the air, CuO/RF aerogels sustain combustion (see movie 1) burning rapidly, leaving behind a solid residue of microparticulate CuO (Figure 4D). By comparison, RF aerogel monoliths neither sustain the flame (movie 1) nor burn once inside the flame (movie 2 and Figure 4B). By considering all data together, it is concluded that CuO mediates the oxidation of CuO/RF aerogels ignited in air via the smelting process:

$$\mathrm{RF} + \mathrm{CuO} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{Cu} \qquad (1)$$

$$2\mathrm{Cu} + \mathrm{O_2(air)} \rightarrow 2\mathrm{CuO} \qquad (2)$$

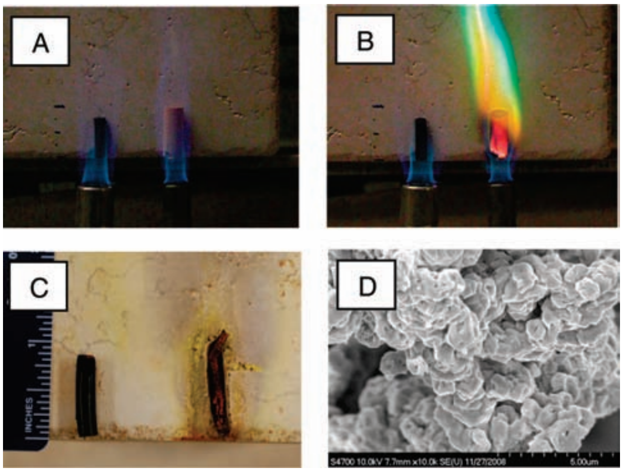

Figure 4. Aerogel monoliths (pure RF, left; CuO/RF, right) glued in vertical position on a ceramic tile. (A) Before ignition (gels behind the flames); (B) 15 s after placing in the flames; (C) after complete combustion (~2 min; Flames were removed 60 s after ignition; Note that only a shadow of the original CuO/RF monolith remains); (D) SEM of the traces of solid residue from the CuO/RF monolith (CuO).

Reportedly, sol−gel RF networks actually *desensitize* energetic materials entrapped in their porous network.[11] In our case, the energetic material is the CuO/RF nanocomposite itself, and even as it stands now it is adequate for pyrotechnics. The catalytic role identified for CuO in the combustion of RF is investigated further in three component mixtures along with an independent oxidizer and RF as fuel. The cogelation of RF and metal oxide networks is a quite general process, and it has been demonstrated in our laboratory with both smeltable (Co_2O_3, NiO, SnO) and nonsmeltable oxides (e.g., Cr_2O_3, HfO_2).

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Supporting Information Available: Titration of $CuCl_2 \cdot xH_2O$, N_2 adsorption isotherms, EDS of as-made CuO/RF aerogels and after ignition in air, XRD experimental. This material is available free of charge via the Internet at http://pubs.acs.org.

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