Porous Semiconducting Gels and Aerogels from Chalcogenide Clusters

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Inorganic porous materials are being developed for use as molecular sieves, ion exchangers, and catalysts, but most are oxides. We show that various sulfide and selenide clusters, when bound to metal ions, yield gels having porous frameworks. These gels are transformed to aerogels after supercritical drying with carbon dioxide. The aerogels have high internal surface area (up to 327 square meters per gram) and broad pore size distribution, depending on the precursors used. The pores of these sulfide and selenide materials preferentially absorb heavy metals. These materials have narrow energy gaps (between 0.2 and 2.0 electron volts) and low densities, and they may be useful in optoelectronics, as photocatalysts, or in the removal of heavy metals from water.

Inorganic porous materials are at the foundation of broad applications such as molecular sieves, ion exchangers, and catalysts (1, 2). Zeolites and aluminosilicate mesoporous materials constitute the vast majority of this class. Aerogels are another kind of porous inorganic amorphous polymer in which nanosized blocks are interconnected to yield high internal surface area, very low densities, and large open pores (3, 4). Although the sol-gel chemistry of oxide-based materials (e.g., SiO2, Al2O3, TiO2) and carbon (5) is well known, successful attempts to apply this approach to non–oxide-based systems are quite rare, especially for chalcogenides. Such systems would be capable of combining the electronic properties of chalcogenide clusters with the unique properties of aerogels.

In this work, we report the synthesis of porous aerogel materials based on chalcogenide clusters (e.g., chalcogen–metal–chalcogen–metal clusters). These materials have been used as adsorbents for heavy metals such as Cu2+, Pb2+, and Cd2+. The porous materials have very high internal surface areas and low densities, and they may be useful in a variety of applications, including adsorption of heavy metals, air purification, and water treatment.

Fig. 4. Quantum state tomography. (A) Real part of the reconstructed density matrix for \( B = 0 \) and \( t_0 = 1.3 \mu s \). About 2200 entanglement events were collected for each of nine measurement settings. (B) For \( B = -0.13 \) G and \( t_0 = 2.8 \mu s \), the atomic superposition state rotates by \( \pi \). The observed data correspond to a \( |\Psi^-\rangle \) Bell state, with fidelity of 82.9(6)%.

References and Notes

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genides with internal porosity. Aerogels based on aggregated simple binary nanocrystals (e.g., CdS, CdSe) and on amorphous GeS$_2$ have been reported (6, 7).

We report on a strategy to create highly porous semiconducting aerogels derived from chalcogenide-based clusters and platinum as the linking metal ion (8). A family of chalcogenide gels was prepared in aqueous solution with anionic [MQ$_4$]$^-$, [M$_2$Q$_6$]$^-$, and [M$_4$Q$_{10}$]$^-$ (M = Ge, Sn; Q = S, Se) building blocks (Fig. 1A) in the presence of platinum (II) salt, according to the following metathesis reactions:

\[
(R_4N)_{4}[M_4Q_{10}]+2K_2PtCl_4 \rightarrow Pt_2[M_4Q_{10}]+4KCl+4R_4NCl \quad (1)
\]

\[
K_4[M_2Q_6]+2K_2PtCl_4 \rightarrow Pt_2[M_2Q_6]+8KCl \quad (2)
\]

\[
A_4[MQ_4]+2K_2PtCl_4 \rightarrow Pt_2[MQ_4]+4KCl+4ACl \quad (3)
\]

where R= methyl, ethyl; M = Ge, Sn; Q = S, Se; and A = Na, K. In these reactions (e.g., Eq. 1), all chloride ligands of [PtCl$_4$]$^-$ can be replaced by the Q terminal atoms of chalcogenido clusters, generating materials with a formula of Pt$_2$[M$_4$Q$_{10}$]. Energy-dispersive spectroscopy (EDS) revealed that two platinum atoms per complex anion are incorporated in almost every case, giving a charge-balanced formula (Table 1). K$^+$ or Cl$^-$ ions, used as counterions in the synthesis, were not detected in the product—a result consistent with complete metathesis. This linking/polymerization reaction produced a continuous, extended Pt/M/Q framework of covalently bonded atoms that encapsulates solvent molecules into their pore system during the process of polymerization and finally makes hydrogels (fig. S1, A to C). Because the gels formed are based on all-chalcogenide species, we term these hydrogels “chalcogels” by analogy to the naming of cyanogels (9).

Table 1. Elemental analysis, colors, and optical energy gaps for the chalcogel series.

<table>
<thead>
<tr>
<th>Chalcogel</th>
<th>Zintl anion</th>
<th>Pt/M/Q ratio$^*$</th>
<th>Empirical formula</th>
<th>Color</th>
<th>Energy gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chalcogel-1</td>
<td>[Ge$<em>4$S$</em>{10}$]$^-$</td>
<td>2.0:4:9.6</td>
<td>Pt$<em>{2.0}$Ge$</em>{4.9}$</td>
<td>Pinkish brown</td>
<td>2.0</td>
</tr>
<tr>
<td>Chalcogel-2</td>
<td>[Ge$<em>4$Se$</em>{10}$]$^-$</td>
<td>2.0:4:8.7</td>
<td>Pt$<em>{2.0}$Ge$</em>{4.8}$</td>
<td>Black</td>
<td>1.3</td>
</tr>
<tr>
<td>Chalcogel-3</td>
<td>[Sn$<em>4$Se$</em>{10}$]$^-$</td>
<td>2.1:4:9.5</td>
<td>Pt$<em>{2.1}$Sn$</em>{4.9}$</td>
<td>Black</td>
<td>1.0</td>
</tr>
<tr>
<td>Chalcogel-4</td>
<td>[Sn$<em>4$Se$</em>{10}$]$^-$</td>
<td>1.4:2:5.7</td>
<td>Pt$<em>{1.4}$Sn$</em>{2.6}$</td>
<td>Black</td>
<td>0.8</td>
</tr>
<tr>
<td>Chalcogel-5</td>
<td>[SnSe$_4$]$^-$</td>
<td>2.0:1:4.0</td>
<td>Pt$<em>{2.0}$Sn$</em>{2.8}$</td>
<td>Black</td>
<td>0.2</td>
</tr>
<tr>
<td>Chalcogel-6</td>
<td>[SnS$_4$]$^-$</td>
<td>1.4:1:4.0</td>
<td>Pt$<em>{1.4}$Sn$</em>{1.8}$</td>
<td>Dark pinkish brown</td>
<td>1.4</td>
</tr>
</tbody>
</table>

$^*$Based on EDS results. Listed values are an average of seven measurements on independently prepared samples.

Transmission electron microscopy (TEM) images of our aerogel samples revealed empty mesopores with no long-range order (Fig. 2, A to C). Indeed, they appear to be morphologically similar to the silica aerogels where particles are connected to each other, making continuous amorphous (2D) networks. The micro- and mesoporosity were confirmed by nitrogen physisorption measurements. The adsorption-desorption isotherms show a type IV adsorption branch with a combination of H1- and H3-type hysteresis loops characteristic of an interconnected mesoporous system (Fig. 3) (11). This indicates that the mesopores have cylindrical and slit-shaped geometries. Pore size distribution plots calculated by the Barrett-Joynes-Halenda method show a narrow distribution with a peak at around 2nm.

Fig. 1. (A) Different building blocks used in chalcogel formation (blue spheres, metal centers; red spheres, chalcogenide atoms). (B and C) Monolithic hydrogels before (B) and after (C) supercritical drying, showing very little volume loss.

Fig. 2. (A and B) TEM images of Chalcogel-1 (A) and Chalcogel-2 (B). Pores between the particles in the meso- and macrophase regime are clear from these pictures, although they are not ordered. (C) TEM image of Chalcogel-2 shows small pores inside the particle. Large macropores are absent here. (D) Wide-angle powder x-ray diffraction data for Chalcogel-1. The amorphous nature of the aerogel and the lack of other crystalline phases are obvious.
Brunauer-Emmett-Teller (BET) surface areas obtained from the aerogels range from 108 to 327 m^2/g, depending on the chalcogenido cluster (Table 2). The surface area of 327 m^2/g obtained from [Ge_4S_{10}]^4− in Chalcogel-2 is the highest of the six chalcogels, followed by 323 m^2/g for [Ge_4S_{10}]^− in Chalcogel-1. The smallest cluster, [SnS_4]^2− in Chalcogel-6, gave the lowest BET surface area value of 117 m^2/g. Given that the formula weights of these chalcogels are high, on a per-mole basis the surface area values are actually very large. The silica equivalence (12) BET surface area of Chalcogel-2 is 1674 m^2/g and that of Chalcogel-3 is 1580 m^2/g (Table 2). Values for silica aerogels range from 100 to 1600 m^2/g and typical values are 600 m^2/g. The bulk density of these chalcogels is very low; for example, Chalcogel-1 showed 0.12 to 0.17 g/cm^3 with a skeletal density of 3.1 g/cm^3.

To probe the local structure of the amorphous aerogels, we used the atomic pair distribution function (PDF) (13) technique, which analyzes both diffuse and Bragg scattering by recovering atom-atom correlations in real space in the form of a radial distribution function. A single correlation occurring at 2.36 Å is evident in the PDF of Chalcogel-1 (Fig. 4A), corresponding to the first-neighbor Ge-S and Pt-S bond distances. A clustering of correlations is evident around 3.52 Å, which corresponds to the second-neighbor Ge−Ge, S−S, and Pt−Ge distances. The PDF of Chalcogel-2 is remarkably similar to that of Chalcogel-1, although it exhibits a shift in correlations to longer interatomic distances r as a result of the larger atomic radius of Sn versus S. Again a single correlation is evident in the PDF of Chalcogel-2 at 2.49 Å (Ge-Se and Pt-Se bond distances), and several appear centered around 3.75 Å. The higher intensity of the first correlation in Chalcogel-2 arises from the larger scattering factor of Se over that of S. Both PDFs show a lack of well-defined features past 6 Å that suggests a lack of long-range translational symmetry. However, a well-defined local structure is evident from the PDF and clearly shows that the adamantane clusters remain intact. The splitting of the correlations (3.52 Å and 3.75 Å) is likely due to subtle distortions, arising from linking of the adamantane clusters, that ultimately disrupt the long-range translational symmetry. The PDF data, together with the complete metathesis chemistry, elemental analysis, and x-ray photoelectron spectroscopy (XPS) (fig. S2), suggest a nonperiodic structure of the type shown in Fig. 4B. Further support for the integrity of the starting clusters in the final aerogels was provided by nuclear magnetic resonance (NMR) (fig. S3), electrospray ionization mass spectroscopy (ESI-MS) (fig. S4), and infrared spectroscopy (fig. S5).
Stabilization of Labile Carbonyl Addition Intermediates by a Synthetic Receptor

Tetsuo Iwasawa, Richard J. Hooley, Julius Rebek Jr.*

Products of unfavorable chemical equilibria are not readily observed because their high energy and increased reactivity result in low concentrations. Biological macromolecules use binding forces to access unfavorable equilibria and stabilize reactive intermediates by isolating them from the medium. In a similar vein, we describe here a synthetic receptor that allows direct observation of labile tetrahedral intermediates: hemiaminals formed in the reaction of an aldehyde carbonyl group with amines. The receptor encapsulates alkyl-substituted primary amines, then orients them toward a covalently tethered aldehyde function. The hemiaminal intermediates appear at high concentration, confined from the bulk solution and observable at ambient temperature by conventional nuclear magnetic resonance spectroscopy.

Chemical reactions often proceed through many intermediate stages between starting materials and products. The reactive intermediates at such stages are generally not observed directly, because their concentrations are vanishingly small, but are treated through steady-state approximations and detected by kinetic or other methods (1, 2). The reaction of carbonyl compounds with nucleophiles invariably involves an addition step that gives an unstable tetrahedral carbon intermediate followed by an elimination step. For example, the reaction of primary amines with aldehydes to give imines (Fig. 1) proceeds through an intermediate hemiaminal (3). The process is catalyzed by acids or bases, and the proton transfers involved generate additional transient, charged intermediates. The hemiaminal is, except in very special cases (4–6), not observed. It is energetically disfavored, because the cost of breaking the carbonyl pi bond and the entropic price of bringing the two reactants together are not compensated by the new covalent bonds formed. Accordingly, the unstable hemiaminal dissociates to starting materials or proceeds to imine with loss of water. We tailored a molecular receptor to favor formation of this intermediate and found that the hemiaminal was stabilized for minutes to hours, long

When the carbonyl group in a donor aldehyde is protected by S-alkylation, the stable hemiaminal dissociates to starting material and product. The receptor allows the reaction to proceed without significant loss of reactants, trapping the unstable transient, charged hemiaminal intermediate. The receptor contains a tethered aldehyde group and primary amines. The receptor and amines are covalently linked through an adjacent aldehyde function. The dication 1 serves as a reservoir of primary amines, which are delivered to the receptor in the form of the amine salt 2. The amine is released at the site of reaction as shown in Figure 1. The amine dissociates to neutral amines 3, which are immediately captured by the receptor 1.

References and Notes

8. See supporting material on Science Online.
12. The molecular formulas were normalized to two sulfur or two selenium atoms to compare well with SiO2 (e.g., Pt2Ge2S4 is converted to Pt0.4Ge0.8S2 having formula weight of 230.27 for equivalent surface area calculation.
14. The capacity of Chalcogel-1 to remove Hg2+ from aqueous solution is extremely high (645 ng/ml or 3.21 nmol). This tremendous affinity is also reflected in the calculated distribution coefficient Kd (defined as the amount of adsorbed metal (in micrograms) on 1 g of adsorbing material divided by the metal concentration (in milligrams per milliliter) remaining in the treated water (d)). Kd values varied from 0.92 x 10^6 (at 92 ppm Hg2+) to 1.61 x 10^4 (at 645 ppm Hg2+).
16. The specific binding of chalcogels with heavy metals was demonstrated by adding 5 ml each of 89 ppm Zn2+ and 92 ppm Hg2+ solutions to 10 mg Chalcogel-2 and stirring for 24 hours at room temperature. The final solution contained 52.8 ppm Zn2+ and 0.1 ppm Hg2+.
17. The BET surface area remained high after storing the chalcogels for longer times. For example, the surface area of Chalcogel-2 decreased from 327 to 303 m2/g after 5 weeks and to 265 m2/g after 3 months.
23. We thank T. J. Pinsavalia and D. Holmes for use of the nitrogen sorption measurement and NMR handling, respectively. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

Supporting Online Material

www.sciencemag.org/cgi/content/full/317/5837/490/DC1

Materials and Methods

Fig. S1 to S6

References

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