Inorganic Paper

Highly Flexible and Nonflammable Inorganic Hydroxyapatite Paper

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Abstract: A highly flexible and nonflammable inorganic hydroxyapatite (HAP) paper made from HAP ultralong nanowires is reported. The paper can be used for printing and writing and is promising for the permanent and safe storage of information, such as archives and important documents. The HAP paper is also an excellent and recyclable adsorbent for organic pollutants.

Paper is a versatile material with many uses. The most common use is for printing and writing upon, and it is also widely used as a packaging material. Traditional paper is typically produced from plant cellulose pulp derived from wood or grass along with some additives and bleaching agents. To meet the requirements for high-performance printing, paper needs an inorganic coating. By using modern technology, disposable paper has become a cheap commodity, leading to a high level of consumption and waste.[4, 5] Currently, the amount of paper and related products is enormous, and its environmental impact is also very significant. The consumption of paper has greatly increased in the last few decades. According to a report from the Worldwatch Institute, global paper use has grown more than six-fold over the latter half of 20th century, and one fifth of the paper harvested in the world ends up in paper. In addition, paper made from the mechanical pulp contains a significant amount of lignin, a major component of wood, which forms yellow materials in the presence of light and oxygen, that is why newsprint and other mechanical papers yellow with age. Traditional paper is also at risk of acid decay because cellulose itself forms formic, acetic, lactic, and oxalic acids. Another major weakness of traditional cellulose paper is its flammability; books and documents are completely ruined by fire.

Effort has been made to explore new kinds of paper to tackle the issues facing traditional paper. For example, organic composite sheet materials made from blends of recycled polystyrene and polyethylene have been reported; however, these sheets were generally inferior to cellulose paper, and they may cause secondary pollution to the environment.[7] Producing new kinds of paper from inorganic materials is highly desirable to solve these issues, but development has been hindered by their drawbacks, especially poor flexibility. As a result, paper-like materials made from pure inorganic components have rarely been reported.[8] Ideally, materials for producing paper should be white in color, nontoxic, highly flexible, and easy to make into thin membranes; however, few inorganic materials can meet these requirements. To the best of our knowledge, highly flexible and nonflammable inorganic hydroxyapatite paper with white color has not been reported until now.

Hydroxyapatite \( (\text{Ca}_{10}\text{(OH)}_{2}\text{(PO}_{4})_{6}; \text{HAP}) \), a well-known member of the calcium phosphate family with high biocompatibility and essentially no toxicity, is the major inorganic component of bone and tooth in the vertebrate body.[9, 10] HAP is also abundant in oceanic water. In past decades, various HAP-based materials have been synthesized and explored for applications in biomedical fields.[12–22] However, HAP materials usually exhibit very poor flexibility. Some effort has been made to improve the flexibility of HAP materials.[14, 23] For example, a HAP-based transparent membrane was prepared by pulsed laser deposition by using the NaCl crystal substrate; however, thermal heating of the substrate was generally needed for the deposition of high-quality HAP thin films, and the HAP film became cracked on the NaCl crystal substrate after heating. Currently, the synthesis of highly flexible ultralong HAP nanowires remains a big challenge because HAP usually forms short nanorods or nanoneedles.

Herein, we report a new method for the fabrication of highly flexible and nonflammable inorganic HAP paper by using ultralong HAP nanowires. HAP nanowires with high aspect ratios are synthesized by using calcium oleate as the precursor, and their hydrophilicity/hydrophobicity can be readily tuned. The as-prepared HAP paper is highly flexible and nonflammable, and it can be bent and rolled without visible damage. The as-prepared HAP paper can be used as printing or writing paper with excellent nonflammability and high thermal stability, properties that are promising for the permanent and safe storage of information, such as for archives and important documents. In addition, HAP paper has a good performance as an adsorbent for organic pollutants.

Ultralong HAP nanowires were synthesized by using the as-prepared calcium oleate, along with its mother reaction solution, as the precursor and \( \text{NaH}_2\text{PO}_4\cdot2\text{H}_2\text{O} \) in an aqueous solution, all of which were treated by the solvothermal method. The calcium oleate precursor was synthesized by using \( \text{CaCl}_2 \), NaOH, and oleic acid in mixed solvents of ethanol and water.
at room temperature. For comparison, the amounts of reagents and solvothermal reaction times were varied. The samples synthesized with different amounts of NaH₂PO₄·2H₂O (labeled as x gram, for example, 0.120 g) and different solvothermal reaction times (labeled as y hours, for example, 5 h), while the other experimental conditions were kept the same, were labeled as “H-x g–y h” (e. g., H-0.120 g–5 h). The experimental details are described in the Experimental Section and in the Supporting Information. For the fabrication of HAP paper by suction filtration and the adsorption of organic solvents with HAP paper, refer to Figures S1 and S2 in the Supporting Information.

The X-ray diffraction (XRD) pattern in Figure 1 e indicates that the precursor is a single phase of calcium oleate. The XRD patterns in Figure 1 e and Figure S3 (see the Supporting Information) show that the product obtained from the solvothermal treatment of the calcium oleate precursor is single-phase hydroxyapatite. The scanning electron microscopy (SEM) micrographs and transmission electron microscopy (TEM) micrograph in Figure 1 a–c and Figures S4 and S5 (see the Supporting Information) show that the product obtained from the solvothermal treatment of the precursor consists of HAP ultralong nanowires with a single-crystalline structure (inset of Figure 1 c). The as-prepared HAP nanowires have lengths of tens of micrometers and very high aspect ratios (>100). We have found that the as-prepared ultralong HAP nanowires are highly flexible and can be bent and rolled without being broken (arrows in Figure 1). When a dispersion of ultralong HAP nanowires in ethanol is stirred with a glass rod, the HAP nanowires form long fibers (28 mm, Figure 1 d) that exhibit very high flexibility. The high flexibility of the ultralong HAP nanowires may be mainly attributed to their high aspect ratios. Ultralong HAP nanowires with high aspect ratios have been previously reported.[14, 24] However, it is difficult to prepare ultralong HAP nanowires with aspect ratios larger than 100 because HAP usually forms short nanorods or nanoneedles. These highly flexible HAP nanowires are expected to be a promising raw material for the preparation of flexible HAP products.

The synthesis of HAP nanostructured materials with tunable hydrophilicity and hydrophobicity is of great importance for their applications. Generally, hydrophilic HAP materials are preferred for biomedical applications. The synthesis of hydrophobic HAP nanostructured materials has been rarely reported. Kandori et al.[25] reported the preparation and characterization of hydrophobic calcium hydroxyapatite particles with grafted oleylphosphate groups. We have found that the hydrophilicity/hydrophobicity of the HAP product can be readily adjusted by varying experimental parameters, and both hydrophilic and hydrophobic HAP nanowires can be obtained. The contact angles of the tablet samples prepared by pressing the HAP powders were investigated (Figure 1 f–j). The HAP sample synthesized by using 0.0926 g of NaH₂PO₄·2H₂O with a solvothermal reaction time of 5 h is highly hydrophobic, generating a contact angle of ≈137° (Figure 1 f), whereas the contact angle decreases to 108° when the solvothermal reaction time is prolonged to 23 h (Figure 1 g). When the amount of NaH₂PO₄·2H₂O is increased to 0.120 g, the contact angles of the HAP samples are 95° and 20° for solvothermal reaction times of 5 and 9 h, respectively (Figure 1 h and i), and a HAP sample with excellent hydrophilicity is obtained for a solvothermal reaction time of 23 h (Figure 1 j). The difference in hydrophilicity/hydrophobicity may be attributed to the adsorption of oleic acid molecules or oleate groups with long hydrophobic hydrocarbon chains on the surface of the HAP nanowires. This conclusion is supported by Fourier transform infrared (FTIR) spectroscopy (Figure S6) and thermogravimetric (TG) analysis (Figure S7, see the Supporting Information).

We have also found that the ultralong HAP nanowires can be used as a raw material for fabricating highly flexible and nonflammable inorganic paper by a simple process of suction filtration. The thickness and area of the HAP paper can be easily tuned by varying the amount of HAP nanowires. Figure 2 a shows a square of HAP paper with a length of 108 mm. The HAP paper has high flexibility, which means it can be laid flat (Figure 2 b), bent (Figure 2 c), or rolled (Figure 2 d) without visible damage. HAP papers fabricated under other experimental conditions also have high flexibilities (Figure S8 in the Supporting Information). In contrast, short HAP nanorods obtained

![Figure 1](image-url)
Paper is heated in an electric oven at a high temperature. Furthermore, when the HAP paper is heated with a spirit lamp for 5 min, no visible damage is observed although it has been served even after being heated with a spirit lamp for 5 min. (f) The HAP paper with the characters remains well preserved after heating (h). The characters on the commercial printing paper and HAP paper are written by using a dispersion of graphite powder in ethanol.

in the absence of oleic acid cannot form the highly flexible HAP paper, indicating the important role of the highly flexible ultralong HAP nanowires in the formation of the highly flexible HAP paper. Such highly flexible HAP paper can be used to prepare HAP products with unique shapes. For example, we have successfully prepared a hollow cylindrical HAP scaffold by simply heating a rolled HAP paper at 1000 °C for 4 h (Figure 2 e) without using any template.

The as-prepared HAP paper has an excellent performance in printing and writing (Figure 2 f); English words and Chinese characters with different colors have been printed on the HAP paper by using a commercial ink-jet printer. More importantly, the HAP paper has a high flexibility, excellent nonflammability, and high thermal stability, all of which are great merits compared with traditional cellulose paper. On heated with a spirit lamp, commercial printing paper catches on fire imme-

Ni,SiO3 as an inorganic binder. Figure 2 g shows that a piece of HAP paper made from ultralong HAP nanowires and Na2SiO3 as an inorganic binder is able to withstand the weight of a steel autoclave (~450 g) without breaking.

Figure 3. Illustration of the excellent nonflammability and resistance to high temperature of the highly flexible inorganic HAP paper. (a–c) Commercial printing paper is heated by a spirit lamp: (a) before heating; (b) flaming paper; (c) the ash after combustion in seconds. (d–f) The as-prepared HAP paper is heated by a spirit lamp: (d) before heating; (e) the HAP paper is nonflammable in fire; (f) the HAP paper with the characters remains well preserved after 5 min in fire. (g–i) The as-prepared HAP paper is heated in an electric oven at 450 °C for 1 h: (g) before heating, (h, i) after heating. The HAP paper with the characters remains well preserved after heating (h). The characters on the commercial printing paper and HAP paper are written by using a dispersion of graphite powder in ethanol.

In recent years, the applications of hydrophobic products for treating spilled crude oil, petroleum products, and toxic organic solvents, all of which are great threats to the environment, have been increasingly investigated. But the practical applications of these materials have been hindered by drawbacks such as low adsorption capacity, poor recyclability, and toxicity. New materials for adsorbents that can effectively and safely tackle these problems are highly desirable. To the best of our knowledge, the widely used HAP biomaterials, which have high biocompatibility and essentially no toxicity, have been rarely reported for treating organic pollutants. In this work, the highly flexible and nonflammable inorganic HAP paper is used as an excellent adsorbent for organic pollutants; it exhibits high adsorption capacities for various organic pollutants (Figure 4a, Figure S9 in the Supporting Information), for example, the HAP paper of H-0.120 g–5 h has a high adsorption capacity of 7.3 g g⁻¹ for chloroform. Other samples of the HAP paper obtained under different conditions also have high adsorption capacities for organic solvents (Figure S9). Thus, the highly flexible and nonflammable inorganic HAP paper is promising for applications as an adsorbent for treating organic pollutants.
The recovery of pollutants and regeneration of used adsorbents are usually required for reducing resource consumption and economic cost. The highly flexible and nonflammable inorganic HAP paper can be easily separated from organic solvents with tweezers and regenerated by heating in a distillation unit (Figures S1 and S2 in the Supporting Information). The adsorbed organic solvents can be completely removed from the HAP paper for recycling. No visible damage to the HAP paper is observed in the regenerated HAP paper after such cycles of solvent removal. The regenerated HAP paper can be reused for the adsorption of organic pollutants and has similar adsorption capacities compared with the freshly prepared HAP paper for at least five cycles (Figure 4b, Figure S9). For most organic polymer adsorbents, the solvents and adsorbents cannot be recovered by heating owing to their poor thermal stability, leaving only the choice of chemical extraction, which can rarely recover the organic solvents completely and leads to high costs. In addition, polymeric adsorbents may cause pollution to the environment. By contrast, the HAP paper, as the main inorganic component of bone and tooth and as a widely used biomaterial, is highly stable to heat and fire, and not toxic to the environment, and shows better recyclability. According to the recyclable HAP paper is promising for the application in organic pollutant treatment.

The highly flexible and nonflammable inorganic HAP paper has also been successfully used as a filler to make a filtration column for the treatment of organic pollutants in water. A mixture of toluene (dyed by oil red O) and water was used for the investigation. As illustrated in Figure 4c, when the mixture of toluene and water is poured into the filtration column, water goes through the HAP paper filler, whereas toluene is adsorbed completely by the filler. By using this simple procedure, toluene can be completely separated from water and the polluted water is effectively purified.

In summary, a new strategy has been demonstrated for fabricating a prototype of a new kind of highly flexible and nonflammable inorganic HAP paper by using ultralong HAP nanowires. HAP nanowires with high aspect ratios are synthesized by the solvothermal method using calcium oleate as the precursor, and the hydrophilicity/hydrophobicity of the HAP nanowires can be readily tuned. The as-prepared HAP paper is highly flexible and nonflammable, and it can be bent and rolled without visible damage. The prototype of the HAP paper showed excellent performance in printing and writing, a fact that makes it promising for applications for the permanent and safe storage of information, such as archives and important documents. This work provides a promising perspective for the fabrication and application of highly flexible and nonflammable HAP paper as a possible substitute for the traditional cellulose paper, which has caused serious resource and environmental problems. In addition, HAP paper has also shown excellent performance as an adsorbent for organic pollutants.

**Experimental Section**

Calcium oleate as the precursor was synthesized by separately adding aqueous solutions of CaCl₂ (10 mL, 0.110 g) and NaOH (10 mL, 0.500 g) dropwise into a mixture of ethanol (6.000 g) and oleic acid (6.000 g) under magnetic stirring. Ultralong HAP nanowires were synthesized by using the as-prepared calcium oleate as the precursor for the solvothermal method. In a typical procedure, calcium oleate as the precursor, together with its mother reaction solution, was used for the subsequent synthesis of ultralong HAP nanowires. Under continuing stirring, 5 mL of NaH₂PO₄·2H₂O aqueous solution was added into the precursor solution dropwise. The resulting mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for different times (5–23 h).

The HAP paper made from ultralong HAP nanowires was fabricated through a simple process of suction filtration. The ultralong HAP nanowires were dispersed in ethanol and the suspension was poured onto filter paper in a Büchner funnel. Under suction generated by a vacuum pump, the white HAP paper was formed on the filter paper. The HAP paper was then washed with ethanol and deionized water several times, dried at 60 °C, and separated from the filter paper with tweezers.

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