



Co₂P nanoparticles for microwave absorption

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ABSTRACT

Microwave absorbing materials have critical roles in homeland and information security. In this study, we report for the first time Co₂P nanoparticles as promising microwave absorbing materials. A large reflection loss peak of −39.3 dB, correlating to nearly 99.99% absorption efficiency, is obtained with a 1.10-mm-thick Co₂P nanoparticle absorber. Important relationships are revealed between the reflection loss peak value (RL_{peak}), the reflection loss or absorption peak frequency (f_{peak}), and the reflection loss or absorption peak width (Δf₁₀), with respect to the overall thickness of the Co₂P nanoparticle absorber. The three important parameters that determine the microwave absorption can be approximately expressed with the following general formula: $P = A + B/d^n$, where P is RL_{peak}, f_{peak}, or Δf₁₀; d is the thickness of the Co₂P nanoparticle absorber A (A is zero when P is f_{peak} or Δf₁₀); and B and n are the fitting constants. A non-zero permeability of the Co₂P nanoparticles slows the shift of f_{peak} to a lower value and decreases the narrowing of Δf₁₀ as d increases, while RL_{peak} decreases in a wide thickness range. Because of this, the overall microwave absorbing performance can be well tuned with the thickness of the Co₂P absorber, making Co₂P nanoparticles as strong candidates for microwave absorption.

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1. Introduction

Microwave absorbing materials (MAMs) fulfill many of the important roles in optics, electronics, wireless communications, anti-radar detection systems, etc. [1–3] For example, MAMs have been used as coating materials to reduce the electromagnetic interference between electrical components and circuits in many modern electronics and to reduce the radar signature of various military machines, such as aircraft, ships, and tanks. Thus far, various materials and composites have been investigated for microwave absorption, such as graphite [4], graphene [5–7], carbon nanotubes (CNTs) [8–11], carbon fiber [12–14], conducting polymers [15–18], Fe₂O₃ [19–21], Fe₃O₄ [22–25], MnO₂ [26–29], ZnO [30–32], SiC [33–35], SiCN [36], BaFe₁₂O₁₉ [37–39], BaTiO₃ [39], and SrFe₁₂O₁₉ [40,41]. For a majority of the listed materials,

dielectric and magnetic losses are believed to be the main mechanisms of action for their individual affinities for microwave absorption. For example, in the study of Zhao et al. on the microwave absorbing properties, complex permittivity, and complex permeability of epoxy composites containing Ni-coated and Ag nanowire-filled CNTs, the microwave absorption enhancement of Ni-coated CNTs/epoxy composites resulted from coupled dielectric and magnetic losses, and the microwave absorption of Ag nanowire-filled CNTs/epoxy composites was mainly attributed to the dielectric loss, rather than magnetic loss [3]. In the study by Zou et al., the microwave absorbing properties of activated carbon fiber composites were found to depend largely on the carbon fiber content in the composite [12]. Chen et al. reported that broadband, high-performance microwave absorption can be obtained with light-weight, compressible, graphene foam [5]. Olmedo et al. demonstrated that conducting polymers such as polypyrrole, polyaniline, and poly(3-octylthiophene) can possess a high affinity for microwave absorption [15]. Wang et al. found that a suitable amount of Fe₂O₃ nanoparticles embedded in polyaniline enhanced the microwave absorption properties of the oxide material, because of the simultaneous adjusting of dielectric loss and magnetic loss

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[19]. Zhou et al. demonstrated that hollow, urchin-like MnO_2 nanostructures had shape-dependent microwave absorption properties and that the tetragonal nanorod clusters had better performance because of the proper electromagnetic impedance matching [29]. Zhao et al. showed that porous, hollow ZnO prepared by CO_2 soft-template displayed remarkable microwave absorption performance [30]. Li et al. demonstrated that porous SiC fabricated by the pyrolysis of a polycarbosilane precursor had some interesting microwave absorption properties [34]. Yang et al. found that the BaTiO_3 /polyaniline and $\text{BaFe}_{12}\text{O}_{19}$ /polyaniline composites had good compatible dielectric and magnetic properties for broadband microwave absorbing properties [39]. These progresses are just some of the many examples that demonstrate the recent reviving research activities in this field.

Distinct from the previously reported carbonaceous and ferrite materials, we recently demonstrated that by changing the dielectric properties of TiO_2 [42–45], ZnO [45], and BaTiO_3 [46] nanoparticles, through the perturbation of their crystalline structure by hydrogenation treatment, the microwave absorption performances of these materials can be largely enhanced. Gao et al. also found that the microwave dielectric properties of TiO_2 nanoparticles can be largely altered by introducing partial crystalline phases in these nanoparticles [47]. However, we noticed that great strategies have been demonstrated in fabricating various nanoparticles [48]. These findings have provided a large flexibility for choosing materials that are optimal for certain specific microwave absorption applications. As such, it is highly desirable to discover new material candidates for microwave absorption, as different materials are characterized by unique advantages and disadvantages.

In this study, we report for the first time Co_2P nanoparticles as a promising microwave absorbing material. The Co_2P nanoparticles were obtained by a facile thermal phosphorization process. A large reflection loss of -39.3 dB, with nearly 99.99% absorption efficiency, was obtained with a 1.10-mm Co_2P nanoparticle absorber. The relationships were investigated between the microwave absorption performance and the thickness of the Co_2P nanoparticle absorber. Specifically, the thickness (d) of the absorber largely affected the reflection loss peak value (RL_{peak}), the reflection loss or absorption peak frequency (f_{peak}), and the reflection loss or absorption peak width (Δf_{10}). In addition, the influence of permeability on the microwave absorption performance was also investigated. The microwave absorbing performance (RL_{peak} , f_{peak} , and Δf_{10}) could be well tuned by varying the thickness of the Co_2P absorber, independent of the permeability properties of the Co_2P nanoparticles.

2. Material and methods

$\text{Co}(\text{OH})_2$ and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ powders were obtained from Sigma-Aldrich and used as received. The Co_2P nanoparticles were obtained by a thermal phosphorization process following our previous work, where Co_2P nanoparticles were explored as a promising catalyst for electrochemical hydrogen production [49]. Briefly, suitable amounts of $\text{Co}(\text{OH})_2$ and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ were grinded and heated under argon atmosphere at 350°C for 3 h at 1 atm, followed by a thorough washing in HCl and a drying process at 100°C overnight. Co_2P nanoparticles were believed to form from the phosphorization reaction at an elevated temperature between the $\text{Co}(\text{OH})_2$ and PH_3 gas produced *in situ* by the thermal decomposition of the precursor NaH_2PO_2 . This high-temperature reaction allows the formation of highly crystalline Co_2P nanoparticles. Pure Co_2P phase was obtained by adjusting the molar ratio of $\text{Co}(\text{OH})_2$ to $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ and the reaction temperature [49].

The crystal structure of the formed Co_2P nanoparticles was examined using a Rigaku Miniflex X-ray diffractometer (XRD) with

a Cu $K\alpha$ ($\lambda = 0.15418$ nm) radiation source. Suitable amounts of Co_2P nanoparticles were pasted carefully into a thin layer on an amorphous silicon substrate for the XRD measurement. The morphologies and crystallinity were probed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). A few milligrams of Co_2P nanoparticles were first dispersed in ethanol under sonication for 15 min, then a few drops of the dispersion were put on a holey carbon TEM grid, and finally dried overnight at room temperature for the TEM and HRTEM measurements, which were conducted on an FEI Tecnai F20 STEM at an electron accelerating voltage of 200 kV. The surface chemical properties and valence states were studied by X-ray photoelectron spectroscopy (XPS) collected on a Kratos Axis 165 X-ray photoelectron spectrometer with an Al/Mg dual-anode X-ray source, using a photon beam of 1486.6 eV. A small amount of Co_2P nanoparticles were pressed into a thin layer on a conductive carbon tape on an XPS sample holder for the XPS measurements, which were conducted at room temperature. All the XPS spectra were calibrated with the C 1s peak from the carbon tape to 284.6 eV. The complex permittivity and permeability were measured in the frequency range of 1.0–18.0 GHz using an HP8722ES network analyzer with small ring-shaped samples containing 60 wt% Co_2P nanoparticles dispersed in paraffin wax, which was cast into a ring mold with a thickness of 1.0–4.0 mm, an inner diameter of 3.0 mm, and an outer diameter of 7 mm. The thickness of the pellet was carefully controlled by polishing after the pellet was pressed. The measurements were performed at room temperature.

3. Results and discussion

Fig. 1A shows the XRD patterns for the Co_2P nanoparticles with the Co_2P standard (JCPDF no 32-0306). The well-matched diffraction patterns between the prepared Co_2P nanoparticles (curve (a)) and the standard (curve (b)) indicate the successful formation of Co_2P phase. The sharp diffraction peaks in the pattern also suggest that the Co_2P nanoparticles were highly crystallized. The average crystalline size was calculated using the Scherrer formula: $\tau = (K\lambda)/(\beta \cos\theta)$, where τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size, K is the shape factor with a typical value of 0.9, λ is the X-ray wavelength, β is the line broadening full width at half maximum peak height in radians, and θ is the Bragg angle [42–45]. The average crystalline size of the Co_2P nanoparticles was about 25.6 nm using the diffraction (121) and (211) peaks at 40.73° and 43.3° , respectively. Fig. 1B displays the XPS survey spectrum of the Co_2P nanoparticles. Only Co, P, C, and O signals were observed. The Co and P signals were from the Co_2P nanoparticles, while the C and O signals were from the atmospheric carbon deposition and the adsorbed water molecules on the surface of the Co_2P nanoparticles, respectively. All the XPS spectra were calibrated from the C 1s peak mapped to 284.6 eV. The P 2p core-level XPS spectrum of the Co_2P nanoparticles is plotted in Fig. 1C. The strong peaks located at 128.1 and 132.1 eV correspond to the P $2p_{3/2}$ and $2p_{1/2}$ of P^{3-} ions in the Co_xP nanoparticles, respectively. In the Co 2p core-level spectrum shown in Fig. 1D, the two peaks at 778.1 and 781.0 eV were from the $2p_{3/2}$ of the Co^+ and Co^{2+} ions in the Co_xP nanoparticles, respectively; the two peaks at 792.9 and 797.3 eV were from the Co $2p_{1/2}$ of Co^+ and Co^{2+} ions in the Co_xP nanoparticles; and the two weak bands at 785.8 and 802.7 eV are the Co $2p_{3/2}$ and $2p_{1/2}$ satellite signals, respectively. The TEM image in Fig. 1E shows that the Co_2P nanoparticles were between 20 and 35 nm in diameter. The HRTEM image in Fig. 1F clearly demonstrates the lattice fringes, indicating the high crystallinity of the Co_2P nanoparticles. The lattice spacing was about 0.544 nm, corresponding to the (111) plane of the Co_2P nanoparticles.

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