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# Graphitic carbon nitride nanosheets for microwave absorption

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ABSTRACT

In this study, we have demonstrated for the first time that the graphitic carbon nitride (g-$C_3N_4$) nanosheets can possess interesting microwave absorption performance. A large reflection loss (RL) value of −36.1 dB has been demonstrated, corresponding to absorption efficiency over 99.9%. Meanwhile, we have also elucidated the independent contributions of the permittivity and permeability to the microwave absorption. Without the contribution of the electrical or magnetic relaxations, the microwave absorption efficiency decreases. Specifically, the microwave absorption performance decreases much faster without the contribution of the magnetic relaxation than without the contribution of the electrical relaxation. Therefore, the magnetic relaxation in g-$C_3N_4$ nanosheets has a large role in their microwave absorption. The origins of those relaxations can be traced back to the dipole rotation and magnetic domain resonance inside the materials. In addition, we have also proposed a macroscopic interference model for the microwave absorption behavior of the g-$C_3N_4$ nanosheets, so that the frequency to reach maximum RL can be precisely predicted given the thickness of the g-$C_3N_4$ nanosheet absorber.



## Introduction

Microwave absorbing materials have widely studied for many applications such as wireless communications and antiradar detection [1–3]. For example, they are used to reduce the electromagnetic interference in many electronics and to reduce the radar signature of aircraft, ships, and tanks. So far, various materials and composites have been investigated, such as graphite [4], graphene [2,5], carbon nanotubes (CNTs) [6,7], carbon fiber [8], conducting polymers [9,10], $Fe_2O_3$ [11], $Fe_3O_4$ [12], $MnO_2$ [13], ZnO [14,15], $TiO_2$ [3,16,17], $BaFe_{12}O_{19}$ [18], $BaTiO_3$ [19,20], $SrFe_{12}O_{19}$ [21], SiC [22], SiCN [23], $Co_2P$ [24], FeP [25], etc. The main mechanisms for microwave absorption are believed to be from the dielectric and magnetic losses inside the materials. For example, the broadband, high-performance microwave absorption in light-weighted, compressible graphene foam has been attributed to the polarization relaxation of defects or π-electron and interfacial polarization between graphene and other materials [2]. The microwave absorption enhancement of Ni-coated CNTs/epoxy composites is assigned to the dielectric and magnetic losses, while the microwave absorption of Ag nanowire-filled CNTs/epoxy composites is due to the dielectric loss rather than magnetic loss [26]. The microwave absorption of conducting polymers such as polypyrrole, polyaniline, and poly(3-octylthiophene) are caused by the dielectric relaxation in the materials and the interfaces [9]. The enhanced microwave absorption properties of polyaniline with the addition of a suitable amount $Fe_2O_3$ nanoparticles are accredited to the simultaneous adjusting of dielectric loss and magnetic loss [27]. The shape-dependent microwave absorption properties of $MnO_2$ with hollow urchin-like nanostructures and the tetragonal nanorod clusters are ascribed to the proper electromagnetic impedance matching [13]. Similar conclusion is drawn in microwave absorption of porous hollow ZnO as well [28]. On the other hand, enhanced microwave absorption performances of hydrogenated $TiO_2$ [1,3,16,17], ZnO [15], and $BaTiO_3$ [20] nanoparticles have been proposed to be from the perturbation of the crystalline structure to introduce partially crystalline phases in changing the dielectric properties. The excellent microwave absorption performance of

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$Co_2P$ and FeP nanoparticles has been suggested due to the good coupling between the dielectric and magnetic relaxations in the asymmetric polar lattice and the possible magnetic $Co^{2+}$ and $Co^{+}$ domains in the nanoparticles [24,25]. The microwave absorption in SiC nanoparticles [29] and porous SiCN ceramics [23] has been credited to the dipole relaxation in vacancies and interfaces. Despite of these progresses and the general explanation of the microwave absorption with the dipole rotation and magnetic resonance mechanisms, there lacks of a general model to explain the phenomena that have been observed in almost all the materials in that the frequency of the microwave absorption varies with the thickness of the absorber which is somehow different from what we normally see in optical absorption, for example, ultraviolet–visible (UV–vis) light absorption, where the absorbance increases but the peak's frequency does not change with the concentration or the length of the absorber. Meanwhile, although dipole rotations and magnetic domain resonance are commonly invoked to explain the microwave absorption performance, however, their roles have not yet been explicitly revealed.

In this study, we report for the first time the microwave absorption properties of g-$C_3N_4$ nanosheets which have been recently widely studied as attractive photocatalysts [30–42]. A large reflection loss (RL) value of −36.1 dB is obtained, with an over 99.9% absorption efficiency. The peak frequency ($f_{peak}$) can be precisely predicted given the thickness (d) of the absorber. The microwave absorption performance are analyzed in terms of the RL $f_{peak}$, reflection loss peak value ($RL_{peak}$), and the critical RL peak width ($\Delta f_{10}$), and their relationships with the thickness of the absorber (d). Here, the RL of −10 dB is used as a 'critical value', as in it indicates a 90% threshold for the incident microwave electromagnetic field to be effectively unreflected for signal detection. $\Delta f_{10}$ means the frequency region within which the RL is more negative than −10 dB. Apparently, it is the effective microwave shielding frequency range. The contributions of the permittivity and permeability to microwave absorption performance are evaluated. Specifically, the microwave absorption efficiency decreases much faster without the contribution of the magnetic relaxation than without the contribution of the electrical relaxation. These effects can be traced back to the dipole rotation and magnetic domain resonance inside the g-$C_3N_4$ nanosheets that induce the permittivity and permeability properties. We have also proposed a macroscopic interference model to explain the microwave absorption behavior of the g-$C_3N_4$ nanosheets with the change of the thickness of the absorber.

## Materials and methods

The g-$C_3N_4$ nanosheets were prepared by thermal condensation of melamine at elevated temperatures. Melamine was purchased from ACROS ORGANICS. In a typical synthesis, 10.0 g of melamine was heated at 550°C for 4 h in air in a small crucible with cap on. After it cooled down to room temperature, it was grinded into fine powder to get g-$C_3N_4$ nanosheets. The crystal structure of the g-$C_3N_4$ nanosheets was examined on a Rigaku Miniflex X-ray diffractometer (XRD) with a Cu Kα (λ = 0.15418 nm) radiation source. A suitable amount of the sample was pasted carefully into a thin layer on an amorphous silicon substrate for the XRD measurement. The UV–vis absorption spectrum was collected with an Agilent Cary 60 UV–Vis spectrometer with a fiber optical reflectance unit using the diffusive reflectance method. MgO power was used as the reference material. The Fourier transform infrared (FTIR) spectrum was collected on a Thermo-Nicolet iS10 FTIR spectrometer equipped with an attenuated total reflectance (ATR) unit where the g-$C_3N_4$ nanosheets were pressed onto the ZnSe crystal of the ATR unit. The Raman spectrum was collected on an EZRaman-N benchtop Raman spectrometer with the excitation wavelength of 785 nm. The spectrum range was from 100 $cm^{-1}$ to 3100 $cm^{-1}$. The spectrum collection time was 4 s and was averaged over three measurements to improve the signal-to-noise ratio. The transmission electron microscopy (TEM) measurements were performed on a FEI Tecnai F200 TEM instrument with an electron accelerating voltage of 200 kV. A few drops of g-$C_3N_4$ nanosheets dispersed in water were dropped onto a thin holey carbon film, and dried overnight before TEM measurement. The surface chemical bonding and valence band information of the samples was obtained with X-ray photoelectron spectroscopy (XPS) on a PHI 5400 XPS system equipped with a conventional (non-monochromatic) Al anode X-ray source with $K_\alpha$ radiation. Small amount of the g-$C_3N_4$ nanosheets were pressed onto conductive carbon tape for XPS measurements. The binding energies from the samples were calibrated, with respect to the C 1s peak, from the carbon tape at 284.6 eV. The scanning electron microscopy (SEM) image and the energy-dispersive X-ray spectroscopy (EDX) measurement were conducted on a Vegas 3 Tescan SEM instrument equipped with a Bruker EDX unit. The complex permittivity and permeability were measured at the frequency range of 1.0–18.0 GHz using an HP8722ES network analyzer with small ring-shape samples containing 60 wt% g-$C_3N_4$ nanosheets 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 prepared. The measurements were performed at room temperature.

## Results and discussion

The formation of g-$C_3N_4$ nanosheets was believed to be based on the polymerization of melem building blocks. Fig. 1A shows the XRD pattern of the $C_3N_4$ nanosheets. The XRD pattern had two distinct peaks at 2θ of 13.08 and 27.52° the hexagonal phase of polymeric g-$C_3N_4$ (JCPDS #87-1526) [40–44]. The strong peak at 27.52° was related to interlayer stacking of the (002) melem planes, and the peak at 12.8° was attributed to the (100) planes corresponding to inplane ordering of the nitrogen-linked heptazine units [40–43]. The peak at 18.04 was attributed to the (310) plane of the polymeric g-$C_3N_4$ [44]. The interlayer distance of the (002) planes and between the (100) planes calculated were of 0.32 and 0.69 nm for $d_{002}$ and $d_{100}$, respectively, both close to their theoretical values of 0.34 and 0.73 nm, respectively. The crystallite domain size (L) was calculated according to the Scherrer's equation for the full width at half maximum intensity (FWHM, β) of a diffraction peak β(2θ): $L = K\lambda/\beta(2\theta)\cos\theta$ where λ is the wavelength of the X-rays, θ is the Bragg's angle and K is a constant equal to 0.94 for cube or 0.89 for spherical crystallites [40–45]. In this study K was rounded to 0.9 for simple estimation. The average g-$C_3N_4$ crystallite size was estimated with Scherrer equation from FWHM of the (002) diffraction peaks at of 8.0 nm. The XRD pattern was consistent with the findings of pure g-$C_3N_4$ nanosheets in the literature [46–48].

Fig. 1B displays the diffusive UV–vis absorption spectrum. It showed a long-tail absorption from 635.0 to 455.1 nm and a large band absorption below 455.1 nm. The optical bandgap was estimated near 2.73 eV, calculated from the intersection of the long-tail and band absorption at 455.1 nm. The bandgap transition energy $E_g$ was also estimated using the Tauc's equation: $\varepsilon h\nu = C(h\nu\text{-}E_g)^p$, where $\varepsilon$ is the molar extinction coefficient, which can be obtained from the Beer–Lambert's law, hν is the energy of incident photons, C is a constant, $E_g$ is bandgap energy of the material, and p depends on the type of transition [36–42]. For direct semiconductors like g-$C_3N_4$ $p = 1/2$. The $E_g$ was around 2.92 eV with this method from the