Solid-State Synthesis of UV-Plasmonic Cr$_2$N Nanoparticles

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Abstract:

Materials that exhibit plasmonic response in the UV region can be advantageous for many applications such as biological photodegradation, photocatalysis, disinfection, and bioimaging. Transition metal nitrides have recently emerged as chemically and thermally stable alternatives to metal-based plasmonics materials. However, most free-standing nitride nanostructures explored so far have plasmonic response in the visible and near-IR region. Herein, we report the synthesis of UV-plasmonic Cr$_2$N nanoparticles using a solid-state nitridation reaction. The nanoparticles had an average diameter of 9 ± 5 nm and a positively charged surface that yields stable colloidal suspension. The particles were composed of a crystalline nitride core and an amorphous oxide/oxynitride shell whose thickness varied between 1 - 7 nm. Calculations performed using finite element method predicted the localized surface plasmon resonance (LSPR) for these nanoparticles to be in the UV-C region (100 - 280 nm). While a distinctive LSPR peak could not be observed using absorbance measurements, low-loss electron energy loss spectroscopy showed the presence of surface plasmons between 80 - 250 nm and bulk plasmons centered around 50 - 60 nm. Plasmonic coupling was also observed between the nanoparticles resulting in resonances between 250 - 400 nm.
I. INTRODUCTION

Plasmonic metal nitrides have recently received significant interest as reports outlining multiple synthetic methods to prepare free-standing nanoparticles (NPs),\textsuperscript{1-3} demonstrating their thermal stability,\textsuperscript{4} and high photothermal efficiency\textsuperscript{4,5} have emerged. Many of these studies have predominantly focused on TiN which exhibits broad absorption with localized surface plasmon resonance (LSPR) maximum typically in the near-IR region.\textsuperscript{6} As such, TiN has been explored for solar light driven processes such as water evaporation\textsuperscript{4,5} and photocatalysis\textsuperscript{7-9} and applications that require absorption in the biological transparency window such as photothermal therapy\textsuperscript{10} and photoacoustic tomography.\textsuperscript{11} Moving down the group, ZrN and HfN have also been explored which possess LSPR in the visible region of the electromagnetic spectrum.\textsuperscript{12,13} They have been shown to have higher photothermal efficiencies compared to TiN due to stronger electron-phonon coupling.\textsuperscript{14-16} Detailed experimental studies on plasmonic metal nitride NPs beyond those containing group 4 transition metals are scarce. Therefore, most of the plasmonic applications involving nitrides have predominantly focused on light-material interactions in the visible and near-IR region.

Materials with plasmonic responses in the UV region (100 - 400 nm) are of interest for disinfection, biological imaging, sensing, and developing metamaterials.\textsuperscript{17} Metals such as Al, Mg, Ga, In, Rh, Pd, Pt, Sn, Tl, Sb, Pb, Bi, and Ru have a bulk plasma frequency below 400 nm and have been explored for UV applications.\textsuperscript{18-24} However, these metals can be either expensive, oxidize under ambient conditions, or have low melting points making them incompatible with high-temperature fabrication techniques.\textsuperscript{22,23} Computational studies have predicted that chromium metal nitrides (CrN and Cr\textsubscript{2}N) can possess LSPR in the blue
to UV region of the electromagnetic spectrum. The high melting points of these nitrides (> 1500 °C) make them an attractive alternative to metals such as Al and Mg. However, synthetic methods to prepare these nitride NPs and a better understanding of their plasmonic behavior are required to truly assess their applicability.

Recently, plasmonic Cr$_2$N NPs with size ranging between 0.8 - 30 nm were synthesized using a single step pulse laser irradiation. The absorption spectra of these particles showed multiple LSPR between 320 - 420 nm with maximum at 372 nm. This broad absorption was hypothesized to be due to hot spot formation from particle-particle interaction. However, it currently remains unclear what the optical properties of Cr$_2$N NPs without the interparticle interactions look like. This study focuses on exploring the plasmonic properties of Cr$_2$N NPs using UV-Vis absorbance spectroscopy, electron energy loss spectroscopy (EELS), and numerical methods. The NPs were prepared using a solid-state reaction between Cr$_2$O$_3$ and Mg$_3$N$_2$ which resulted in water dispersible NPs and were characterized using various analytical and microscopy techniques. The NPs had bulk and surface plasmon resonances below 200 nm which corroborated with the calculations performed using finite element method.

II. EXPERIMENTAL METHODS

Materials. Chromium oxide (Cr$_2$O$_3$, 99.9%, 18 nm), and magnesium nitride (Mg$_3$N$_2$, 99%, -325 mesh) were purchased from U.S. Research Nanomaterials Inc., and hydrochloric acid (HCl) was purchased from Anachemica (37%). Sodium hydroxide (NaOH) was purchased from Alfa Aesar (98%). Deionized water (DI-water) was obtained from a Sartorius Arium
water purification system. All glassware was cleaned thoroughly with DI-water then acetone and placed in oven to dry prior to use.

Synthesis of Cr$_2$N NPs. The synthesis procedure to make Cr$_2$N particles was adapted from a previously reported method.$^{12}$ Briefly, Cr$_2$O$_3$ (0.152 g, 1.0 mmol) nanopowder was mixed with Mg$_3$N$_2$ (0.403 g, 4.0 mmol) using a spatula. This step was performed in a nitrogen-filled glovebox to avoid Mg$_3$N$_2$ decomposition in the presence of moisture. The mixing step can also be carried out on the benchtop if the relative humidity is below 40%. The powder mixture was transferred to a CoorsTM high alumina combustion boat and the boat was immediately placed in a quartz tube. The reaction mixture was heated to 1000 °C at a ramp rate of 10 °C/min and held at that temperature for 3 hours under argon flow in a Lindberg Blue M™ furnace. The reaction mixture was cooled to room temperature and the resulting product was transferred to a 100 mL beaker and the reaction boat was rinsed with 20 mL DI-water. 25 mL of 1.0 M aqueous HCl solution was slowly added to the reaction product and stirred together for one hour to remove magnesium oxide (MgO) and unreacted Mg$_3$N$_2$. The reaction solution was centrifuged for 15 min at 3300 rpm and the supernatant containing acid and soluble by-products was discarded (after the first centrifugation step, the supernatant is colorless). The solid was resuspended in 5.0 mL DI-water by sonication and centrifuged for 15 min at 3300 rpm. The colored supernatant containing Cr$_2$N NPs was collected, and the precipitate was resuspended in 5 mL DI-water by sonication and centrifuged again for 15 min at 3300 rpm. The colored supernatant was collected and mixed with the supernatant from the previous step. To collect the powder XRD pattern of the
dispersed NPs, the solution pH was adjusted to ~6 using NaOH solution (1.0 M), and the particles were allowed to settle overnight and centrifuged to isolate the solid.

Characterization techniques. Powder X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV X-Ray diffractometer with Cu Kα radiation (λ = 1.54 Å). The samples were placed on to a zero-background Si wafer and the spectra were collected at 3 counts/s. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Versaprobe instrument with an Al Kα source (1486.6 eV). Powders of each sample were dispersed in water, then dried as a near-coverage layer onto a diced Si wafer at 70 ºC. CasaXPS software (VAMAS) was used to interpret high-resolution (HR) XP spectra. The background was subtracted using a Shirley-type background to remove most of the extrinsic loss structure. Absorption spectra were collected using an Agilent CARY 5000 spectrometer. NP suspensions were placed in a quartz cuvette and DI-water was used as the blank. Dynamic light scattering (DLS) measurements were conducted using Zetasizer Nano Series Nano-ZS (Malvern Panalytical) instrument with a built-in 623 nm laser. For the size measurements, dilute NP solutions were placed in a plastic cuvette, whereas for the zeta potential measurements, a DTS1070 folded capillary cell was used. Zetasizer software was used for data analysis. Transmission electron microscopy (TEM) samples were prepared by drop-casting nanoparticle suspensions onto a copper grid coated with holey carbon film and the images were collected on either a Thermo Scientific Talos 200 X microscope or a Hitachi-9500 electron microscope at an operating voltage of 200 kV. The core-loss electron energy loss spectroscopy (EELS) data was acquired in Digital Micrograph environment using a Gatan CMOS detector. Image J was used to measure particle size and aspect ratios.
High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected on a Thermo Scientific Talos 200 X microscope. Low-loss EELS data was acquired on a double-corrected FEI Titan scanning transmission electron microscope operated at 80 kV and equipped with a monochromator and Gatan Quantum GIF spectrometer. The beam was monochromated to achieve an energy resolution of approximately 100 meV, using a dispersion of 25 meV/channel (bulk plasmon spectra) or 10 meV/channel (surface plasmon spectra) on a CCD camera with a convergence angle of 14.2 mrad and a collection angle of 25.4 mrad. Data processing on the low-loss EELS was done using custom Python software.27

Computational Studies. The optical properties of Cr₂N NPs were computed using a finite element method (FEM) solver for Maxwell’s equations in COMSOL MultiPhysics. To simulate the optical characteristics of the materials, Lorentz oscillator parameters of Cr₂N were obtained from Aouadi et al.28 to determine real and imaginary part of dielectric function of the material. In simulations, particles were modelled as three dimensional nanospheres suspended in water. To ensure the accuracy of the results, rigorous convergence analysis and perfectly matched layers (PML) boundary conditions. Three-dimensional models were meshed via the built-in meshing algorithm in COMSOL with a maximum element size of 0.1r, where r is the radius of nanospheres.

III. RESULTS AND DISCUSSION

The solid-state nitridation of metal oxide nanopowders with Mg₃N₂ has been previously used by our group to successfully synthesize free-standing group 4 plasmonic
transition metal nitride nanostructures. A similar procedure was utilized in here to synthesize Cr$_2$N NPs. Cr$_2$O$_3$ nanopowder with an average particle size of 45 ± 10 nm and ellipsoidal shape (Figure S1) was commercially purchased. While most particles (~90%) were below 100 nm in size, a few larger (> 100 nm) particles were also present in the oxide sample (Figure S1B). The powder XRD pattern of the oxide precursor showed reflections characteristic of cubic phase Cr$_2$O$_3$ (Figure 1A). This was reacted with Mg$_3$N$_2$ at 1000 ºC for 3 hours and the resulting reaction product was treated with 1 M aqueous HCl solution to remove MgO and unreacted Mg$_3$N$_2$. The nitride product was isolated through a series of washes as outlined in the experimental section. The powder XRD pattern of the dried NP dispersion showed reflections characteristic of Cr$_2$N with a hexagonal crystal structure and no peaks corresponding to the starting materials or reaction byproducts were observed. The TEM analysis showed most of the NPs to be pseudospherical with an average diameter of 9 ± 5 nm (Figure 1B and C). While most particles were between 5 - 15 nm, a small portion of larger NPs ranging between 15 - 25 nm were also formed (Figure S2). Additionally, the chemical composition of the Cr$_2$N was investigated using EELS elemental mapping. The EELS analysis showed good overlap between Cr (Figure 1E) and N (Figure 1F) confirming the presence of a chromium nitride phase, whereas O (Figure 1G) was found to be predominantly in N deficient regions. The nitride NPs prepared using this method have been shown to oxidize after the HCl workup to form surface oxynitride and oxide species which is likely the origin of O species in the EELS map. Zeta potential measurements were conducted on the Cr$_2$N NP colloidal suspensions to determine surface charge and colloidal stability. The Cr$_2$N NPs dispersed in water exhibited a zeta potential of 45.4 ± 0.7 mV, indicating that the NP surface is positively charged, and they form a stable...
colloidal suspension. The positive charge most likely originates from the protonated hydroxyl functional groups (-OH$_2^+$) groups on the surface that result from the acid workup. The NP suspension had a hydrodynamic diameter of 47.0 ± 0.5 nm as determined by the DLS.

![Figure 1](image_url)

**Figure 1:** (A) Powder X-ray diffraction pattern of Cr$_2$O$_3$ and Cr$_2$N NPs. (B) TEM image of Cr$_2$N NPs. Inset: Higher magnification TEM image of a single Cr$_2$N NP showing the oxide shell. (C) Cr$_2$N particle size distribution. (D) HAADF-STEM image and EELS map of (E) chromium (F) nitrogen and (G) oxygen content of Cr$_2$N NPs.

To further probe the surface chemical state of the Cr$_2$N, the NPs were analyzed using XPS technique. The high-resolution XP spectrum of the Cr 2p region (Figure 2A) for the precursor had 2p$_{3/2}$ peak fits at binding energies of 576.5, 578.9, and 580.6 eV corresponding to Cr$_2$O$_3$, Cr(OH)$_3$, and CrO$_3$, respectively.$^{31,32}$ The combined 2p$_{1/2}$ fit, and
the satellite peak maxima were at 586.7 and 597.5 eV, respectively.\textsuperscript{33} No distinctive peak was observed in the N 1s region in the starting material (Figure 2B). The Cr 2p spectrum of Cr$_2$N NPs had 2p$_{3/2}$ peak fits at binding energies of 573.8, 575.7, and 576.8 eV corresponding to Cr$_2$N, CrO$_x$N$_y$, and Cr$_2$O$_3$, respectively (Figure 2C).\textsuperscript{34,35} The chemical identity of the small peak located at 579.7 eV is currently unclear but could be due to Cr(V) species.\textsuperscript{36} The data indicates presence of an oxide and oxynitride shell around the Cr$_2$N NP core similar to previous reports.\textsuperscript{12,37} This is further confirmed using TEM analysis which showed the presence of an oxide shell around the NPs (Figure S3). The thickness of this shell varied between 1 - 7 nm for various NPs and was found to be non-uniform even within the same particle. The N 1s spectrum of Cr$_2$N NPs showed a weak signal ca. 395.5 eV corresponding to the nitride (Figure 2D).\textsuperscript{34} Given the oxide shell thickness, it is likely that not many electrons from the Cr$_2$N core are detected.
Figure 2. High resolution XP spectra of Cr 2p and N 1s regions of Cr$_2$O$_3$ nanopowder and Cr$_2$N NPs.

The real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) components of the dielectric function of Cr$_2$N between 100 and 700 nm are shown in Figure 3A. A negative real permittivity is observed in this wavelength range indicating free electron behaviour.$^{25}$ The magnitude of the imaginary component of the dielectric function increases with decreasing frequency indicating higher optical losses at longer wavelengths.$^{38}$ The absorption spectrum of Cr$_2$N NPs with diameter of 9 and 25 nm was calculated using finite element method (Figure 3B). The NP size chosen for the calculations are equal to the average and large particle size in the sample. The data suggest that the LSPR maximum of Cr$_2$N NPs is in the deep UV region (around 60 nm for 9 nm NPs and at 145 nm for 25 nm particle size) and the LSPR peak of the experimental sample should be relatively broad covering all of the UV and parts
of the visible spectrum. The Cr$_2$N NP solution has a brown color (Figure 3B inset) and showed a broad absorbance (Figure 3B, solid line) when suspended in DI-water. The characteristic LSPR peak was not observed in the measured spectrum, however the calculations show this to be present below the spectrometer’s wavelength cutoff (190 nm). The absorbance spectrum showed a shoulder peak at ~310 nm which could be due to plasmon coupling between NPs as observed by Gubert et al.$^{26}$ The computational analysis on the absorption and scattering of Cr$_2$N NPs was performed to evaluate the extinction behavior of the NPs of different sizes. The normalized absorption and scattering coefficients ($Q_{\text{abs}}$ and $Q_{\text{sca}}$) are defined by the calculated absorption or scattering cross sections of NPs ($C_{\text{abs}}$ and $C_{\text{sca}}$) using FEM normalized to the geometrical cross section of the NPs. The extinction coefficient of the NPs can be then defined as: $Q_{\text{ext}} = Q_{\text{abs}} + Q_{\text{sca}}$. As shown in Figure 3C, for smaller NPs ($\leq 50$ nm) the absorbance is higher in the UV-C region (~100 - 280 nm) whereas for the larger NPs (70 - 100 nm), the absorbance is higher in the UV-B and UV-A regions (280 - 400 nm). It is also clear that the absorption and scattering maxima of particles shifts to longer wavelengths and becomes broader with an increase in NP size (Figure 3C and D).
Figure 3. (A) Real and imaginary components of the dielectric function of Cr₂N. (B) Calculated absorption cross-section and measured absorbance of Cr₂N NPs. Inset: Photograph of Cr₂N NP suspension in water. Calculated (C) absorption and (D) scattering coefficients of Cr₂N NPs between 10 - 100 nm.

While a distinctive LSPR could not be observed in the absorbance spectrum limited by the instrument wavelength cutoff, EELS was used as an alternative technique to map both bulk and surface plasmon intensity and energy with high spatial resolution. Since the EELS experiments are conducted under high vacuum, some variations can be expected compared to the NPs suspended in a solvent. Figure 4A inset shows regions from which the EELS spectra were acquired. All the spectra obtained in these studies were normalized to the zero-loss peak. The large signal with peak centered around 20 - 25 eV (i.e., ~50 - 62 nm) is indicative of the bulk plasmon (Figure 4A). The shoulder peaks observed in spots 3 -
5 spectra are indicative of surface plasmons, however, these are difficult to differentiate from the bulk plasmon signal. To further confirm the presence of surface plasmons, aloof EELS experiments were conducted where the electron beam does not interact with the sample directly but does so through long-range Coulomb interactions with the evanescent field of the surface plasmon resonances.\textsuperscript{40} As shown in Figure 4B inset, four different areas were chosen that are close to the NPs but not directly on the sample. The bulk plasmon peaks that appear at higher energies are no longer present in the aloof mode which is expected since the electron beam is not directly interacting with the particles (Figure 4B). It is possible that in spot 1 the interaction with the electron beam might be too weak to observe a surface plasmon peak from \text{Cr}_2\text{N}. In the spots 2 - 4, the aloof EELS spectra indicate the presence of a surface plasmon signal between 5 and 15 eV (i.e., \textasciitilde80 - 250 nm), which aligns with the calculations that indicate LSPR to be present in this energy region for NPs with diameter below 50 nm.
Figure 4. (A) Low-loss EELS spectra and (B) aloof EELS spectra of Cr₂N NPs. Inset: STEM-HAADF images indicating spots where the spectra were collected (scale bar = 20 nm).

Figure S4 shows EELS loss probability maps with the energy ranges that were chosen based on the peak positions in the low-loss EELS spectra. Between the energies of 3.06 and 4.9 eV, signal is mostly arising in between the particles indicating plasmonic coupling which was also observed in the solution absorbance measurements. At energies between 6.96 and 8.60 eV, the map shows higher intensities around the NPs likely originating from surface plasmons. At higher energies (> 9 eV), most of the sample appears bright which can be attributed to both the surface and bulk plasmons.

IV. CONCLUSIONS

Plasmonic Cr₂N nanocrystals were successfully synthesized using solid-state nitridation of Cr₂O₃ with Mg₃N₂. This resulted in the formation of water dispersible Cr₂N NPs with an average diameter size of 9 ± 5 nm and positively charged surface. The
particles had a varying thickness of oxide and oxynitride layer around the nitride core as determined from XPS and TEM analysis. The calculations predicted these NPs to have LSPR below 200 nm which aligned with the experimental observations. While a strong LSPR was not observed in the absorbance spectrum limited by the wavelength cutoff, low-loss EELS spectra showed presence of surface and bulk plasmon resonances below 200 nm. Cr$_2$N can be a promising material for UV-plasmonic applications and future studies will focus on exploring their thermal behaviour.

**SUPPLEMENTARY MATERIAL**

See supplementary material for TEM images of Cr$_2$O$_3$ and Cr$_2$N NPs and EFTEM maps of Cr$_2$N particles (Figures S1 – S4).

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CONFLICT OF INTEREST

Authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request. Python software used to process EELS data is available here: https://zenodo.org/record/807763#.YsuIhnbMLb0.

REFERENCES


