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One-Step Synthesis of Robust 2D Ti_3C_2-MXene/AuNPs Nanocomposite by Electrostatic Self-Assembly for (Bio)Sensing †

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Abstract: In this study, we present a single-step approach for the synthesis of Ti_3C_2 MXene and gold nanoparticle (AuNP) composites via electrostatic self-assembly. The surface of the AuNPs was modified to induce a positive charge using cetyltrimethylammonium bromide (CTAB), which enabled effective electrostatic interactions with negatively charged MXene sheets. The successful synthesis of the MX-AuNP composite was confirmed using UV–Visible spectroscopy (UV–Vis), dynamic light scattering (DLS), and scanning electron microscopy (SEM). In conclusion, our single-step synthesis method offers a sustainable platform for producing MXene-AuNP composites with enhanced properties. This approach can be extended to other metal nanoparticles and holds great promise for a wide range of applications, particularly in biosensing and nanomaterial-based technologies.

Keywords: Ti_3C_2 MXene; Positively charged gold nanoparticles; nanocomposite; MXene@AuNPs; electrostatic self-assembly

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1. Introduction

Recently, biosensing has emerged as a prominent and rapidly growing research area. The use of low-dimensional materials appears to be an effective strategy to meet the need for efficient and sensitive biosensors with low detection limits. In this context, two-dimensional carbides and nitrides of transition metals, commonly known as MXenes, gainedsignificant attention from the biosensing community owing to their exceptional features for sensing applications [1,2]. MXenes are layered structures composed of carbides, nitrides, and carbonitrides produced from their parent MAX phase precursors by eliminating interleaved A layers under controlled etching [3]. In addition to their hydrophilicity, conductivity, and dispersibility, MXenes possess a unique structure with intrinsic functional groups, making them compatible to form composites with other metals [4]. Consequently, this can significantly enhance the detection efficiency of MXene-based sensing platforms. Ti_3C_2 MXene is a pioneering member in the family of MXenes that proved its immense potential in biosensing [4] and many other promising research areas [5]. Gold nanoparticles (AuNPs) exhibit remarkable properties and have been widely employed in MXene research. Rakhi et al. [6] reported an amperometric biosensor for glucose sensing using a Ti_3C_2/Au nanocomposite, achieved through a chemical reduction approach to decorate MXene with Au clusters. Another study reported the synthesis of MXene hybrids with Au, Ag, and Pd nanoparticles via the self-reduction of precursor salts [7]. Yang et al. [8] studied the synthesis of

Nb_2C/Au composites via electrostatic self-assembly after modifying the MXene surface with APTES, resulting in excellent SERS performance. However, it is worth noting that modification of the MXene surface with APTES and other polymers can affect its intrinsic conductivity. MXene can intrinsically function as a reducing agent and reduce aqueous metal salts to corresponding nanoparticles. However, such approach has been commonly used for the reduction of noble metal nanoparticles. Also, the in situ reduction of gold presents challenges such as controlling the shape and size of AuNPs, and requires facile control [9]. Therefore, designing a universal approach is crucial. Electrostatic self-assembly is a simple and highly efficient method for fabricating composites. Owing to their negative surface, MXenes can serve as an active platform to host oppositely charged particles. As proposed by Xie et al., Au nanorods were deposited on $Ti_3C_2T_x$ nanosheets via electrostatic self-assembly [10]. However, there are strong limitations to the size yield of nanorods, and controlling their size is challenging [11]. Thus, it is imperative to develop a robust and controllable method to prepare MXene-AuNP composites without using stabilizers, in situ reduction, or creating an intermediate matrix, such as APTES and polymers.

Spherical AuNPs produced using Turkevich protocols are highly regarded due to their facile synthesis, easy control, and high reproducibility [12]. To the best of our knowledge, a composite of MXene with spherical AuNPs via electrostatic self-assembly while preserving the properties of MXene is rarely reported. Herein, we present a one-step synthesis of a Ti_3C_2 MXene/AuNP composite through electrostatic self-assembly. To achieve this, cetyltrimethylammonium bromide (CTAB) is utilized as a cationic surfactant to introduce a positive charge to gold nanoparticles (AuNPs) produced using the conventional Turkevich protocol [13]. The synergies between both materials (MXene and positively charged AuNPs) can significantly enhance the properties of the composite, making it a promising candidate for various applications, particularly in biosensing.

2. Materials and Methods

2.1. Materials

Ti_3AlC_2 MAX precursor (Particle Size $\leq$ 40 µm) was acquired from Carbon-Ukraine. Hydrochloric acid (HCl, $\geq$37%, ACS reagents), lithium chloride (LiCl, 99%), gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), sodium citrate, ascorbic acid, silver nitrate, and cetyltrimethylammonium bromide (CTAB) were purchased from Sigma-Aldrich. Ethanol ($\geq$99.5%) was obtained from Merck Millipore. Durapore 0.22 µm and 47 mm PVDF hydrophobic membranes were used for vacuum filtration. Ultrapure deionized water was dispensed using a MilliQ system (18.2 MΩ cm resistivity) and used for all experiments.

2.2. Synthesis of MXene

MXene was synthesized via wet chemical etching route with slight modifications [14]. Ti_3AlC_2 MAX powder (1 g) was slowly added to a Nalgene bottle containing MilliQ water (9 mL), HCl (18 mL), and HF (3 mL) and continuously stirred for 24 h at 35 °C. The solution was thoroughly washed with MilliQ water by centrifugation at 4200 rpm for 5 min for each cycle, until the pH reached ~6–7. Delamination was performed in a solution of MilliQ + LiCl (50 mL + 1 g) at 35 °C for 24 h at 600 rpm under constant argon bubbling. The solution was subsequently washed until clay-like sediment appeared. The clay-like sediment was then redispersed, hand-shaken, and centrifuged to obtain delaminated flakes. The delaminated flakes were repeatedly washed to ensure MXene quality and were stored at 4 °C.

2.3. Synthesis of Positively Charged Gold Nanoparticles

Gold nanoparticles (AuNPs) were synthesized using the classic Turkevich method with slight modifications [15]. Briefly, 0.5 mL (25.4 mM) of $HAuCl_4 \cdot 3H_2O$ was spiked in 50 mL MilliQ under vigorous magnetic stirring until boiling. Subsequently, 1 mL of sodium citrate (80 mM) was added with constant stirring for approximately 20 min, while maintaining a constant temperature. The color of the solution first changed from yellowish to dark and finally to wine red. To remove citrate impurities, the solution was washed at

6000 rpm for 30 min, and the pellet was redispersed in ultrapure water (Milli-Q). The final AuNP solution was stored in the dark at 4 °C in the refrigerator.

Gold growth was initiated using a gold growth solution [16]. To achieve this, 0.384 mL of $HAuCl_4 \cdot 3H_2O$ (40 mM) was added to 6 mL CTAB (200 mM) under gentle stirring. The color of the suspension turned bright yellow-orange. Subsequently, 0.228 mL of $AgNO_3$ (10 mM) was added to control the gold growth process, ensuring the formation of spherical particles. Subsequently, 0.960 mL of ascorbic acid (100 mM) was added, and the solution immediately turned colorless. Ascorbic acid acts as a weak reducing agent, causing the reduction of Au(III) to Au(0), as indicated by the colorless change [17]. The solution was then diluted with 11 mL ultrapure water under gentle stirring for 20 min. Finally, Turkevich gold nanoparticles (AuNPs) were mixed with the growth solution. The solution appeared reddish-pink, indicating an increase in the nanoparticle size due to the surfactant. To remove the surfactant, the solution was washed twice with ultrapure water at 7000 rpm for 30 min, and the pellet was redispersed in water to achieve an optical density (OD) of 1.0. Here, CTAB serves a dual purpose: stabilizing the nanoparticles i.e., preventing aggregation, and controlling their growth (size and shape) through the CTAB bilayer. These actions result in the introduction of a positive charge on the surface of the AuNPs through its quaternary ammonium head group. This charge modification is crucial for achieving well-dispersed, positively charged spherical AuNPs that are suitable for electrostatic self-assembly.

2.4. Synthesis of MXene and Gold Nanoparticle Composite (MXene@AuNP)

The MXene/AuNP nanocomposite was synthesized via electrostatic self-assembly to decorate the $Ti_3C_2T_x$ MXene sheets with AuNPs. Briefly, 4 mL of an aqueous solution of AuNPs (7.15×10^{10} NPs/mL) was added dropwise to 4 mL of a colloidal solution of MXene (1 mg/mL) under gentle stirring at room temperature for 1 h. The samples were then centrifuged at 3500 rpm for 30 min to remove excess AuNPs, and the precipitate was redispersed in MilliQ water. The samples were sonicated for 30 min to ensure homogeneity. The resulting sample was denoted as MX@AuNPs.

3. Results and Discussion

The UV–Vis absorbance spectra were recorded on a UV/Vis spectrophotometer (model 6715 Jenway, Cole-Parmer Company) with a resolution of 0.1 nm. Dynamic light scattering (DLS) measurements were conducted using a Zetasizer Nano ZS instrument (Malvern Instruments). The measurements were performed at 25 °C with an equilibration time of 100 s. Prior to the analysis, the samples were homogenized by sonication, and each measurement was repeated three times. Zeta potential measurements were performed using the same instrument, and the results were recorded as the mean value of the zeta potential ± standard deviation. The morphology of the MXene@AuNP composite was examined using a Zeiss ΣIGMA field-emission scanning electron microscope (FESEM).

3.1. MXene Synthesis and Delamination:

The UV–Vis spectra were recorded for $Ti_3C_2T_x$ MXene, AuNP, and MXene@AuNPs composites. The colloidal solution of delaminated $Ti_3C_2T_x$ MXene (black line) exhibited a characteristic absorption peak at ~795 nm, as shown in Figure 1a [18]. The inset shows that the MXene dispersion exhibits a typical greenish color, which signifies successful delamination [19].

3.2. AuNPs Synthesis

The AuNPs displayed a peak at approximately 530 nm in the visible light region, corresponding to the surface plasmon resonance (SPR) of spherical Au nanoparticles (Figure 1d). The estimated size based on this SPR was 40–50 nm, which was consistent with the DLS results (Figure 1e).

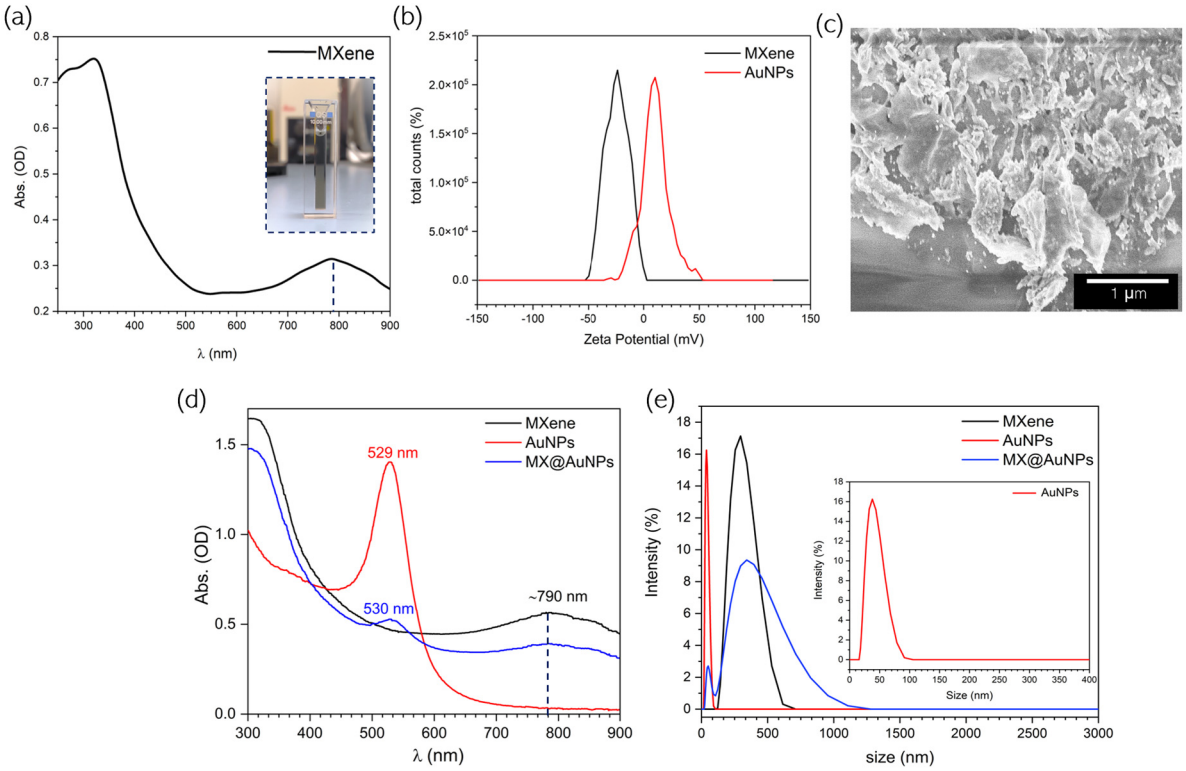

Figure 1. (**a**) UV–visible spectra of freshly delaminated Ti_3C_2 MXenes depicting their standard spectra. (**b**) Zeta potential of $Ti_3C_2T_x$ MXene (black) and AuNPs (red) with contrasting polarities, thus showing compatibility with electrostatic binding. (**c**) SEM micrograph of MXene@AuNPs composite showing AuNP decorated over the MXene sheets. (**d**) UV–visible spectra of spherical MXene, AuNPs, and colloidal solution of MX@AuNPs composite. (**e**) DLS analysis of MXene, AuNPs, and MX@AuNPs.

3.3. MX@AuNPs Composite Synthesis

Zeta potential (ζ-potential) measurements were performed to confirm the electrostatic interactions between Ti_3C_2 MXene and AuNPs, and the ζ-potential measurements were performed as shown in Figure 1b. The mean zeta potential of MXene is −24 mV, owing to the presence of negative surface terminations (−F and −OH) at neutral pH [20]. AuNPs showed a ζ-potential of +11 mV, indicating the possibility of electrostatic self-assembly. When positively charged spherical AuNPs come into proximity with negatively charged MXene nanosheets, they induce electrostatic interactions, leading to the formation of the MXene/AuNP composite. The SEM image (Figure 1c) shows the uniform distribution of AuNPs across the MXene sheets without any noticeable agglomeration. Figure 1d shows the UV–visible spectra of AuNPs, with a peak at ~529 nm in the visible light region. In contrast, the AuNP peak is evident with a typical MXene peak, indicative of MX@AuNPs' composite formation. DLS studies suggested that the MXene sample has an average diameter of approximately 300 nm, representing small flakes dispersed in the solution (Figure 1e). This size reduction can also be attributed to the sonication performed both before the measurements and during composite synthesis. An increase in the diameter of the flakes after loading MXenes with AuNPs was also observed. This can be ascribed to electrostatic interactions between oppositely charged species, leading to an increase in the hydrodynamic size, signifying composite formation.

4. Conclusions

This paper presents a single-step approach for the synthesis of Ti_3C_2 MXene and surface-charged modified Turkevich gold nanoparticle (AuNP) composites through electrostatic self-assembly. Ti_3C_2 MXene was produced via the HF + HCL approach and

delaminated by Li-ions intercalation. Delamination yielded high-quality MXene single flakes with a significantly negative zeta potential (−24 mV), allowing them to be uniformly dispersed in water. Cetyltrimethylammonium bromide (CTAB) induced a positive core around the AuNPs (ζ-potential = +11 mV), thus enabling effective electrostatic interactions with the negatively charged surface of the MXene sheets. The UV–visible spectra confirmed the delamination of MXene. The UV–visible spectra, DLS measurements, and SEM images showed the successful dispersion of AuNPs over the MXene sheets. In conclusion, our preliminary studies suggest a single-step method as a quick and sustainable approach for producing MXenes@AuNPs composites. This approach can be extended to other nanomaterials and holds great promise for a wide range of applications, particularly in biosensing.

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