Simple Synthesis of Silver Nanocluster Composites AgNCs@PE-g-PAA by Irradiation Method and Fluorescence Detection of Cr^{3+}

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Abstract

Silver nanoclusters (AgNCs) represent a novel class of nanomaterials with molecular-like properties, offering unique application prospects. The fabrication of AgNC composites through combination with various matrix materials can substantially broaden their application scope. Utilizing irradiation technology, we have developed a facile two-step synthetic method for preparing silver nanocluster composites. First, polyacrylic acid (PAA) chains are grafted onto the surface of a PE film to obtain a solid template (PE-g-PAA). Subsequently, silver ions are reduced in situ on the template surface to yield the AgNC composite (AgNCs@PE-g-PAA). The loading degree of AgNCs on the composite film can be readily controlled by adjusting the reaction conditions. The loaded AgNCs are anchored onto the carboxyl groups of PAA and encapsulated within the grafted chains. The AgNCs exhibit a particle size of merely 4.38$±$0.85 nm with a highly uniform size distribution. AgNCs@PE-g-PAA displays the fluorescence characteristics of AgNCs. The fluorescence of AgNCs@PE-g-PAA can be efficiently quenched by Cr3+ ions. This composite material can be utilized as a fluorescent test strip for visual detection of Cr3+.

Full Text

Preamble

Simple Synthesis of Silver Nanocluster Composites AgNCs@PE-g-PAA by Irradiation Method and Fluorescence Detection of Cr^{3+}

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ABSTRACT

Silver nanoclusters (AgNCs) are a new class of nanomaterials with molecular-like properties and unique applications. The utility of AgNCs can be significantly expanded by combining them with different matrix materials to form AgNC composites. Using irradiation techniques, we developed a simple two-step method for preparing silver nanocluster composites. First, polyacrylic acid (PAA) chains were grafted onto the surface of a PE film as templates (PE-g-PAA). Subsequently, silver ions were reduced in situ on the template surface to obtain the AgNC composites (AgNCs@PE-g-PAA). The loading degree of AgNCs on the composite film was easily controlled by adjusting the reaction conditions. The loaded AgNCs were anchored to the carboxyl groups of PAA and wrapped within the graft chains. The AgNCs exhibited a particle size of only $4.38\pm0.85nmwithaveryuniformsizedistribution.TheAgNCs@PE-g-PAAdisplayedfluorescencecharacteristicsderivedfromtheAgNCs,andthisfluorescencewasreadilyquenched$ ions. The composite can be used as a fluorescence test paper for the visual detection of Cr^{3+}.

KEYWORDS: Silver nanoclusters, Irradiation grafting, Irradiation reduction, In situ preparation, Fluorescence detection

INTRODUCTION

Metal nanoclusters (MNCs), particularly gold nanoclusters (AuNCs) and silver nanoclusters (AgNCs), represent a novel class of nanomaterials with widespread applications across various fields [1-4]. Due to their extremely small size, MNCs exhibit unique properties that differ from those of conventional metal nanoparticles (MNPs). When the size of MNCs approaches the Fermi wavelength of electrons, discrete energy levels emerge, endowing MNCs with molecular-like properties [5]. A distinctive characteristic of MNCs, especially silver nanoclusters, is photoluminescence [5]. AgNCs possess excellent photostability, low toxicity, and biocompatibility [6], leading to extensive research and applications [7,8]. Compared to semiconductor quantum dots or organic dyes, AgNCs offer superior photostability, lower toxicity, and larger Stokes shifts [9]. These unique photoluminescent properties provide an excellent platform for constructing luminescent probes for biological imaging and sensing applications [10-12].

Given their outstanding performance, developing facile fabrication methods for

AgNCs is of practical significance for their widespread application. Current synthesis of AgNCs primarily relies on traditional chemical reduction [13], with ultraviolet reduction [14] and ultrasonic reduction [15] also being explored. These methods typically employ strong reducing agents such as sodium borohydride or energy-intensive complex instruments to reduce Ag^+ ions to AgNCs in the presence of templates, often limiting practical applications. Therefore, developing simpler preparation methods is essential for promoting the practical use of AgNCs. Radiation reduction offers a promising alternative due to the reducing atmosphere generated by the interaction between water molecules and γ-rays [16], the strong penetrating ability of γ-rays [17], and the spontaneous generation of γ-rays by radionuclides [18]. Under γ-irradiation, water molecules ionize to produce highly reactive species, including hydrated electrons with strong reducing power [16], which reduce Ag^+ ions to Ag atoms that subsequently form AgNCs under the influence of templates [16]. We previously prepared aqueous silver nanocluster solutions via radiation reduction [19]. Compared to conventional methods, radiation reduction synthesis requires simpler conditions, offers easier process control, and is more amenable to industrialization. Based on these advantages, radiation reduction represents an excellent method for the practical synthesis of AgNCs.

Unlike silver nanoparticles (AgNPs), AgNCs possess unique photoluminescence capabilities [20] and have been employed as fluorescent sensors for detecting various chemical substances, including metal ions [23], organic reagents [24], and biological molecules [21]. Dong and Wei et al. prepared DNA-AgNCs for adenosine triphosphate (ATP) detection [25], while Dong et al. synthesized DNA-stabilized AgNCs for mercury ion quantification [26]. However, most studies utilize AgNC solutions for fluorescence detection. In solution, AgNCs tend to aggregate and lose their fluorescence characteristics due to their small size and high activity [20]. An effective approach to prevent this is anchoring AgNCs to solid material surfaces. Various solid materials have been used to load AgNCs for different applications: Yang et al. incorporated AgNCs into DNA hydrogels to obtain multifunctional materials with both fluorescence and antibacterial properties [27], while another group introduced DNA-stabilized AgNCs into graphene materials for tumor marker detection [28]. Irradiation grafting is a simple and universal method for obtaining grafted polymer materials through free radical polymerization induced by γ-rays on matrix surfaces [29-31]. Due to the non-selective nature of γ-rays, irradiation grafting is highly versatile and expandable. By grafting template monomers onto polymer matrices using irradiation grafting techniques to create solid templates, silver nanoclusters can be synthesized in situ, enabling simple and effective preparation of silver nanocluster composites. This straightforward and general synthesis route offers strong expandability, which is beneficial for promoting the practical applications of Ag nanoclusters and broadening their scope of use.

Trivalent chromium (Cr^{3+}) is widely present in wastewater from tanneries, electroplating, dyeing, and other industries [32]. Cr^{3+} can seriously affect cell structure by binding to DNA and cause significant harm to human health [33,34],

making it an environmental pollutant of concern. Current Cr ion detection often relies on complex instruments and laboratory environments [35,36]. Fluorescence detection based on the fluorescence characteristics of AgNCs offers a simple and effective alternative for Cr^{3+} detection. Although existing AgNC-based Cr^{3+} detection methods using solution systems can achieve high sensitivity [37], AgNCs in solution are inconvenient for practical production processes. Therefore, detecting Cr^{3+} fluorescence using solid materials such as test paper is comparatively simpler and more convenient.

Herein, we obtained AgNC-loaded composites using polyacrylic acid (PAA) as a template via a two-step irradiation process. First, the template monomer acrylic acid (AA) was grafted onto a PE matrix by irradiation grafting to obtain PE-g-PAA film. Second, Ag^{+} ions were reduced in situ on the PE-g-PAA film by irradiation reduction to obtain film materials loaded with AgNCs (AgNCs@PE-g-PAA). The degree of nanocluster loading in AgNCs@PE-g-PAA was effectively regulated by controlling reaction conditions. The bonded PAA molecular chains served as templates to prevent AgNC aggregation, while the loaded AgNCs endowed the film materials with photoluminescent properties. The prepared AgNCs@PE-g-PAA film exhibited obvious fluorescence quenching in response to Cr^{3+} and could be used as a fluorescence detection paper. Furthermore, we explored the fluorescence quenching mechanism, which was determined to be static quenching.

MATERIALS AND METHODS

2.1 Materials

Acrylic acid (AA), ferric chloride, acetone, silver nitrate, and isopropyl alcohol were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Chromium nitrate, aluminum nitrate, iron nitrate, copper nitrate, and mercury nitrate were also obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All chemicals and solvents were analytical reagents (AR) and were used as received without further purification. PE film was used as the matrix material, and all experiments were conducted using water purified by a Millipore system.

2.2 Instrumentation

Steady-state absorption measurements were performed on a HITACHI U-3900 UV-vis spectrophotometer scanning from 300–800 nm. Steady-state luminescence measurements were conducted using a spectrofluorometer (FS5) with a quartz cuvette, an integration time of 0.1 s, and excitation and emission slits maintained at 3 nm. Infrared (IR) analysis was performed using an FTIR650 spectrophotometer over 600–4000 cm^{-1} at 2 cm^{-1} resolution. For lifetime measurements, AgNCs were excited at 540 nm using an IBH-NanoLED source (N-340), with emissions collected at magic-angle polarization using a Hamamatsu MCP photomultiplier (Model R-3809U-50). Transmission electron microscopy

(TEM) images were obtained using a JEM-3000F high-resolution instrument operating at 200 kV, with thin samples prepared via ultrathin frozen-section technique. Field-emission scanning electron microscopy (FESEM) imaging was performed using a JSM-6700F instrument at 10–15 kV accelerating voltage, while energy dispersive X-ray spectroscopy (EDS) images were collected at 15 kV. Elemental valence analysis of the film surface was performed by X-ray photoelectron spectroscopy (XPS; SCIENTIFICESCALAB 250Xi) with software fitting. Thermal properties were studied using a TG 209F4 instrument for thermogravimetric analysis and a METTLER TOLEDO DSC3 apparatus for glass transition temperature and melting point determination. Static contact angles were measured using a THETA Optical tensiometer, and fluorescence was observed using a ZF-1 UV analyzer at 365 nm.

2.3 Synthesis of PE-g-PAA

The PE-g-PAA film was synthesized via irradiation grafting. First, 0.72 g of acrylic acid was dissolved in 20 mL acetone and stirred for 1 h until thoroughly mixed. Subsequently, 0.0072 g of ferric chloride was added and stirred until fully dissolved. Meanwhile, commercial PE film was cleaned with deionized water and dried at 60 °C in an oven. The pretreated PE film was then immersed in the prepared acrylic acid–ferric chloride–acetone solution. The solution was sparged with N_2 for 15 min and irradiated at an absorbed dose of 20 kGy using Co^{60} at room temperature. After irradiation, the grafted film was ultrasonically cleaned with deionized water for 1 h, with the water replaced three times. The films were dried at 60 °C for 24 h and reweighed. The degree of grafting (DG) was determined as the percentage weight increase according to Eq. (1), where Wg and W_0 represent the weights of grafted and ungrafted films, respectively.

2.4 Synthesis of AgNCs@PE-g-PAA

The AgNCs@PE-g-PAA film was synthesized by irradiation reduction. First, 0.34 g of silver nitrate and 0.6 g of isopropyl alcohol were combined in deionized water and stirred for 30 min until well mixed. The previously prepared PE-g-PAA graft film was then immersed in this silver nitrate–isopropyl alcohol–aqueous solution and incubated for 2 h to allow silver ion association with the film material. The solution was sparged with N_2 for 15 min and irradiated at an absorbed dose of 600 Gy using Co^{60} at room temperature. After irradiation, the loaded film was ultrasonically cleaned with deionized water for 6 min, with the water replaced twice. The film was left at room temperature for 24 h, then dried and weighed. The degree of loading (DL) was determined as the percentage weight increase according to Eq. (2), where Wg and W_0 represent the weights of grafted and ungrafted films, respectively. The final AgNCs@PE-g-PAA film was stored at 4 °C for subsequent testing.

2.5 Detection of Cr^{3+}

A stock Cr^{3+} solution was prepared by dissolving chromium nitrate in deionized water and diluted to obtain standard working solutions of various concentrations. The AgNCs@PE-g-PAA film was immersed in Cr^{3+} solution of the appropriate concentration and incubated at room temperature for 6 h. The film was then removed, dried at room temperature, and analyzed by fluorescence spectroscopy.

RESULTS AND DISCUSSION

Irradiation techniques such as irradiation grafting and irradiation reduction are simple and effective methods for modifying polymer composite materials [38] and reducing metal ions [39]. As coordination sites for silver nanoclusters, PAA chains were first grafted onto commercial PE film by irradiation grafting, followed by in situ reduction of Ag^{+} ions to silver nanoclusters (AgNCs) via irradiation reduction to obtain AgNC-loaded composite film (AgNCs@PE-g-PAA). The preparation process is illustrated in Scheme 1. The addition of PAA provides reliable binding sites for silver nanoclusters, enabling stable loading. The irradiation technique is not dependent on specific functional groups or reagents and exhibits strong universality, making the synthesis of AgNCs@PE-g-PAA both flexible and extensible.

[Figure 1: see original paper] Scheme 1. Preparation of AgNCs@PE-g-PAA.

3.1 Preparation and Characterization of AgNCs@PE-g-PAA

AgNCs are extremely small and highly active, tending to spontaneously aggregate into more stable silver nanoparticles (AgNPs) without template or stabilizer protection, which is detrimental to practical applications [20]. Typically, templates or stabilizers containing O [15], N [40], and S [41] are used in AgNC synthesis to prevent aggregation. Here, PAA chains grafted onto PE films serve as stabilizing sites for AgNCs.

To confirm AgNCs@PE-g-PAA film formation, Fourier-transform infrared spectroscopy (FT-IR) measurements were performed (Fig. 1(a) [Figure 1: see original paper]). The characteristic peak at 1730 cm^{-1} corresponds to the carboxyl group of the grafted acrylic acid monomer, indicating successful PE-g-PAA synthesis. The irradiation grafting mechanism follows traditional free radical polymerization [42], a mature and efficient technique [43]. Therefore, the degree of grafting of PE-g-PAA can be controlled by adjusting reaction conditions such as absorbed dose, AA concentration, and polymerization inhibitor content, thereby affecting AgNC loading. By controlling these factors, graft polymerization was effectively regulated, achieving PE-g-PAA grafting degrees from 0% to 170% (Fig. S1).

A suitable solid template facilitates AgNC loading and stabilization. The PE-g-PAA film enables in situ synthesis and long-term protection of AgNCs. UV-vis spectra (Fig. 1(b) [Figure 1: see original paper]) show no obvious absorption

peaks for PE and PE-g-PAA in the 300–800 nm range, whereas the prepared AgNCs@PE-g-PAA film exhibits a weak absorption peak at 500 nm, corresponding to AgNC absorption [44]. AgNCs@PE-g-PAA produced fluorescence emission at 650 nm under 540 nm visible-light excitation (Fig. S4(a)) and visible fluorescence under 365 nm UV irradiation (Scheme 1), attributed to AgNC photoluminescence.

XPS analysis confirmed AgNC formation (Fig. 1(c) [Figure 1: see original paper]). Peaks at 368 eV and 374 eV in the Ag3d spectrum reveal Ag^0 formation (Fig. 1(d) [Figure 1: see original paper]), collectively indicating successful AgNC synthesis. The interaction between AgNCs and the PE-g-PAA template was further investigated. As AgNCs bind with carboxyl groups, the carboxyl groups on graft chains ionize and participate in coordination, producing a characteristic peak for the PAA carboxylate group at 1550 cm^{-1} (Fig. 1(a) [Figure 1: see original paper]). Analysis of the oxygen chemical state revealed a new peak on the film surface after AgNC loading (Fig. 1(e) [Figure 1: see original paper]) that was absent in the PE-g-PAA spectrum (Fig. 1(f) [Figure 1: see original paper]), likely arising from coordination between oxygen atoms in carboxyl groups and silver atoms in AgNCs, altering oxygen' s chemical state. This carboxyl-AgNC interaction plays a key role in stabilizing AgNCs. When the PE-g-PAA grafting degree was 0%, no AgNCs formed in the material (Fig. S2), further supporting PAA' s crucial stabilizing function.

Irradiation reduction, similar to irradiation grafting, exhibits strong universality [17]. The AgNCs@PE-g-PAA loading degree could be controlled by adjusting the number of anchor sites on the film surface and the reduction degree of Ag^+ ions, analogous to controlling PE-g-PAA grafting degree. By controlling grafting degree, Ag^+ ion concentration, and absorbed dose, AgNCs@PE-g-PAA loading degree was easily regulated between 0% and 35% (Fig. S2).

The morphology and distribution of AgNCs in AgNCs@PE-g-PAA films were investigated by TEM and SEM. As shown in Fig. 1(g) [Figure 1: see original paper], the prepared AgNCs were spherical with an average particle size of 4.38$±$0.85 nm, wrapped within the AgNCs@PE-g-PAA film. Uniform AgNC distribution was more clearly observed through nanoscale elemental analysis (Fig. S3). SEM imaging at larger scales revealed the morphological changes in film surface and cross-sectional profiles. The ordinary commercial PE film exhibited a typical planar structure with a dense nonporous cross-section (Fig. 2(a) [Figure 2: see original paper]). After PAA grafting and AgNC loading, the film surface and cross-sectional morphology (Fig. 2(b) and 2(c) [Figure 2: see original paper]) did not change significantly. EDS mapping (Fig. 2(d) [Figure 2: see original paper]) shows uniform oxygen distribution on the PE film surface, indicating even distribution of grafted PAA chains, which facilitates uniform AgNC loading. As expected, silver was also evenly distributed on the film surface (Fig. 2(d) [Figure 2: see original paper]), demonstrating successful uniform AgNC loading. Interestingly, EDS mapping of the AgNCs@PE-g-PAA film cross-section reveals oxygen and silver distribution throughout the cross-

section, indicating that AA grafting and AgNC loading occur not only on the surface but also within the film interior. This may be attributed to PE swelling during reaction. As a good PE solvent, acetone does not dissolve PE at room temperature but causes swelling, allowing AA molecules to penetrate the PE film and undergo grafting reactions within the interior, forming PAA chains inside the film. Due to the good hydrophilicity of grafted PAA chains, the PE-g-PAA template film exhibits similar swelling behavior in aqueous solution, enabling silver ion reduction within the film and facilitating interior AgNC loading. Consequently, template PAA chains and AgNCs were stably distributed throughout the material (Fig. 2(d) [Figure 2: see original paper]).

The film morphology remained unchanged during AgNCs@PE-g-PAA synthesis, indicating that the synthesis process did not cause serious matrix damage, enhancing the method' s universality. The matrix material used was commercial PE film comprising a nonpolar -CH_2-CH_2- structure. The contact angle of commercial PE film was 97° (Fig. 3(a) and 3(b) [Figure 3: see original paper]), indicating hydrophobicity. After PAA grafting, the PE-g-PAA contact angle decreased to 80° due to the strong polarity of PAA carboxyl groups, making the material hydrophilic and facilitating subsequent Ag^+ ion adsorption from aqueous solution for AgNC loading. After AgNC loading, the AgNCs@PE-g-PAA film contact angle further decreased to 58° (Fig. 3(b) [Figure 3: see original paper]). The combination of AgNCs with carboxyl groups on PAA chains increased material polarity and hydrophilicity [45], enabling the AgNCs@PE-g-PAA film to detect metal ions in aqueous solutions.

Thermal analysis using TG and DSC further investigated material changes during synthesis. The PE thermogravimetric curve (Fig. 4(a) [Figure 4: see original paper]) shows mass loss at 468.8 °C due to polymer backbone decomposition. After PAA grafting, PE-g-PAA exhibited additional mass loss at 170 °C from dehydration of adjacent carboxyl groups to form anhydride [29]. The AgNCs@PE-g-PAA film thermal decomposition curve was almost identical to that of PE-g-PAA. The maximum thermal decomposition temperature was 472.5 °C for PE-g-PAA and 462.2 °C for AgNCs@PE-g-PAA, with final weight loss of ~70%. The mass percentage difference between AgNCs@PE-g-PAA and PE-g-PAA was consistent with the AgNC loading degree. The DSC scan (Fig. 4(b) [Figure 4: see original paper]) shows a slight melting point decrease after AA grafting, with no further change after AgNC loading, indicating minimal matrix damage during synthesis. Additionally, the PE film melting enthalpy gradually decreased with AA grafting and AgNC loading (Fig. 4(b) [Figure 4: see original paper]), suggesting that the crystal region was disrupted by irradiation, though this did not affect its application as a metal ion sensor.

3.2 Fluorescence Properties of AgNCs@PE-g-PAA

Unlike larger AgNPs, bright fluorescence emission is unique to AgNCs. Under 365 nm UV light, AgNCs@PE-g-PAA produced bright red fluorescence (Scheme 1). Upon 540 nm excitation, AgNCs@PE-g-PAA exhibited maximum fluores-

cence at 650 nm (Fig. S4(a)). Compared to conventional organic dyes, silver nanoclusters have larger Stokes shifts, beneficial for improving identification efficiency [15]. Moreover, since the AgNC excitation wavelength falls within the visible light range, AgNCs@PE-g-PAA could still be excited under natural light, appearing light red (Scheme 1), facilitating visual ion detection by film materials under natural light. The quantum yield of AgNCs@PE-g-PAA was 0.125, comparable to AgNCs reported elsewhere [46]. The excited-state decay profile (Fig. S4(c)) revealed a fluorescence lifetime of 1.43 ns for AgNCs. The nanosecond fluorescence lifetime indicates photoluminescence rather than phosphorescence, with excited electrons returning directly to the ground state without passing through the triplet state [15].

Notably, the fluorescence emission of synthesized AgNCs@PE-g-PAA films was excitation-wavelength dependent. Under 480 nm excitation, the film presented two fluorescence peaks at 640 nm and 730 nm, with the 730 nm peak being stronger (Fig. S4(b)). As excitation wavelength increased, the long-wavelength emission peak gradually weakened while the short-wavelength peak strengthened, eventually resolving to only the short-wavelength emission. With increasing excitation wavelength, the short-wavelength emission peak maximum gradually red-shifted and its intensity initially increased, then decreased slightly when excitation exceeded 530 nm (Fig. S4(b)). This indicates that AgNC fluorescence emission on AgNCs@PE-g-PAA film originated from AgNCs containing different numbers of silver atoms. The failure to form monodisperse AgNCs may be attributed to the polymer template, which hindered fixed structure formation, consistent with AgNCs formed using other polymer templates [44].

3.3 Detection of Cr^{3+}

Trivalent chromium (Cr^{3+}) is an important environmental pollutant widely used in industry and agriculture [47], necessitating low-cost detection methods. Based on the bright fluorescence of AgNCs, AgNCs@PE-g-PAA film can serve as fluorescent test paper for metal ion detection. When exposed to Cr^{3+}, the film fluorescence was quenched (Fig. 5(a) [Figure 5: see original paper]), demonstrating its potential as a Cr^{3+} detection platform.

The degree of fluorescence quenching depended on Cr^{3+} concentration (Fig. 5(a) and 5(b) [Figure 5: see original paper]). At low Cr^{3+} concentrations, fluorescence did not change significantly, with minimal intensity decrease at 650 nm. When Cr^{3+} concentration exceeded 10^{-4} M, fluorescence intensity decreased dramatically (Fig. 5(b) [Figure 5: see original paper]). The fluorescence quenching time varied with Cr^{3+} concentration, occurring more rapidly at higher concentrations (Fig. S5). Even at low Cr^{3+} concentrations, the synthesized film could detect Cr^{3+} within 3 h (Fig. S5).

Selectivity evaluation against other common metal ions (Fe^{3+}, Cu^{2+}, Al^{3+}, and Hg^{2+}) at Cr^{3+} response concentrations revealed that under 365 nm UV light, only films exposed to Cr^{3+} and Fe^{3+} lost fluorescence, while others retained

bright fluorescence (Fig. 5(c) [Figure 5: see original paper]). Compared to the control, films exposed to Fe^{3+} and Cr^{3+} showed fluorescence intensity decreases by an order of magnitude, with Cr^{3+} causing the most significant reduction (Fig. 5(d) [Figure 5: see original paper]). In natural light, AgNCs@PE-g-PAA appeared yellow with iron ions and blue with chromium ions (Fig. S6), demonstrating good Cr^{3+} selectivity through both color change and fluorescence quenching. Reliability testing using domestic water instead of deionized water confirmed that AgNCs@PE-g-PAA could detect Cr^{3+} in complex ionic environments (Fig. S7).

As shown in Table 1 , compared to other methods such as AAS and ICP-MS, AgNCs@PE-g-PAA detection performance still shows a significant gap. However, these traditional methods often require complex pretreatment processes and laboratory conditions. The low requirements for original samples and testing environments represent advantages of AgNCs@PE-g-PAA for ion detection, confirming its good Cr^{3+} selectivity and suitability as a test paper for Cr^{3+} detection.

Table 1. Comparison of different Cr^{3+} detection methods

Method	Test substance	Detection limit
Resonance Rayleigh scattering	Cr^{3+}	2–4 pM
CEC-ICPMS	Cr^{3+}	1.0 pM
LA-ICPMS	Cr^{3+}	<0.02 M
Ion interaction chromatography	Cr^{3+}	0.02 mM
Electrochemistry	Cr^{3+}	0.4 M
Atomic absorption spectrometry	Cr^{3+}	4.1 nM
AgNCs@PE-g-PAA (This work)	Cr^{3+}	3.8 nM

3.4 Detection Mechanism

The mechanism underlying AgNCs@PE-g-PAA detection of Cr^{3+} was investigated. Unlike AgNC solutions where dynamic quenching can occur, the AgNCs in AgNCs@PE-g-PAA films are immobilized on the film surface, making interparticle contact difficult and dynamic quenching unlikely. In UV-vis spectra (Fig. 6(a) [Figure 6: see original paper]), the AgNC absorption peak at 500 nm disappeared after Cr^{3+} treatment, indicating that Cr^{3+} introduction formed a new complex that altered AgNC light absorption. Based on this analysis, Cr^{3+} quenches AgNC fluorescence via a static quenching mechanism.

AgNCs@PE-g-PAA contains numerous carboxyl groups with strong coordination ability for metal ions [39]. Cr^{3+} ions in solution can be captured and adsorbed by these carboxyl groups. The XPS profile (Fig. 6(b) [Figure 6: see original paper]) shows an intense Cr absorption peak on the AgNCs@PE-g-PAA film surface after Cr^{3+} treatment, confirming effective Cr^{3+} adsorption. The carboxyl groups in AgNCs@PE-g-PAA also stabilize AgNCs through coordination. When the film was immersed in Cr^{3+} solution, Cr^{3+} was adsorbed

onto AgNCs@PE-g-PAA via carboxyl groups, forming a non-fluorescent Cr^{3+}-AgNCs@PE-g-PAA complex that quenched AgNC fluorescence. The oxygen chemical state in AgNCs@PE-g-PAA differed significantly from PE-g-PAA due to carboxyl group coordination with AgNCs (Fig. 1(e) [Figure 1: see original paper] vs. Fig. 1(f) [Figure 1: see original paper]). After Cr^{3+} adsorption, a new low-intensity peak appeared in the XPS O1s spectrum (Fig. 6(c) [Figure 6: see original paper]), attributed to Cr-O bonding. The unchanged Ag chemical state after Cr^{3+} adsorption (Fig. 6(d) [Figure 6: see original paper]) indicates that Cr^{3+} did not directly contact AgNCs, confirming that Cr^{3+}-AgNCs@PE-g-PAA complex formation caused static fluorescence quenching.

CONCLUSIONS

In summary, AgNCs@PE-g-PAA films were synthesized via a two-step irradiation process. First, a poly(acrylic acid) (PAA) template was grafted onto PE by irradiation to obtain PE-g-PAA template material. Second, Ag^{+} ions were reduced in situ on the PE-g-PAA film by irradiation to obtain AgNCs@PE-g-PAA. The loading degree was controlled by varying reaction conditions, yielding extremely small, uniformly distributed AgNCs on the film. AgNCs@PE-g-PAA exhibited clear red fluorescence emission derived from AgNCs, which was quenched by Cr^{3+}, enabling the system to function as a test paper for Cr^{3+} detection via a static quenching mechanism. This irradiation technique provides a simple, controllable method for loading AgNCs onto solid materials, improving approaches for immobilizing metal nanoclusters on various matrices and expanding the practical applications of metal nanoclusters.

AUTHOR CONTRIBUTIONS

All authors contributed to study conception and design. Material preparation, data collection, and analysis were performed by Fei Han, Wen-Rui Wang, Dan-Yi Li, Mou-Hua Wang, and Ji-Hao Li. The first draft was written by Fei Han under the guidance of Lin-Fan Li, and all authors commented on previous versions. All authors read and approved the final manuscript.

DATA AVAILABILITY STATEMENT

The data supporting this study are openly available in Science Data at http://resolve.pid21.cn/31253.11.sciencedb.j00186.0007 and https://www.doi.org/10.57760/sciencedb.j00186.0

REFERENCES

[1] C.-C. Hsu, Y.-Y. Chao, S.-W. Wang, et al. Polyethylenimine-capped silver nanoclusters as fluorescent sensors for the rapid detection of ellagic acid in cosmetics. Talanta. 204. (2019). doi: 10.1016/j.talanta.2019.06.047
[2] L. Lu, X. An and W. Huang. Quantitative determination of calcium ions by means of enhanced fluorescence of silver nanocluster complex. Analytical

Methods. 9. 1 (2017). doi: 10.1039/C6AY02477G
[3] Y. Tang, Y. Zhang, Y. Su, et al. Highly sensitive resonance light scattering bioassay for heparin based on polyethyleneimine-capped Ag nanoclusters. Talanta. 115. (2013). doi: 10.1016/j.talanta.2013.06.028
[4] J. Yang and R. C. Jin. New Advances in Atomically Precise Silver Nanoclusters. ACS Mater. Lett. 1. 4 (2019). doi: 10.1021/acsmaterialslett.9b00246
[5] L. Shang, S. J. Dong and G. U. Nienhaus. Ultra-small fluorescent metal nanoclusters: Synthesis and biological applications. Nano Today. 6. 4 (2011). doi: 10.1016/j.nantod.2011.06.004
[6] L. B. Zhang and E. K. Wang. Metal nanoclusters: New fluorescent probes for sensors and bioimaging. Nano Today. 9. 1 (2014). doi: 10.1016/j.nantod.2014.02.010
[7] H. Haidari, R. Bright, Z. Kopecki, et al. Polycationic Silver Nanoclusters Comprising Nanoreservoirs of Ag^{+} Ions with High Antimicrobial and Antibiofilm Activity. Acs Appl Mater Inter. 14, 1 (2021). doi: 10.1021/acsami.1c21657
[8] Y. M. Su, X. Y. Li, Z. Wang, et al. Structural rearrangement of Ag-60 nanocluster endowing different luminescence performances. J. Chem. Phys. 155. 23 (2021). doi: 10.1063/5.0070138
[9] S. Ghosh, U. Anand and S. Mukherjee. Luminescent Silver Nanoclusters Acting as a Label-Free Photoswitch in Metal Ion Sensing. Anal. Chem. 86. 6 (2014). doi: 10.1021/ac500122v
[10] H. Chen, Y. Li, Y. Song, et al. A sandwich-type electrochemical immunosensor based on spherical nucleic acids-templated Ag nanoclusters for ultrasensitive detection of tumor biomarker. Biosensors and Bioelectronics. 223. (2023). doi: 10.1016/j.bios.2022.115029
[11] Y. Jiang and P. Miao. DNA dumbbell and chameleon silver nanoclusters for mirna logic operations. Research. 2020. (2020). doi: 10.34133/2020/1091605
[12] K. Zheng, X. Yuan, N. Goswami, et al. Recent advances in the synthesis, characterization, and biomedical applications of ultrasmall thiolated silver nanoclusters. Rsc Adv. 4. 105 (2014). doi: 10.1039/c4ra12054j
[13] S. Choi, Y. Zhao and J. Yu. Generation of luminescent silver nanodots in the presence of amino silane and sodium polyacrylate. J. Photochem. Photobiol. A-Chem. 374. (2019). doi: 10.1016/j.jphotochem.2019.01.018
[14] Z. Shen, H. W. Duan and H. Frey. Water-soluble fluorescent Ag nanoclusters obtained from multiarm star poly(acrylic acid) as "molecular hydrogel" templates. Advanced Materials. 19. 3 (2007). doi: 10.1002/adma.200601740
[15] H. X. Xu and K. S. Suslick. Sonochemical Synthesis of Highly Fluorescent Ag Nanoclusters. Acs Nano. 4. 6 (2010). doi: 10.1021/nn100987k
[16] J. V. Rojas and C. H. Castano. Radiation-assisted synthesis of iridium and rhodium nanoparticles supported on polyvinylpyrrolidone. J Radioanal Nucl Ch. 302. 1 (2014). doi: 10.1007/s10967-014-3291-y
[17] A. A. Zezin, D. I. Klimov, E. A. Zezina, et al. Controlled radiation-chemical synthesis of metal polymer nanocomposites in the films of interpolyelectrolyte complexes: Principles, prospects and implications. Radiat Phys Chem. 169. (2020). doi: 10.1016/j.radphyschem.2018.11.030

[18] S. Strohmaier and G. Zwierzchowski. Comparison of Co-60 and Ir-192 sources in HDR brachytherapy. J. Contemp. Brachytherapy. 3. 4 (2011). doi: 10.5114/jcb.2011.26471
[19] F. Han, J. Li, W. Wang, et al. Synthesis of silver nanoclusters by irradiation reduction and detection of Cr(3+) ions. Rsc Adv. 12. 51 (2022). doi: 10.1039/d2ra06536c
[20] I. Diez and R. H. A. Ras. Fluorescent silver nanoclusters. Nanoscale. 3. 5 (2011). doi: 10.1039/c1nr00006c
[21] L. S. Ardekani, T. T. Moghadam, P. W. Thulstrup, et al. Design and Fabrication of a Silver Nanocluster-Based Aptasensor for Lysozyme Detection. Plasmonics. 14. 6 (2019). doi: 10.1007/s11468-019-00954-5
[22] Q. L. Wen, J. Peng, A. Y. Liu, et al. DNA bioassays based on the fluorescence 'turn off' of silver nanocluster beacon. Luminescence. 35. 5 (2020). doi: 10.1002/bio.3775
[23] D. Li, B. Li, G. Lee, et al. Facile Synthesis of Fluorescent Silver Nanoclusters as Simultaneous Detection and Remediation for Hg^{2+}. Bull. Korean Chem. Soc. 36. 6 (2015). doi: 10.1002/bkcs.10294
[24] J. H. Chen, X. Zhang, S. X. Cai, et al. A fluorescent aptasensor based on DNA-scaffolded silver-nanocluster for ochratoxin A detection. Biosens. Bioelectron. 57. (2014). doi: 10.1016/j.bios.2014.02.001
[25] Q. Qiu, R. R. Gao, A. M. Xie, et al. A ratiometric fluorescent sensor with different DNA-templated Ag NCs as signals for ATP detection. J. Photochem. Photobiol. A-Chem. 400. (2020). doi: 10.1016/j.jphotochem.2020.112725
[26] D. T. Lu, Z. Chen, Y. F. Li, et al. Determination of Mercury(II) by Fluorescence Using Deoxyribonucleic Acid Stabilized Silver Nanoclusters. Anal. Lett. 48. 2 (2015). doi: 10.1080/00032719.2014.940527
[27] J. H. Geng, C. Yao, X. H. Kou, et al. A Fluorescent Biofunctional DNA Hydrogel Prepared by Enzymatic Polymerization. Advanced Healthcare Materials. 7. 5 (2018). doi: 10.1002/adhm.201700998
[28] Y. Y. Wang, S. S. Wang, C. S. Lu, et al. Three kinds of DNA-directed nanoclusters cooperating with graphene oxide for assaying mucin 1, carcinoembryonic antigen and cancer antigen 125. Sens. Actuator B-Chem. 262. (2018). doi: 10.1016/j.snb.2018.01.235
[29] H. Oraby, M. M. Senna, M. Elsayed, et al. Fabrication of reverse-osmosis membranes for the desalination of underground water via the gamma-radiation grafting of acrylic acid onto polyethylene films. J Appl Polym Sci. 134. 41 (2017). doi: 10.1002/app.45410
[30] F. X. Sha, G. J. Cheng, Z. Y. Xuan, et al. Free-radical evolution and decay in cross-linked polytetrafluoroethylene irradiated by gamma-rays. Nucl Sci Tech. 33. 5 (2022). doi: 10.1007/s41365-022-01039-5
[31] F. Wang, Q. F. Wu, Y. R. Jiang, et al. Effect of irradiation on temperature performance of dispersion-compensation no-core cascade optical-fiber sensor coated with polydimethylsiloxane film. Nucl Sci Tech. 33. 9 (2022). doi: 10.1007/s41365-
[32] W. Liu and Y. Yu. Removal of recalcitrant trivalent chromium complexes from industrial wastewater under strict discharge standards. Environmental

Technology & Innovation. 23. (2021). doi: 10.1016/j.eti.2021.101644
[33] R. BENCHEIKH-LATMANI, A. OBRAZTSOVA, M. R. MACKEY, et al. Toxicity of Cr(III) to Shewanella sp. Strain MR-4 during Cr(VI) Reduction. Environ. Sci. Technol. 41. 41 (2007). doi: 10.1021/es0622655
[34] M. Chen, Y. Liu, H. Cao, et al. The secondary and aggregation structural changes of BSA induced by trivalent chromium: A biophysical study. Journal of Luminescence. 158. (2015). doi: 10.1016/j.jlumin.2014.09.021
[35] J. Wang, N. Graham, K. Sun, et al. Ultra-low concentrations of detection for fluoride and trivalent chromium ions by multiple biomimetic nanochannels in a PET membrane. Journal of Cleaner Production. 389. (2023). doi: 10.1016/j.jclepro.2023.136055
[36] Y. Ye, H. Liu, L. Yang, et al. Sensitive and selective SERS probe for trivalent chromium detection using citrate attached gold nanoparticles. Nanoscale. 4. 20 (2012). doi: 10.1039/C2NR31985C
[37] S. H. Ren, S. G. Liu, Y. Ling, et al. Fabrication of silver nanoclusters with enhanced fluorescence triggered by ethanol solvent: a selective fluorescent probe for Cr^{3+} detection. Anal. Bioanal. Chem. 411. 15 (2019). doi: 10.1007/s00216-019-
[38] K. I. Kim, S. H. Oh, H. D. Kwen, et al. Polymer-copper-modified MWNTs by radiation-induced graft polymerization and their efficient adsorption of odorous gases. J Appl Polym Sci. 126. (2012). doi: 10.1002/app.35453
[39] D. I. Klimov, E. A. Zezina, S. B. Zezin, et al. Radiation-induced preparation of bimetallic nanoparticles in the films of interpolyelectrolyte complexes. Radiat Phys Chem. 142. (2018). doi: 10.1016/j.radphyschem.2017.02.034
[40] J. Y. He, X. Shang, C. L. Yang, et al. Antibody-Responsive Ratiometric Fluorescence Biosensing of Biemissive Silver Nanoclusters Wrapped in Switchable DNA Tweezers. Anal. Chem. 93. 33 (2021). doi: 10.1021/acs.analchem.1c02444
[41] S. Jin, W. Liu, D. Q. Hu, et al. Aggregation-Induced Emission (AIE) in Ag-Au Bimetallic Nanocluster. Chem.-Eur. J. 24. 15 (2018). doi: 10.1002/chem.201800189
[42] M. Ma and S. Zhu. Grafting polyelectrolytes onto polyacrylamide for flocculation - 1. Polymer synthesis and characterization. Colloid and Polymer Science. 277. 2-3 (1999). doi: 10.1007/s003960050375
[43] M. N. Z. Abidin, M. M. Nasef and T. Matsuura. Fouling Prevention in Polymeric Membranes by Radiation Induced Graft Copolymerization. Polymers-Basel. 14. 1 (2022). doi: 10.3390/polym14010197
[44] L. Shang and S. J. Dong. Facile preparation of water-soluble fluorescent silver nanoclusters using a polyelectrolyte template. Chemical Communications. 9 (2008). doi: 10.1039/b717728c
[45] L. G. Wang, X. G. Zhang, S. F. Hou, et al. Preparation and Characterization of Hydrophilic PVDF Membrane via graft modification by Acrylic Acid. Univ Jinan, Jinan, PEOPLES R CHINA. 306-307. (2011). doi: 10.4028/www.scientific.net/AMR.306-
[46] Y. L. Li, W. Y. Xi, I. Hussain, et al. Facile preparation of silver nanocluster self-assemblies with aggregation-induced emission by equilibrium shifting.

Nanoscale. 13. 33 (2021). doi: 10.1039/d1nr03445f
[47] S. A. Cavaco, S. Fernandes, M. M. Quina, et al. Removal of chromium from electroplating industry effluents by ion exchange resins. J Hazard Mater. 144. 3 (2007). doi: 10.1016/j.jhazmat.2007.01.087
[48] M. Chen, H.-H. Cai, F. Yang, et al. Highly sensitive detection of chromium (III) ions by resonance Rayleigh scattering enhanced by gold nanoparticles. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 118. (2014). doi: 10.1016/j.saa.2013.09.058
[49] W.-H. Chen, S.-Y. Lin and C.-Y. Liu. Capillary electrochromatographic separation of metal ion species with on-line detection by inductively coupled plasma mass spectrometry. Analytica Chimica Acta. 410. 1 (2000). doi: 10.1016/S0003-2670(00)00713-3
[50] J. P. Lafleur and E. D. Salin. Speciation of Chromium by High-Performance Thin-Layer Chromatography with Direct Determination by Laser Ablation Inductively Coupled Plasma Mass Spectrometry. Anal. Chem. 80. 17 (2008). doi: 10.1021/ac8010582
[51] J. Threeprom, S. Purachaka and L. Potipan. Simultaneous determination of Cr(III)-EDTA and Cr(VI) by ion interaction chromatography using a C18 column. Journal of Chromatography A. 1073. 1 (2005). doi: 10.1016/j.chroma.2004.09.053
[52] R. M. Cespón-Romero, M. C. Yebra-Biurrun and M. P. Bermejo-Barrera. Preconcentration and speciation of chromium by the determination of total chromium and chromium(III) in natural waters by flame atomic absorption spectrometry with a chelating ion-exchange flow injection system. Analytica Chimica Acta. 327. 1 (1996). doi: 10.1016/S0003-2670(96)00062-1

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