

Boosting Photocatalytic Free Cyanide Degradation Through Hydrogen Co-Reduction of Graphene Oxide/TiO₂ Composites

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Abstract

This study investigates the synthesis of anatase TiO_2 coupled with laboratory-synthesized graphene oxide (GO) and evaluates the influence of GO loading (0.1, 0.3, and 0.5 wt%) on the photocatalytic oxidation of cyanide in aqueous solution. Among the composites examined, the 0.3 wt% GO/ TiO_2 material exhibited the highest photocatalytic activity, achieving complete oxidation of free cyanide within 210 min, including a 30 min adsorption stage. The effect of reductive treatment on both pristine TiO_2 and GO/ TiO_2 composites was also investigated, revealing a significant enhancement in photocatalytic performance. Reduced TiO_2 (TiO_{2-x}) achieved complete cyanide oxidation within 150 min, while the simultaneously reduced 0.3 wt% rGO/ TiO_{2-x} composite demonstrated the best performance, reaching complete oxidation in only 90 min.

The stability of the reduced composite was assessed over three consecutive photocatalytic cycles. Compared with the initial cycle, the photocatalytic activity decreased by 10% and 18% during the second and third cycles, respectively. Post-reaction characterization revealed surface functionalization through the formation of amide groups, attributed to the interaction between cyanate species, generated during cyanide oxidation, and residual oxygen-containing functionalities on the reduced graphene oxide. The simultaneous reductive treatment promoted structural and surface modifications in the rGO/ TiO_{2-x} composite, increasing the availability of active adsorption sites and enhancing cyanate uptake. The results demonstrate a strong synergistic effect between GO incorporation into TiO_2 and hydrogen co-reduction, leading to improved charge separation, enhanced adsorption capacity, and superior photocatalytic efficiency for cyanide remediation.

1. Introduction

The presence of free cyanide in wastewater poses a severe environmental and public health challenge due to its acute toxicity, potential for bioaccumulation, and persistent threat to ecosystems and human well-being [1, 2]. Industrial activities, such as mining, electroplating, chemical synthesis, and metal processing, are primary sources of cyanide contamination, as cyanide is widely used as a reagent in these sectors [3, 4]. In gold mining, for example, cyanide leaching is a standard method for gold extraction, generating cyanide-laden wastewater that is often stored in tailings dams. Poor management of these dams can lead to catastrophic environmental contamination of soil and water resources [5–7].

Addressing cyanide pollution requires a multifaceted approach that combines effective treatment technologies, stringent regulatory frameworks, and proactive management strategies to mitigate its ecological and health impacts [4]. Current and emerging cyanide remediation methods can be classified into five categories: chemical (e.g., alkaline chlorination, ozonation, hydrogen peroxide oxidation); physical (e.g., adsorption, membrane filtration); biological (e.g., bacterial, fungal, or enzyme-based degradation); electrochemical (e.g., electrooxidation, electrocoagulation); and photocatalytic (e.g., semiconductor-mediated processes using TiO_2 and other photocatalysts) [3, 8–12].

Despite decades of research, with nearly 150 published articles on the topic (1980–present, Scopus), photocatalytic degradation of free cyanide remains underdeveloped, with most studies focusing on TiO₂-based catalysts. The ideal outcome is the complete mineralization of cyanide ($2\text{CN}^- + 2\text{O}_2 + h\nu \rightarrow 2\text{CO}_2 + \text{N}_2$) via photogenerated hydroxyl radicals and holes [13]. However, the reaction mechanism, particularly the roles of hydroxyl radicals and holes in converting cyanide to intermediates (e.g., cyanate) or achieving full mineralization, has been the subject of various interpretations. While pilot-scale tests using real wastewater and TiO₂ catalysts have been conducted, no scalable industrial photocatalytic process for treating free cyanide currently exists.

Existing catalytic materials often fail to meet the three critical criteria for industrial application: high photocatalytic activity, long-term stability, and non-toxic byproducts [10]. Notably, carbonaceous materials like graphene, which have shown promise in other photocatalytic applications, have been rarely explored for cyanide degradation [3, 14]. Graphene oxide (GO) offers unique advantages as a dopant for semiconductors such as TiO₂, which often suffer from rapid charge recombination. GO's functional groups enable it to act as an electron trap, facilitating the generation of reactive oxygen species (e.g., superoxide radicals ($\text{O}_2^{\bullet-}$), hydrogen peroxide (H_2O_2), and hydroxyl radicals ($\text{HO}^\bullet$)), thereby enhancing oxidative performance [3]. The reduction of GO is a critical step in composite formation, as it determines the final oxidation level, which is influenced by synthesis and post-treatment methods [15, 16]. Interestingly, residual functional groups and structural defects, though typically unavoidable, can paradoxically improve photocatalytic activity, leading many studies to focus on reducing GO either before or during composite synthesis [17].

The primary methods for reducing graphene oxide (GO) to reduced graphene oxide (rGO) include thermal, chemical, electrochemical reduction, and photochemical reduction. These processes significantly restore the material's electrical conductivity, mechanical strength, and hydrophobicity by removing oxygen-containing functional groups [18]. In particular, the thermal reduction consists of heating GO at high temperatures (200–1000°C) in a vacuum or an inert or hydrogen atmosphere, removing oxygen groups as CO₂ and H₂O [19]. This method offers the advantage of controlling the heating rate and duration, enabling the production of reduced graphene oxide (rGO) with diverse surface compositions.

In prior research, our group demonstrated that pristine GO could degrade ~ 80% of free cyanide (50 mg/L) in water within 400 minutes, primarily forming surface-bound amide species (CONH₂) with minimal cyanate (CNO⁻) detected [20]. Building on this, we synthesized reduced GO/TiO₂ (rGO/TiO₂) composites using TiO₂ P25, which outperformed pristine GO or TiO₂ alone due to strong GO-TiO₂ interactions, confirmed by Raman, FTIR, UV-Vis, and photoluminescence analyses. These interactions reduced charge recombination, enhanced UV activation, and improved charge transfer, leading to superior cyanide degradation [21]. Recently, we further modified the anatase phase of TiO₂ via hydrogen treatment, producing grey TiO₂ with significantly higher activity and stability for free-cyanide degradation [19].

This study explores the synthesis of rGO/TiO_{2-x} composites via the co-reduction of graphene oxide and anatase, testing various GO loadings (0.1%, 0.3%, and 0.5%) for cyanide (CN⁻) degradation. While reduced TiO₂ alone required 150 minutes for complete cyanide oxidation, the 0.3% rGO/TiO_{2-x} composite achieved full degradation in just 90 minutes, demonstrating its enhanced photocatalytic performance.

2. Materials and Methods

2.1 Chemicals and Reagents

All chemicals were used as received without further purification: Potassium cyanide (KCN, Aldrich), Titanium dioxide (anatase TiO₂, Aldrich), Potassium hydroxide (KOH, Riedel-de Haën), Boric acid (H₃BO₃, Ensure), Industrial-grade graphite, Sulfuric acid (H₂SO₄, Fermont), Potassium permanganate (KMnO₄, J.T. Baker), Hydrogen peroxide (H₂O₂, Sigma-Aldrich).

2.2 Synthesis of rGO/TiO_{2-x} composites

Graphene oxide (GO) was synthesized utilizing the Hummers method [22]. A specified amount of the GO powder was dispersed in deionized water, magnetically stirred for 30 minutes, and sonicated for 10 minutes to achieve a homogeneous suspension. This suspension was transferred to a Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 180°C for 20 h. After cooling to room temperature, the solid product was collected, thoroughly washed with deionized water, and dried at 100°C for 12 h. The weight percentages of GO in the composites were 0.1, 0.3, and 0.5; the samples were labeled as follows: TiGO.1, TiGO.3, and TiGO.5. Additionally, the 0.3% wt GO/TiO₂ composite was thermally reduced in a quartz tube reactor under a 10% v/v H₂/Ar atmosphere at a flow rate of 50 mL/min (STP). The thermal reduction was conducted at 600°C for 2 h with a heating rate of 10°C/min. The resulting sample was designated as TiGO.36.

2.3 Characterization Techniques

Fourier-transform infrared (FTIR) spectra were recorded on a NEXUS spectrometer (Thermo Scientific, Waltham, MA, USA) using the KBr pellet transmission technique over a range of 4000 to 400 cm⁻¹. Raman spectroscopy was performed using an InVia Renishaw system (Renishaw plc, Gloucestershire, UK) equipped with a cooled CCD detector (-73°C) and a holographic super-Notch filter. Samples were excited using a 532 nm Ar laser line; spectra were acquired with a resolution of ~4 cm⁻¹ through 5 accumulations of 10 s each. X-ray diffraction (XRD) patterns were collected on a Bruker D2 Phaser 2nd Gen diffractometer using Cu Kα radiation (λ = 1.5406 Å) at 30 kV and 10 mA, over a 2θ range of 5° to 80°.

Electrochemical measurements were conducted in a three-electrode cell using a Gamry Instruments Reference 3000 potentiostat, with a 30 mg/L KCN aqueous solution serving as the supporting electrolyte. Ag/AgCl (in KCl) and a graphite foil were used as the reference and counter electrodes, respectively. The working electrodes were prepared by depositing catalyst films onto cleaned fluorine-

doped tin oxide (FTO) glass. Briefly, 3 mg of each catalyst was dispersed in 200 μL of a Nafion/ethanol solution and vigorously stirred to form a homogeneous suspension. An 80 μL aliquot of this suspension was drop-cast onto a 1×1 cm FTO substrate and dried at room temperature. A second 80 μL coating was applied to ensure uniform distribution, after which the FTO glass was annealed in an oven at 70°C for 1 h.

Open-circuit potential (OCP) was measured over two cycles, alternating between dark conditions (180 s) and illumination (120 s) using a 100 W Hg arc lamp. Linear sweep voltammetry (LSV) was performed from 0.6 to -0.6 V using 50 mV steps, incorporating multiple illumination cycles.

2.4 Photocatalytic Activity Evaluation

A 30 mg/L solution of free cyanide was prepared in deionized water, and the pH was adjusted and strictly maintained at 12.0 using potassium hydroxide (KOH). Photocatalytic tests were conducted by adding 50 mg of the composite material to 50 mL of the free cyanide solution in a batch reactor, yielding a catalyst concentration of 1 g/L. The suspension was sonicated for 10 minutes and transferred to a Luzchem photoreactor. To establish adsorption-desorption equilibrium, the mixture was magnetically stirred in complete darkness for 30 minutes. An initial aliquot was collected before activating the UV lamps to initiate photocatalytic oxidation. Subsequent samples were collected every 30 minutes over a 4-h period. All samples were filtered through a $0.45 \mu\text{m}$ Millipore microdisk before analysis.

Free cyanide concentration was quantified via pulse voltammetry on a Metrohm 797 VA polarograph equipped with a three-electrode system: a mercury drop working electrode, a platinum auxiliary electrode, and an Ag/AgCl reference electrode. For the analysis, 100 μL of the filtered sample was mixed with 10 mL of a supporting electrolyte (KOH and boric acid) and purged with nitrogen for 300 seconds to remove dissolved oxygen and prevent interference. Concentrations were determined using a previously established standard calibration curve.

The primary oxidation product, cyanate, was monitored spectrophotometrically utilizing the anthranilic acid method [20]. Briefly, 0.5 mL of the sample was mixed with 0.5 mL of a 0.01 M anthranilic acid solution and heated at 40°C for 10 minutes. After cooling, 1.0 mL of 6 N HCl was added. The solution was immersed in a boiling water bath for one minute to complete the reaction. Cyanate was quantified by measuring the absorbance of the resulting complex at 310 nm against a calibration curve.

To identify the primary reactive species involved in photocatalytic oxidation, scavenger experiments were performed under identical operating conditions to the standard degradation tests. Specific scavengers (0.01 M) were introduced into the initial suspension: tert-butyl alcohol for hydroxyl radicals, ascorbic acid for superoxide radicals, sodium persulfate for electrons, and EDTA for holes. Sampling and analysis protocols remained consistent with those used in the primary experiments to determine the individual contribution of each reactive species.

3. Results and discussion

The TPR profiles, presented in Fig. 1a, compare pure TiO_2 (Ti, red line) with the 0.3 wt.% GO/ TiO_2 composite (TiGO.3, blue line). Pure TiO_2 shows only a weak hydrogen consumption signal, mainly above 500 °C. This behavior is expected because anatase TiO_2 is generally difficult to reduce, and reduction of lattice oxygen typically occurs at elevated temperatures [19]. The composite exhibits substantially higher hydrogen consumption over the entire temperature range. Different reduction regions can be distinguished for TiGO.3: (i) Low-temperature region ($\approx 250\text{--}350$ °C), a broad peak centered around 300 °C; and (ii) Intermediate-temperature region (400–600 °C). Nowadays, the reduction mechanisms of GO under thermal annealing are still under debate. The hydrogen consumption observed in this sample can be related to the reduction of oxygen-containing functional groups present on graphene oxide (epoxy, hydroxyl, carbonyl, and carboxyl groups) [23–27]. Moreover, there are only a few works related to the reduction of GO by thermal annealing under hydrogen flow, suggesting that this reductive atmosphere (H_2) can improve the structural quality of GO, diminishing overall defects as the temperature is increased [28]. These findings suggest that sp^2 character of GO is restored by using this reductive method [28].

The structural properties of the synthesized composites were evaluated by X-ray diffraction (XRD). The diffraction patterns shown in Fig. 1(b) revealed no significant changes in peak positions among the composites containing different GO loadings, except for a low-intensity diffraction peak assigned to the (001) plane of GO. This result indicates that GO incorporation did not modify the crystalline structure of the TiO_2 matrix. All samples exhibited well-defined diffraction peaks at 2θ values of 25.3° , 37.8° , 48.0° , 53.9° , 55.0° , 62.7° , and 75.0° , corresponding to the (101), (004), (200), (105), (211), (204), and (215) crystallographic planes of the anatase TiO_2 (JCPDS Card No. 21-1272), respectively. Also, a small diffraction peak was observed at approximately 27.4° , which can be attributed to the (110) plane of the rutile TiO_2 (JCPDS Card No. 21-1276). These results confirm that anatase is the predominant crystalline TiO_2 phase, consistent with the specifications for commercial TiO_2 (98% anatase). The preservation of the diffraction pattern across all composites confirms that the crystal structure of TiO_2 remained intact throughout the synthesis process.

The XRD pattern of the reduced sample 0TiGO.36 showed no significant shifts in peak position or changes in the characteristic anatase reflections. These results indicate that the reduction treatment did not alter the crystalline phase of TiO_2 , highlighting the thermal stability of the anatase structure under the applied reduction conditions.

Raman spectroscopy was performed to analyze the characteristic signals of the TiO_2 crystalline phases, with all patterns displaying the expected five Raman-active modes of anatase. These modes were observed at 637 cm^{-1} (E_g), 514 cm^{-1} ($\text{A}_{1g} + \text{B}_{1g}$), 395 cm^{-1} (B_{1g}), 194 cm^{-1} (E_g), and 144 cm^{-1} (E_g) [19], as shown in Figure 2b. The D band, associated with disordered carbon structures such as defects and oxygen-containing functional groups on graphene oxide (GO), is characterized by A_{1g} symmetry, indicating sp^3 carbon bonds. Meanwhile, the G band corresponds to the first order scattering of the E_{2g} mode, signifying sp^2 -bonded carbon or ordered carbon structures.

All GO/TiO₂ composites exhibited both D and G bands in their Raman spectra. The most pronounced signals were observed in Ti6G0.3 and TiG0.36 composites. For Ti6G0.3 and other composites (TiG0.1 and TiG0.5), the D band was more intense than the G band, suggesting a higher degree of disorder in their carbon structures. In contrast, TiG0.36 exhibited a more intense G band than D, indicating a more ordered carbon structure, likely due to the reduction process in this composite. The I_D/I_G ratio for TiG0.36 was less than one, further confirming the higher order of its carbon structure. The reduction treatment improved the structural order and enhanced the surface area and electrical conductivity of the reduced graphene oxide (rGO) [29–31].

The photoelectrochemical behavior of the synthesized composites was evaluated by open-circuit potential (OCP) measurements in a 30-ppm cyanide solution under alternating dark and illumination conditions (Figure 2c). Upon irradiation, all samples exhibited a shift of the OCP toward more negative potential, confirming the n-type semiconducting nature of the materials. This negative displacement indicates the accumulation of photogenerated electrons in the semiconductor and the efficient generation of charge carriers under illumination.

The magnitude of the photopotential strongly depended on the incorporation of reduced graphene oxide (rGO). Compared with pristine TiO₂, the TiG0.3 composite exhibited a more than fourfold increase in photopotential, indicating a substantial improvement in charge-separation efficiency. The introduction of rGO promotes electron extraction from the TiO₂ conduction band, suppressing electron-hole recombination. However, increasing the graphene content to TiG0.5 reduced the photopotential enhancement, suggesting that excessive rGO may partially shield the TiO₂ surface from incident light or create additional recombination sites, thereby limiting the photoelectrochemical response.

Among all materials, the thermally reduced composite TiG0.36 exhibited the highest photopotential, exceeding that of pristine TiO₂ by more than eightfold. This remarkable improvement can be attributed to the thermal reduction process, which removes oxygen-containing functional groups from graphene oxide, restores the sp² carbon network, and significantly increases electrical conductivity [32]. Consequently, rGO acts as an efficient electron acceptor and transport pathway, facilitating charge separation and reducing recombination losses.

A slight decrease in the photopotential observed during the second illumination cycle for the rGO-containing materials may be associated with the presence of surface defects or localized electronic states capable of temporarily trapping photogenerated electrons. The accumulation of trapped charges can modify the interfacial electric field and reduce the magnitude of the subsequent photopotential response. Nevertheless, the materials retained a stable and reproducible photoresponse, indicating good photoelectrochemical stability.

The photocurrent behavior of the composites was investigated by linear sweep voltammetry (LSV) under intermittent illumination (Figure 2d). All samples exhibited anodic photocurrent generation, characteristic of n-type semiconductors. The photocurrent intensity increased with applied potential, reflecting

enhanced separation and transport of photogenerated charge carriers. Among the evaluated materials, TiG0.36 displayed the highest photocurrent density throughout the potential range, confirming its superior photoelectrochemical performance. The enhanced photocurrent is consistent with the OCP results and demonstrates that thermal reduction of the graphene-containing composite significantly improves charge carrier separation and transport. The conductive rGO network facilitates electron migration while photogenerated holes remain available at the semiconductor surface to participate in oxidation reactions.

The improved performance of TiG0.36 suggests that photogenerated holes can be efficiently transferred to the electrolyte, where cyanide species are oxidized, while electrons are rapidly transported through the TiO_2 -rGO heterostructure. This efficient charge separation minimizes recombination and promotes photocatalytic oxidation reactions.

The photocatalytic performance of TiO_2 and rGO/ TiO_2 composites was evaluated through the oxidation of free cyanide under UV irradiation at pH 12.0 and a catalyst loading of 1 g L^{-1} . Figure 3a shows the normalized cyanide concentration as a function of irradiation time. During the initial 30 min in the dark, only a slight decrease in cyanide concentration was observed for all materials, indicating that adsorption contributed minimally to cyanide removal and that the subsequent decrease under irradiation was primarily due to photocatalytic oxidation.

Upon UV illumination, all catalysts promoted cyanide degradation; however, significant differences in activity were observed with varying graphene content and thermal treatment. The TiG0.36 composite exhibited the highest photocatalytic activity, achieving nearly complete cyanide removal within approximately 90 min of irradiation. In contrast, pristine TiO_2 and the other TiG composites required substantially longer reaction times and showed lower overall conversion. The enhanced performance of TiG0.36 demonstrates the beneficial effects of incorporating reduced oxide graphene and applying thermal reduction. Furthermore, according to the concentration-versus-time profiles shown in Fig. 3(a), they were well fitted to zero-order kinetics (Table S1), yielding a rate constant of 0.351 mg L^{-1} for the TiG0.36 composite, compared to 0.214 mg L^{-1} for the TiO_2 catalyst reduced to 600°C .

The superior activity of TiG0.36 can be attributed to its improved charge separation and electron transport properties, as evidenced by the photoelectrochemical characterization. The OCP measurements revealed the highest photopotential response for TiG0.36, indicating more efficient accumulation of photogenerated electrons. These characteristics reduce electron-hole recombination and increase the availability of photogenerated holes and reactive oxygen species for cyanide oxidation. The effect of graphene loading is also evident in Figure 3a. While incorporating graphene improves photocatalytic performance relative to pristine TiO_2 , excessive graphene content does not necessarily yield further enhancement. The TiG0.5 sample exhibited lower activity than TiG0.36, suggesting that an optimum graphene concentration exists. At higher loadings, graphene sheets may partially shield the TiO_2 surface from incident UV light or cover active sites, thereby reducing photon absorption and limiting photocatalytic efficiency.

The formation of cyanate (CNO^-), shown in Figure 3b, provides direct evidence of cyanide oxidation. For all photocatalysts, the cyanate concentration increased progressively with irradiation time, confirming that cyanide was converted to the less toxic cyanate species rather than merely adsorbed onto the catalyst surface. The TiG0.36 composite exhibited one of the highest cyanate formation rates, consistent with its superior cyanide degradation performance. The simultaneous decrease in cyanide concentration and increase in cyanate concentration suggest that cyanide oxidation follows the well-established pathway [13,33,34]:



The higher cyanate production observed in the thermally reduced composite further supports the conclusion that thermal reduction improves the conductivity of the graphene phase and facilitates interfacial electron transfer, thereby enhancing the kinetics of photocatalytic oxidation. However, a substantial difference between the proposed mechanisms for the degradation of free cyanide and those previously reported was the high reactivity of the surface species present on the rGO/TiO_{2-x} catalyst, which promotes the surface reaction with the cyanate ions to form amides, as shown in Fig.3 (d) [20].

The stability of the most active catalyst, TiG0.36, was evaluated through three consecutive photocatalytic cycles (Figure 3c). Although the catalyst maintained photocatalytic activity after repeated use, cyanide removal efficiency gradually decreased from the first to the third cycle. This decline may be associated with the accumulation of reaction intermediates or oxidation products on the catalyst surface, which can partially block active sites and hinder charge transfer. Despite this decrease, the catalyst retained a significant fraction of its activity after three cycles, indicating reasonable structural stability and resistance to photocorrosion under the operating conditions. These results demonstrate the potential applicability of TiG0.36 for repeated cyanide treatment processes.

The FTIR spectra of TiG0.36 before and after three photocatalytic cycles are presented in Figure 3d. The appearance and increased intensity of bands assigned to amide-type species after reuse suggest the adsorption of nitrogen-containing intermediates or by-products generated during cyanide oxidation. These surface species may contribute to the partial deactivation observed during the recycling tests by occupying active sites and reducing the photocatalyst surface's accessibility. Nevertheless, the overall spectral profile remains largely unchanged after three cycles, indicating that the fundamental structure of the TiO_2/rGO composite is preserved during photocatalytic operation. This result confirms that the

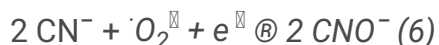
reduction in activity is more likely due to surface fouling rather than to structural degradation of the photocatalyst.

To identify the reactive species involved in the photocatalytic degradation of free cyanide, radical scavenging experiments were conducted using specific quenching agents. Ethylenediaminetetraacetic acid (EDTA), ascorbic acid (AA), tert-butyl alcohol (TBA), and sodium persulfate (PS) were employed as scavengers for holes (h^+), superoxide radicals ($\cdot O_2^-$), hydroxyl radicals ($\cdot OH$), and electrons (e^-), respectively. By selectively suppressing these reactive species, their contributions to the photocatalytic process could be evaluated.

The results of the scavenging experiments are presented in Fig.4. In the absence of any scavenger, the TiGO.36 photocatalyst achieved complete degradation of free cyanide, corresponding to a degradation efficiency of approximately 100%. When sodium persulfate was added, the degradation efficiency remained essentially unchanged, indicating that photogenerated electrons do not play a significant direct role in the oxidation of cyanide under the investigated conditions.

In contrast, the addition of ascorbic acid caused the most pronounced decrease in degradation efficiency, reducing cyanide removal to approximately 65%. This result demonstrates that superoxide radicals ($\cdot O_2^-$) are the dominant reactive species involved in the photocatalytic oxidation process. Similarly, the presence of EDTA and tert-butyl alcohol decreased the degradation efficiency to approximately 75% and 76%, respectively. These reductions confirm that both photogenerated holes (h^+) and hydroxyl radicals ($\cdot OH$) contribute significantly to cyanide degradation, although their influence is less pronounced than that of superoxide radicals.

Overall, the scavenger study reveals that the photocatalytic oxidation of free cyanide over TiGO.36 is primarily governed by superoxide radicals, with additional contributions from hydroxyl radicals and photogenerated holes. The negligible effect of electron scavenging suggests that electrons are not directly involved in the oxidation pathway. These findings indicate a synergistic mechanism in which multiple reactive oxygen species participate in the conversion of free cyanide to cyanate, as reported previously [35].



Conclusions

The photocatalytic performance of the synthesized TiG composites showed a strong correlation with their photoelectrochemical properties. Among all materials evaluated, 0.3 wt. GO/TiO₂ co-reduced with hydrogen at 600°C (TiGO.36) exhibited the highest photocatalytic activity, which was consistent with its superior photoelectrochemical behavior, including the highest photopotential and the greatest photocurrent response. These characteristics indicate more efficient generation, separation, and transport of photogenerated charge carriers, thereby enhancing the availability of oxidative species for cyanide degradation. The close agreement between the photoelectrochemical and photocatalytic results

confirms that thermal co-reduction of the GO/TiO₂ composite is an effective strategy for improving photocatalytic performance, owing to the synergy between rGO and TiO_{2-x} (grey-TiO₂), which promotes the generation of more charge carriers.

Additionally, the composite exhibited the ability to adsorb cyanate and to functionalize its surface, leading to amide groups formation. This process left the water free of contaminants and resulted in a functionalized composite at the end of the photocatalytic reaction. Functionalizing semiconductors remains a crucial strategy in photocatalysis for enhancing their properties and performance. Radical quenching experiments revealed that superoxide radicals ($\cdot\text{O}_2^-$), hydroxyl radicals ($\cdot\text{OH}$), and photogenerated holes (h^+) all contributed to the oxidation process, while electrons played a negligible direct role.

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Author Contribution

Conceptualization: MAV, EAMethodology: EA, LC, JMBA, MYPP, ERGInvestigation: JMBA, MYPP, LAC, ERG, EAFunding acquisition: MAV, EASupervision: EA, LC, JMBA, MYPP, ERGWriting original draft: MAV, EAWriting review & editing: MAV, EA, LC

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Figures

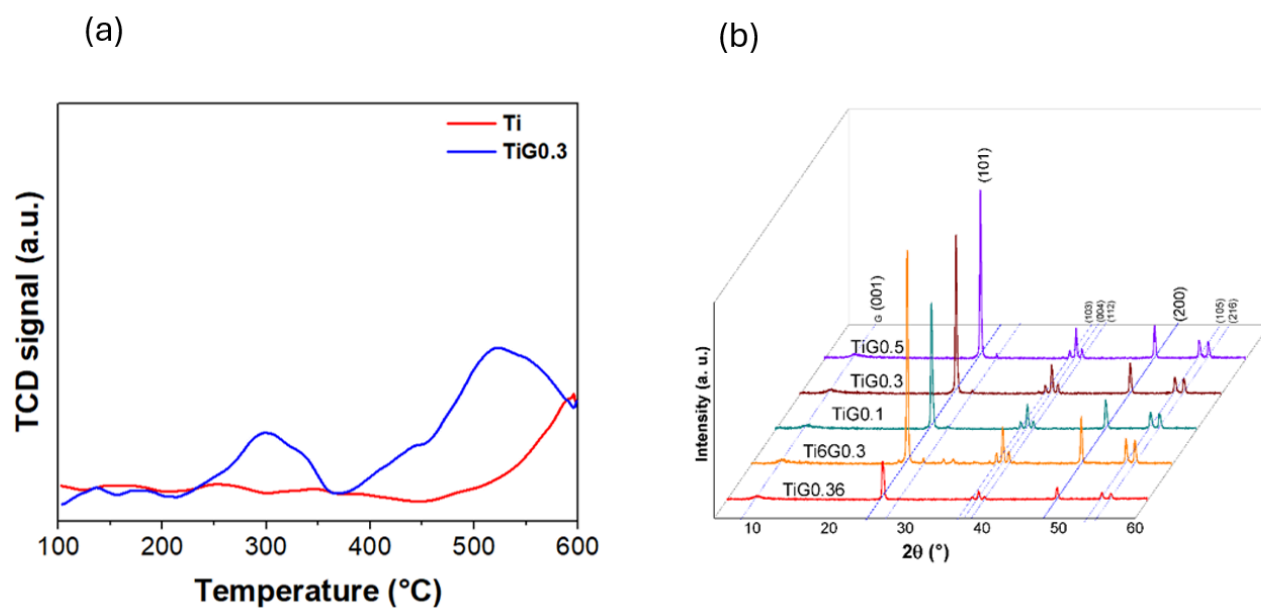


Figure 1

(a) Temperature-programmed reduction (TPR) profiles of TiO_2 anatase (Ti) 0.3 wt.% GO/TiO_2 , (b) XRD patterns of GO/TiO_2 containing different amounts of GO (TiG0.1, TiG0.3, TiG0.5) and TiG0.36, after reduction at 600°C .

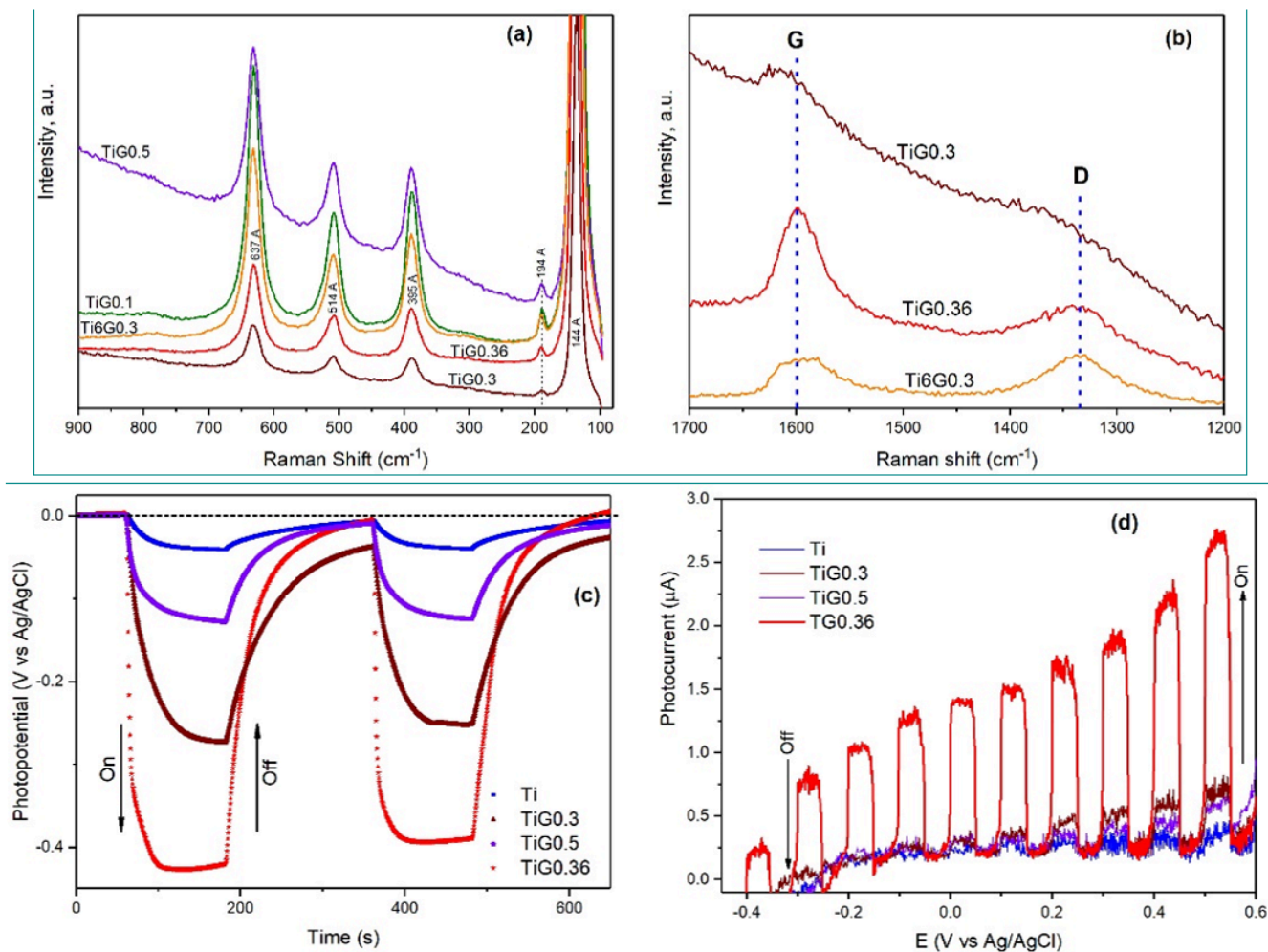


Figure 2

(a). Raman patterns of the composites TiG showing anatase signals. (b) G and D signals for the TiG0.3, Ti6G0.3, and TiG0.36 composites. (c) Photopotential of the composites. (d) Photocurrent for the Ti, TiG0.3, TiG0.5, and TiG0.36.

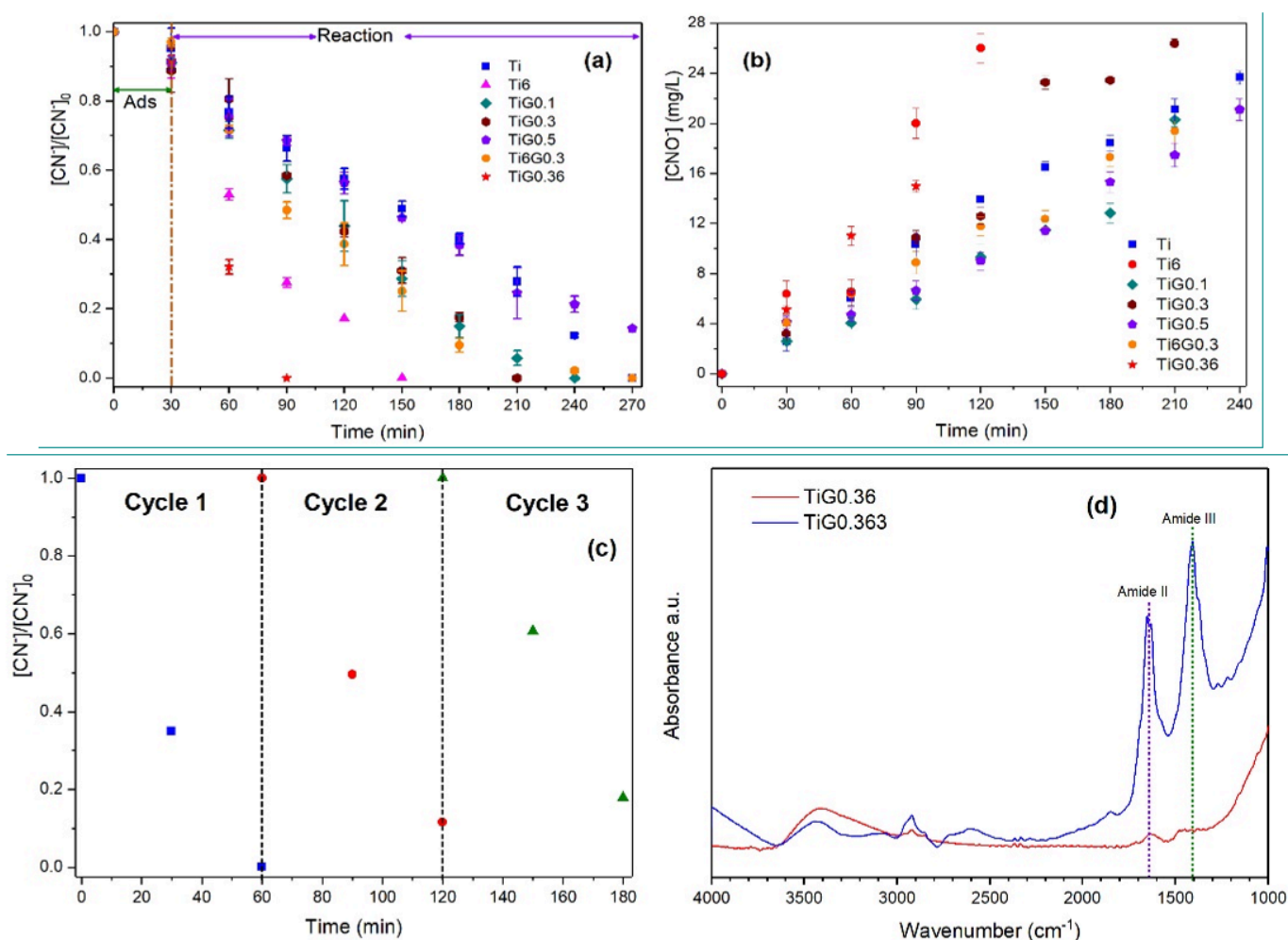


Figure 3

(a) Degradation patterns of free cyanide using Ti Aldrich and TiG composites at pH 12.0, $1gL^{-1}$ of catalyst concentration, and UV light. (b) Cyanate formation for Ti and all the composites. (c) Reaction cycles of TiG0.36 during free-cyanide oxidation at a pH of 12.0, $1gL^{-1}$ catalyst concentration, and UV light. (d) FTIR patterns of the TiG0.36 before (TiG0.36) and after 3 reaction cycles (TiG0.363).

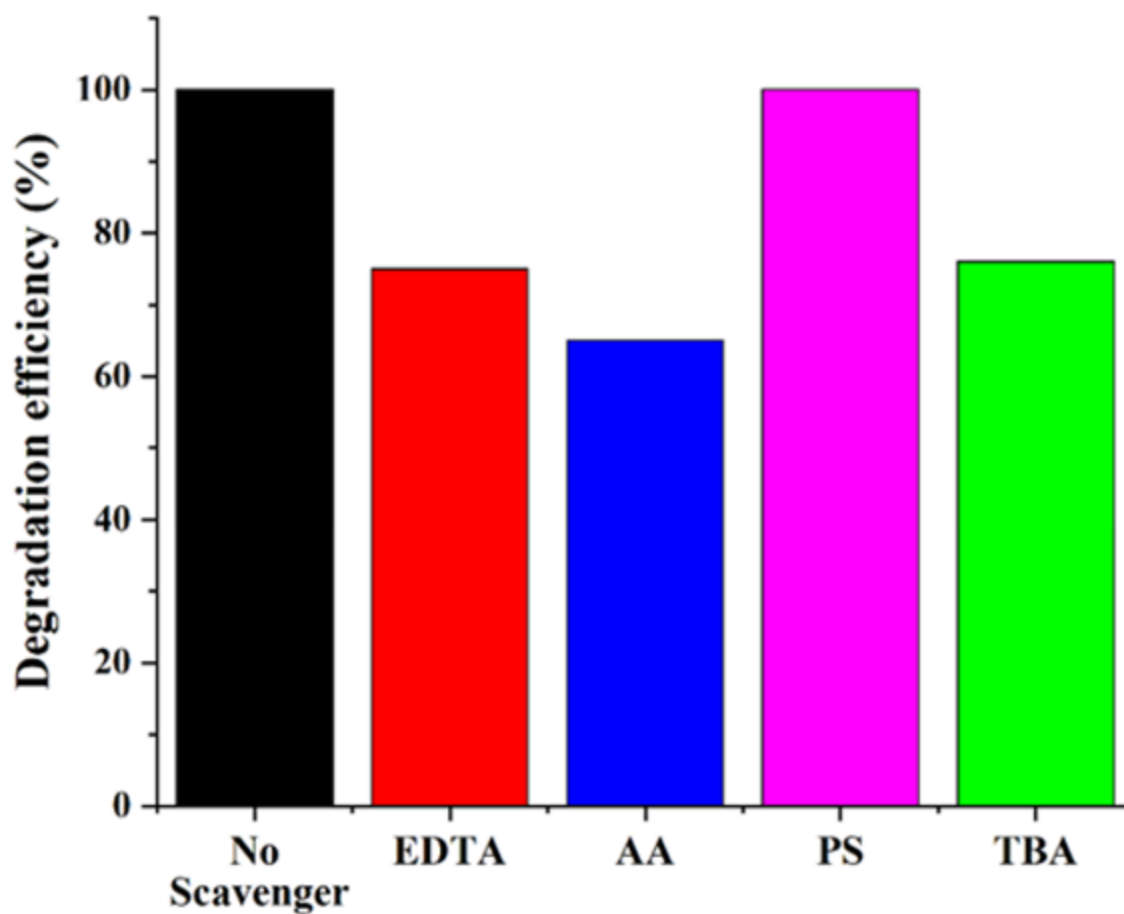


Figure 4

Radical quenching experiments during photocatalytic degradation of free cyanide by using TiO₂ catalyst.

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