Visible-Light-Induced Photocatalytic Degradation of Azodyes in Aqueous AgI/TiO₂ Dispersion

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AgI/TiO₂ was prepared by the deposition–precipitation method and was found to be a novel visible light driven photocatalyst. The catalyst showed high efficiency for the degradation of the nonbiodegradable azodyes reactive red K-2G, reactive brilliant red X-3B, reactive red K-2BP, and reactive yellow KD-3G under visible light irradiation ($\lambda > 420$ nm). The catalyst's activity was maintained effectively after successive cyclic experiments under visible irradiation without the destruction of AgI. On the basis of the characterization of X-ray diffraction, X-ray photoelectron spectroscopy, and Auger electron spectroscopy, the structure of AgI loaded on TiO₂ did not significantly change before and after reaction. K-2G was completely decolorized and partly mineralized. The main intermediates are the small organic acids besides CO₂ and cyanuric acid, which is photostable. The $\cdot\text{OH}$ is the main active oxygen species in the photocatalytic reaction by the studies of electron spin resonance and the effect of radical scavengers.

Introduction

Industrial wastewater is becoming more and more complex with the increasing diversity of industrial products. Dyes are released into the environment mainly from textile and dyestuff industries. Of the dyes available on the market today, approximately 50–70% are azo compounds (1). Some studies suggest that most azodyes are non-biodegradable (1, 2). Heterogeneous photocatalysis has been considered as a cost-effective alternative as a pre- or posttreatment of biological treatment processes for the purification of dye-containing wastewater (3, 4).

TiO₂ photocatalyst has been studied extensively for the destruction of organic pollutants under near UV irradiation (5, 6). One obstacle to its effective utilization is the relatively inefficient use of solar energy; less than 5% (UV light) of the sunlight is absorbed by this photocatalyst. To handle this problem, new photocatalysts capable of using visible light have been developed, including the impurity doping (7, 8) and sensitization (9) of TiO₂, and new visible-light-induced photocatalysts, such as PbBi₂Nb₂O₉ (10) and CaBi₂O₄ (11). However, the variety of visible-light photocatalysts is still very limited. It is still crucial to develop new visible-light photocatalytic materials with high activity to utilize sunlight more efficiently.

Silver halides are well-known as photosensitive materials and widely employed as source materials in photographic films. In the photographic process, silver halides absorb a photon and liberate an electron and a positive hole. The electron will combine with a mobile interstitial silver ion, leading to separation of a silver atom. Upon repeated absorption of photons, a cluster of silver atoms can be ultimately formed. This shows that silver halides are unstable under light irradiation. Because of these properties, silver halides have not been studied much in photocatalytic reactions. Recently, we have reported that the novel visible-light-driven photocatalyst AgBr/TiO₂ shows high efficiency in the degradation of nonbiodegradable azodyes and the killing of *Escherichia coli* under visible light irradiation (12). Our results indicate that AgBr is the main photoactive species for the destruction of pollutants under visible light. Moreover, Ag⁰ species on the surface of AgBr/TiO₂ scavenges $h\nu_{\text{VB}}^+$ and then traps e_{CB}^- in the process of the photocatalytic reaction, inhibiting the decomposition of AgBr. In earlier studies, AgBr was also well dispersed on silica or Al–MCM-41 support and exhibited higher activity and stability for photolysis of CH₃-OH/H₂O solution and the decomposition of acetaldehyde in gas phase under UV or visible light irradiation, respectively (13, 14). These results suggested that silver halides could act as a good visible-light photocatalyst candidate for the removal of pollutants when a suitable environment condition could be chosen to prevent their photodecomposition.

Related to this above work, we report in the present study that AgI was supported on P25-TiO₂ by the deposition–precipitation method in an aqueous solution of AgNO₃ and NH₄OH containing KI. Among azo dyes, those with triazine group are particularly important due to the well-known resistance of the *s*-triazine to light induced fading (15, 16). In the present study, the triazine-containing group azodyes were selected to evaluate the activity and properties of the catalyst. The results indicated that the catalyst exhibited higher visible-light-driven photocatalytic activity and stability for the photocatalytic degradation of triazine-containing azodyes.

Furthermore, the degradation process of reactive red K-2G was analyzed by total organic carbon (TOC), fourier transform infrared spectroscopy (FT–IR), and gas chromatography–mass spectroscopy (GC–MS) techniques. The transformation of the center group, *s*-triazine was followed during the photodegradation of K-2G. Electron spin resonance (ESR) was used to detect the reactive oxygen species involved in the reaction.

Experimental Section

Materials and Reagents. Titania P-25 (TiO₂; ca. 80% anatase, 20% rutile; BET area, ca. 50 m²/g) was purchased from the Degussa Co. Spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) was purchased from the Sigma Chemical Co. Azodyes reactive red K-2G (K-2G), reactive brilliant red X-3B (X-3B), reactive red K-2BP (K-2BP) and reactive yellow KD-3G (KD-3G) (Figure S1, Supporting Information) were kindly supplied by the Shanghai Chemical Co. and were used without further purification. All other chemicals were analytical grade. Deionized and doubly distilled water was used throughout this study.

Preparation of Photocatalysts. AgI/TiO₂ was prepared by the deposition–precipitation method. A 1-g quantity of P-25 TiO₂ was added to 100 mL of distilled water, and the suspension was sonicated for 30 min. Then, 0.205 g of KI was added to the suspension, and the mixture was stirred magnetically for 30 min, then, 0.21 g of AgNO₃ in 2.3 mL of

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NH_4OH (25 wt % NH_3) was quickly added to the mixture. The molar ratio of Ag^+ to I^- was 1:1. The resulting suspensions were stirred at room temperature for 12 h. Then, the amount of Ag^+ in the supernatant was measured by inductively coupled plasma optical emission spectrometry (ICP-OES) on an OPTIMA 2000 (Perkin-Elmer Co.) instrument, confirming that an Ag content of 10 wt % was incorporated into the TiO_2 . The product was filtered, washed with water, and dried at 70 °C. Yellow AgI/TiO_2 was obtained. The Brunauer–Emmett–Teller (BET) surface area of the sample was 23 m^2/g . The samples with 20 and 30% Ag content were prepared in the same procedure. Since the AgI/TiO_2 with 10 Ag wt % exhibited the highest activity (Figure S2–3, Supporting Information), this catalyst was used for all the experiments.

Characterization of Catalysts. The powder X-ray diffraction of the catalysts was recorded on a Scintag-XDS-2000 diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54059 \text{ \AA}$). UV–visible absorption spectra of the samples were recorded on a UV–vis spectrophotometer (Hitachi UV-3100) with an integrated sphere attachment. The analyzed range was 200–800 nm, and BaSO_4 was the reflectance standard. The X-ray photoelectron spectroscopy (XPS) data were taken on an AXIS-Ultra instrument from Kratos using monochromatic Al $\text{K}\alpha$ radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charge effects, the binding energies were calibrated using the C_{1s} hydrocarbon peak at 284.80 eV. Auger electron spectroscopy (AES) measurements were performed on AXIS-Ultra instrument from Kratos. The XPS and AES data were converted into VAMAS file format and imported into CasaXPS software package for manipulation and curve-fitting. ESR spectra were obtained using a Bruker model ESP 300 E electron paramagnetic resonance spectrometer. A 350-W Xe arc lamp with a UV cutoff filter ($\lambda > 420 \text{ nm}$) served as the irradiation light source. The settings were center field, 3480.00 G; microwave frequency, 9.79 GHz; and power, 5.05 mW. Determination of the concentration of H_2O_2 formed in the catalyst aqueous suspension under visible light irradiation was performed with a photometric method described in the literature (17).

Photocatalytic Degradation of Azodyes under Visible Light. The light source for photocatalysis was a 350-W Xe arc lamp (Shanghai Photoelectron Device Ltd.). Light passed through a water filter and a UV cutoff filter ($\lambda > 420 \text{ nm}$, Shanghai Seagull Coloured Optical Glass Co., Ltd) and then was focused onto a 100-mL beaker. The reaction temperature was maintained at 25 °C. Four nonbiodegradable azodyes (K-2G, X-3B, K-2BP, KD-3G) were selected as model chemicals to evaluate the activity and properties of the catalyst. In a typical experiment, aqueous suspensions of azodyes (60 mL, 50 mg/L) and 0.1 g of AgI/TiO_2 powders were placed in the beaker. Prior to irradiation, the suspensions were magnetically stirred in the dark for ca. 30 min to establish adsorption/desorption equilibrium between the dye and the surface of the catalyst under room air equilibrated conditions. At given irradiation time intervals, 3-mL aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.22 μm) to remove the catalyst particulates for analysis. The filtrates were analyzed by recording variations at the wavelength of maximal absorption in the UV–vis spectra of dyes using a model 752N spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd., China). Total organic carbon of the solution was analyzed with the Apollo9000 TOC analyzer. The SO_4^{2-} ions were determined by ionic chromatography (Dionex series 4500!). The final product cyanuric acid (OOOT) was determined by high performance liquid chromatograph (HPLC, Alliance 2695) with a Xterra C18 column. 20% acetonitrile with 80% water plus 1 g/L tetrabutylammoniumhydrogensulfate mobile phase was used. All of the above experiments were repeated three

FIGURE 1. XRD pattern of AgI/TiO_2 (a) fresh, (b) after UV irradiation for 60 h, (c) after photodegradation of K-2G under visible light irradiation.

FIGURE 2. UV–vis diffuse reflectance spectra of AgI/TiO_2 and TiO_2 .

times. Samples for GC–MS and FT–IR analysis were prepared by the following procedure. The suspensions at different irradiation times were filtered to remove AgI/TiO_2 particles. The solutions were evaporated by freeze-dried method. For FT–IR measurement, the dry residue was supported on KBr pellets. The infrared spectrum was recorded on a Nicolet Fourier FT–IR spectrophotometer. For GC–MS analysis, the residue was trimethylsilylated with 0.2 mL of anhydrous pyridine, 0.1 mL of hexamethyldisilazane, and 0.05 mL of chlorotrimethylsilane at room temperature. GC–MS analysis was carried out on an Agilent 6890GC/5973MSD with a DB-5 MS capillary column.

Results and Discussion

Characterization of Photocatalysts. Figure 1 shows the XRD patterns of fresh and used AgI/TiO_2 under UV or visible light irradiation. All samples exhibited the common anatase and rutile phase of P-25 TiO_2 . In addition to this, diffraction peaks attributed to β -AgI were observed for the three different AgI/TiO_2 samples. However, we found that all of the peaks of γ -AgI overlapped with the peaks of (002), (110), and (112) of β -AgI. This confirmed that AgI supported on TiO_2 was a mixture of β -AgI and γ -AgI. No diffraction peaks assigned to Ag^0 were displayed in the three samples, not even in the one irradiated by UV for 60 h. A new diffraction peak 18° appeared in the sample irradiated by UV for 60 h, which was possibly assigned to Ag_2O by JCPDS no. 72–2108. To affirm the metallic state of the silver on the surface of these samples, the fresh and used AgI/TiO_2 under visible light and UV irradiation were further characterized by XPS and AES measurement. On the basis of XPS and AES profiles (Figure S4–5, Supporting Information), the surface Ag species mainly exist as Ag^+ in all the AgI/TiO_2 samples. The atomic ratio of silver and iodine on the surface of AgI/TiO_2 was 1:1 corresponding to the stoichiometric ratio of AgI, for the three samples. The diffuse reflectance UV–vis spectra of AgI/TiO_2 (Figure 2) exhibited a visible-light absorption band around 400–436 nm. The presence of an excitation peak around 425 nm in the

FIGURE 3. Temporal course of the photodegradation of K-2G (50 mg/L, 60 mL) in aqueous dispersions containing (3.2 g/L) of catalysts under visible light irradiation: (a) no catalyst, (b) TiO_2 under visible irradiation ($\lambda > 420$ nm), (c) AgI/TiO_2 under visible irradiation ($\lambda > 450$ nm), and (d) AgI/TiO_2 under visible irradiation ($\lambda > 420$ nm). The inset is the UV/vis spectral changes recorded for (d) as a function of irradiation time.

FIGURE 4. Decolorization and TOC removal of the solution, OOOT and SO_4^{2-} ions formation during the photodegradation of K-2G (50 mg/L, 60 mL) in AgI/TiO_2 aqueous dispersions (3.2 g/L) under visible irradiation.

absorption spectra provides important additional evidence for the mixture of $\beta\text{-AgI}$ and $\gamma\text{-AgI}$ (18).

Photodegradation of Azodyes under Visible Light Irradiation. The K-2G photodegradation was carried out after adsorption equilibrium had been reached between K-2G and the catalyst under different conditions (Figure 3). K-2G almost could be photodegraded completely over AgI/TiO_2 under visible light ($\lambda > 420$ nm) (curve d). Neither visible light nor TiO_2 /visible light showed any activity for K-2G photodegradation (curves a-b). Zhao and co-workers reported that many dyes could be degraded over TiO_2 on the basis of the self-photosensitization process of dyes under visible-light irradiation (19). However, a similar phenomenon did not occur in the degradation of K-2G over TiO_2 . Furthermore, no significant K-2G photodegradation was observed over AgI/TiO_2 under visible light ($\lambda > 450$ nm) irradiation (curve c), where the catalyst hardly absorbed the light radiation, but K-2G had strong light absorption. These results indicated that the dye self-photosensitization process could be ignored, and the photocatalytic process was the predominant process in the system of AgI/TiO_2 with visible light. The temporal UV/vis spectra showed that the K-2G characteristic band centered at 500 nm was decreased promptly upon light irradiation (inset plot in Figure 3), together with a blue shift of the maximum absorption, indicating that at least the chromophoric structure of the dye was destroyed, and other intermediates was formed. Figure 4 shows TOC removal of the solution and the formation of inorganic ions with exposure time during the photodegradation of K-2G. Obviously, the K-2G was decolorized completely after 150 min of

FIGURE 5. Plots showing the formation of H_2O_2 in AgI/TiO_2 aqueous dispersions (1.6 g/L) (a) under visible irradiation, (b) in the dark.

irradiation, whereas the TOC hardly was decreased, and only 16% of the total sulfur of K-2G was converted to SO_4^{2-} at the same time. Subsequently, the TOC was markedly removed and the formation rate of SO_4^{2-} was enhanced, indicating that decolorization was easier than the TOC removal and desulfuration. The results also confirmed that the photocatalytic process occurred in AgI/TiO_2 suspension with visible light irradiation because the photoreaction did not stop after dye disappearing. The total sulfur of K-2G was almost completely transformed to SO_4^{2-} at 30 h of irradiation. After 10 h of illumination, about 60% of TOC content was removed. Further illumination, even up to 30 h, did not reduce the TOC content of the solution much. Meanwhile, cyanuric acid (OOOT) began to appear at 10 h of irradiation, and the maximal amount (3.8 ppm) of OOOT was produced after 30 h irradiation. The results implied that the triazine ring in the structure of K-2G was almost completely converted to OOOT, which is very stable in photocatalysis (16). As shown in Figure S6 (Supporting Information), the azodyes K-2BP, X-3B, and KD-3G were degraded efficiently in AgI/TiO_2 suspension under visible light irradiation as K-2G.

Involved Active Species. To illustrate the mechanism of AgI/TiO_2 visible light photocatalysis, the formation of H_2O_2 was determined in aqueous AgI/TiO_2 suspension without dyes to remove the self-photosensitized contribution under visible light irradiation (Figure 5). In the AgI/TiO_2 system, the quantities of H_2O_2 increased with irradiation time, while there was almost no H_2O_2 formation in the dark. According to the photocatalytic mechanism (5, 6), the H_2O_2 could be formed from these reactions of photogenerated electrons and holes with adsorbed oxygen/water, where $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ were possibly involved. Therefore, the results indicated that $\text{O}_2^{\cdot-}$ and $\cdot\text{OH}$ reactive species were probably produced in aqueous AgI/TiO_2 suspension under visible light irradiation. To confirm this conjecture, the ESR spin-trap technique (with DMPO) was used to detect the nature of the reactive oxygen species generated on the surface of the catalyst under visible irradiation. A 350-W Xe arc lamp with a UV cutoff filter ($\lambda > 420$ nm) was employed to irradiate catalyst aqueous suspension without dye. Four characteristic peaks of DMPO- $\cdot\text{OH}$ were observed in the suspension of AgI/TiO_2 (Figure 6). No such signals were detected in the dark. This means that irradiation was essential for the generation of $\cdot\text{OH}$ on the surface of the catalyst. The DMPO- $\text{O}_2^{\cdot-}$ species were not detected in AgI/TiO_2 dispersions in methanolic media under otherwise identical conditions. The evidence that $\cdot\text{OH}$ radicals are produced on the surface of visible light-illuminated AgI/TiO_2 provides a solid indication that the catalyst can be efficiently excited by visible light to create electron-hole pairs to form reactive oxygen species. Additional examination for the role of the $\cdot\text{OH}$ in the degradation of K-2G came from effects of various scavengers of $\cdot\text{OH}$ radicals on the rate of K-2G degradation (Figure 7). Since there was no significant amount of methanol and isopropanol adsorbed on the catalyst in aqueous systems, they predominantly scavenged

FIGURE 6. DMPO spin-trapping ESR spectra recorded at ambient temperature in aqueous AgI/TiO₂ dispersion under visible irradiation ($\lambda > 420$ nm).

FIGURE 7. Plotted degradation kinetics of K-2G in the AgI/TiO₂ suspension (1.6 g/L) under visible light irradiation on addition of (a) no scavenger added, (b) isopropanol, (c) methanol, (d) NaHCO₃, (e) KH₂PO₄. Scavenger concentration 0.1 M.

the free $\cdot\text{OH}$ radicals in solution. When they were introduced into the photoreaction system, the degradation of K-2G was depressed to some extent (curves b–c). Addition of HCO_3^- and H_2PO_4^- ions led to a marked suppression in the photodegradation rate of K-2G (curves d–e). Both HCO_3^- and H_2PO_4^- had high adsorption on the surface of TiO₂ (20). The both adsorbed anions reacted with the positive holes (h_{VB}^+) and the absorbed $\cdot\text{OH}$ on the surface of AgI/TiO₂. The results provided a solid indication that the absorbed $\cdot\text{OH}$ radicals were the main reactive oxygen species in AgI/TiO₂ photocatalytic process with visible light irradiation. Oppositely, $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ were involved in AgBr/TiO₂ visible photocatalytic process, leading to different photocatalytic behaviors for the degradation of dyes, which will be illustrated in another paper.

Formation of Intermediates. FT–IR and GC–MS were used to monitor the generation of reaction intermediates during the photodegradation of K-2G. It is relatively important to characterize these byproducts for the practical application of photocatalysis. FT–IR spectra of the degraded solutions of K-2G, after irradiation at various time intervals are shown in Figure 8. The characteristic peaks of the azo bond ($-\text{N}=\text{N}-$, at 1498 cm^{-1}) and the benzene ring (at $1400\text{--}1600\text{ cm}^{-1}$) of K-2G disappeared, and the characteristic peaks at 1200 and 1057 cm^{-1} , due to the asymmetric stretching vibration of the $-\text{SO}_3\text{Na}$ group (21) also clearly disappeared. The results indicated that the azo bond and the benzene ring were broken, and desulfuration occurred with the decolorization of K-2G. Meanwhile, several new peaks at 1740 and 1654 cm^{-1} were generated at 10 h of irradiation, and at 1721 , 1689 , and 1654 cm^{-1} at 30 h , which all were attributed to the stretching vibration of $\text{C}=\text{O}$ groups of carboxylic acids. The changes of the characteristic peaks of $\text{C}=\text{O}$ groups of carboxylic acids may be attributed to different structures of carboxylic acids from different reaction times. Some other new peaks appeared at 991 , 807 , and 624 cm^{-1} at 10 h of

FIGURE 8. Changes of FT–IR spectra during the photodegradation of K-2G.

FIGURE 9. Cycling runs in the photodegradation of K-2G in the presence of AgI/TiO₂ under visible light irradiation, AgI/TiO₂ (1.6 g/L); addition of K-2G (50 mg/L, 60 mL, per run).

irradiation, which could be assigned to the substituted benzene. The results of GC–MS further confirmed these results (Table S1, Supporting Information). For the photodegradation of K-2G, samples treated at different irradiation time were analyzed by GC–MS. All the identified compounds were unequivocally identified using the NIST98 library database with fit values higher than 90%. The main products included 1, 2-ethandiol, glycerol and benzoic acid at 2.5 h of irradiation when the K-2G was completely decolorized. Further 10 h of irradiation, 1, 2-ethandiol disappeared, while phthalic acid was formed by hydroxylation of naphthalene ring, and the glycerol and benzoic acid were still present. At 30 h of irradiation, in addition to all the above products, different aliphatic acids, such as 2-hydroxy-propanoic acid and succinic acid, were generated from the oxidation of benzoic acid and phthalic acid. The results from FT–IR and GC–MS analysis suggest that K-2G photodegradation proceeds by cleavage of the azo bond leading to decolorization and desulfuration, followed by opening of phenyl and naphthalene ring to form small molecular organic acids. All the above results confirm that $\cdot\text{OH}$ radicals were the predominant active oxygen species and were responsible for the degradation of dye in visible light-illuminated AgI/TiO₂ suspension.

Photostability of AgI/TiO₂. Figure 9 shows the durability of the AgI/TiO₂ catalyst for the degradation of K-2G under visible light. AgI/TiO₂ was easily recycled by simple filtration without any treatment in these experiments. The photocatalytic activity did not decrease significantly in the degraded K-2G after six successive cycles under visible irradiation. Even after the catalyst was irradiated by UV for 60 h , the catalyst's activity was maintained effectively (Figure S7, Supporting information). The results demonstrated that AgI/TiO₂ is an effective and stable catalyst under visible light and UV irradiation. It was observed that AgI/TiO₂ kept yellow throughout the cyclic experiments and even after UV irradiation, indicating AgI was not decomposed by light. AgI/TiO₂ is more photostable than AgBr/TiO₂. In our previous

work, the mechanism of AgBr/TiO₂ stability has been proposed as follows: the Ag⁰ species on the surface of AgBr/TiO₂ first scavenge h_ν⁺ and then trap e_{CB}⁻ in the process of photocatalytic reactions, inhibiting the decomposition of AgBr. To elucidate the stability of AgI/TiO₂, the AgI/TiO₂ sample irradiated by UV for 60 h and the other sample after photocatalytic reaction under visible irradiation were characterized by XRD (Figure 1). In comparison with XRD patterns of the samples before and after irradiation, all the AgI peaks became sharp after irradiation by UV or visible light, indicating the crystalline growth of AgI. No diffraction peaks of Ag⁰ were observed in these samples. AgI was not destroyed by exposure to visible light or UV. Furthermore, The XPS and AES data (Figure S4–5, Supporting Information) verified that Ag⁰ was not formed, Ag⁺ ions were main silver species in the structure of the fresh and used AgI/TiO₂ samples, indicating AgI were not decomposed at any time as AgBr. AgI is more photostable than AgBr. To confirm the photostability of AgI/TiO₂, AgI also was loaded on SiO₂ and Al₂O₃ by the same method as the preparation of AgI/TiO₂. The structure of AgI loaded on both supports is same as that one on the TiO₂ based on the measurement of UV–vis absorption and XRD. However, by ICP-OES analysis, the concentration of Ag⁺ released from AgI/TiO₂ (1.6 g/L) suspension is less than 10 μg/L under UV and visible light irradiation. In the contrast, the concentration of Ag⁺ from AgI/SiO₂ and AgI/Al₂O₃ suspensions (1.6 g/L) is 0.505 and 2.349 mg/L under the same conditions. The greater dissolution of Ag⁺ led lower visible light activity of the both catalysts for the degradation of K-2G (Figure S8, Supporting Information). The results indicated that the stability and activity of AgI were affected by different supports. Further experiments are necessary to understand the influence of the support.

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Supporting Information Available

The results for structures of the employed dyes, Ag 3d XPS and AES spectra of AgI/TiO₂, and photodegradation of different azodyes under different conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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