ACS Sustainable Chemistry & Engineering

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Photochemical Reduction of CO_2 by Graphitic Carbon Nitride Polymers

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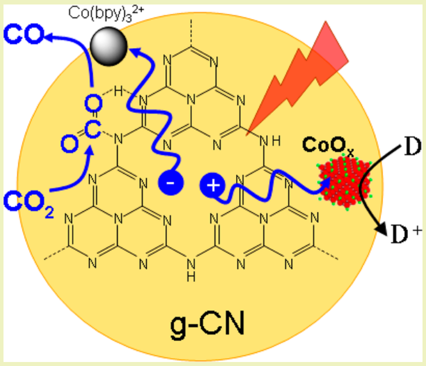
Supporting Information

ABSTRACT: The combination of cobalt redox catalysis and carbon nitride photocatalysis to construct a cascade photoreaction system has been developed for the deoxygenative reduction of CO_2 to CO with visible light. The graphitic carbon nitride has been demonstrated to function both as a capture/activation substrate of CO_2 and a photocatalyst, whereas the introduced cobalt species act as reductive and oxidative promoters to accelerate charge-carrier separation and transfer kinetics. This hybrid photosystem contains inexpensive substances that synergetically catalyze CO_2-to-CO conversion at mild conditions, with a high stability of catalysts. The optimization in the surface and texture structures as well as reaction conditions has been demonstrated. The results represent an important step toward artificial photosynthesis by using cost-acceptable materials.



KEYWORDS: *Photocatalysis, Carbon nitride, CO_2, Cobalt, CO*

INTRODUCTION

The conversion of anthropogenic CO_2 into chemical feedstocks can supplement the natural carbon cycle and might reduce global energy and environment burdens.[1,2] A feasible chemical transformation of CO_2 involves photocatalysis, as inspired by natural photosynthesis, by which solar energy is converted into chemical energy in the form of sugars or biomass in general, using CO_2 and water as starting materials.[3−5]

Since the initial reports by Inoue et al. and Lehn et al. on photochemical reduction of CO_2 in 1980s, there has been great interest in developing stable and efficient carbon fixation systems containing light-absorbing materials and electron transfer mediators.[6−8] Various metal complexes[7,9−11] and inorganic semiconductors[12,13] have been intensively investigated as energy harvesting substances; however, respecting future scale-up consideration, new materials free of expensive/precious metals have to be developed. Cooperative binary catalyst systems that promote both charge-carrier separation and reaction kinetics are also being actively pursued,[14,15] as most photocatalysts are restricted by fast charge recombination and show only poor electrocatalytic activities for CO_2 reduction. Cobalt ions together with suitable organic ligands have been applied to build efficient electron transport chains for supporting the reductive catalysis of CO_2 and H^+,[16] whereas other cobalt species (e.g., Co−Pi, CoO_x) have been demonstrated to act as oxidative cofactors for water splitting.[17,18] It is therefore desirable to integrate these "Janus" redox functions of cobalt species into a single photochemical system to promote both oxidative and reductive catalytic cycles to achieve efficient CO_2 conversion driven with visible light.

It is well known that the key step in CO_2 reduction is the chemical activation of thermodynamically stable CO_2. Transition metals with multiple redox states have been widely employed for this purpose.[19] Recently, metal-free organic molecules have emerged in C1 chemistry as coordination substrates for the capture and activation of CO_2, including frustrated Lewis pairs,[20] N-heterocyclic carbenes,[21] bicyclic amidines,[22] silyl cations,[23] and ionic liquids.[24] A solid-state organocatalyst, graphitic carbon nitride (g-CN), has also been explored to capture, activate, and reduce CO_2 via thermal catalysis in the presence of sacrificial hydrocarbons.[25] The formation of carbamate species is evident by binding of CO_2 to the tris-triazine-based covalent framework with Lewis basic functions. This CO_2 capture and activation process is similar to the first step of biological photosynthesis, in which CO_2 is initially bonded to N atoms to form reactive carbamate intermediates.[26] Unfortunately, the energy input to drive the carbon dioxide splitting catalysis by g-CN is chemical energy from the substrate, instead of photon energy.

g-CN is insoluble in most solvents and is inert against most acids/bases and thermal annealing in air (up to 550 °C), making it an alternative (photo)catalyst.[27−29] It indeed features a suitable semiconductor structure that enables the generation of high energy electron−hole pairs for water redox catalysis

Received: October 21, 2013
Revised: November 18, 2013
Published: December 1, 2013

dx.doi.org/10.1021/sc4004295 | *ACS Sustainable Chem. Eng.* 2014, 2, 353−358

upon light excitation. This cheap easily available polymeric solid was proposed as the basis for a new family of light-absorbing semiconductors, showing promise in CO_2 coordination chemistry[25] already. Very recently, Madea et al. reported on the modification of g-CN with Ru complexes for photocatalytic CO_2 reduction with visible light.[30] Our long-term interest in artificial photosynthesis using noble metal free materials led us to apply g-CN photocatalyst and transition metal-based cocatalysts for photochemical CO_2 conversion by taking its combined benefits of CO_2 capture/activation functions and photocatalytic characteristics. Additional chemical controls in the reaction kinetics and charge-carrier separation at the polymer surface/interface is desirable, using functional cobalt species as redox promoters. This synergetic catalysis effect of cobalt and g-CN for the conversion of atmospheric CO_2 to CO was first designed by using cobalt species and g-CN as reductive cofactors and a light harvester, respectively. Here, we use a homogeneous Co^{2+} ion coordinated with a bipyridine (bpy) ligand acting as a solution-based electron mediator for supporting reductive catalysis. A cobalt oxide was then loaded onto the g-CN as an oxidative catalyst to further accelerate the reaction by promoting the charge separation and transfer of light-generated holes.

EXPERIMENTAL SECTIONS

Preparation of the Photocatalyst. Bulk $g\text{-}C_3N_4$ (denoted as g-CN) was prepared by directly heating melamine at 550 °C for 2 h under air atmosphere. To prepare mesoporous graphitic carbon nitride (MCN), melamine (10g) was dissolved in 10 mL H_2O, followed by dropping 5 g of SiO_2 particles (12 nm) in water (Ludox HS40, Aldrich).[28] The resulting transparent mixtures were stirred at 100 °C to remove water. The dry solid was subjected to sintering at 550 °C for 2 h in a muffle furnace. The resultant yellow powder was treated with NH_4HF_2 (4 M) aqueous solution to remove the silica template. The powders were then washed with distill water and ethanol several times. Finally, the powers were dried at 60 °C in air overnight.

The Pd- and Ru-loaded g-CN samples were prepared by a borohydride reduction process. The experiment was carried out in a 100 mL two-necked round-bottomed flask. An aqueous solution of the metal chloride salt (0.01 mol/25 mL) was prepared using distill water and then added into the g-CN dispersing solution (1g/25 mL). The $NaBH_4$ solution was added, with stirring for 30 min. The contents of the reaction flask were filtered and washed with distilled water, and the resulting powder was dried in vacuum at 45 °C.[31]

The metal oxide/carbon nitride hybrids were prepared by heat treatment. Carbon nitride powders were added to a water solution containing metal ions, followed by stirring and drying in air. Then, these solid mixtures were annealed at 350 °C under air atmosphere.

Characterization. Photoluminescence (PL) spectra were obtained on an Edinburgh FI/FSTCSPC 920 spectrophotometer. A Varian Cary 500 scan UV−vis spectrophotometer was used to record the UV−vis diffuse reflectance spectra of samples with barium sulfate as the reference sample. X-ray diffraction (XRD) patterns were collected using a Bruker D8 Advance X-ray diffractometer (Cu Kα1 irradiation, λ = 1.5406 Å). Fourier transformed infrared (FT-IR) spectra were recorded using a Nicolet Magna 670 FT-IR spectrometer, and the samples were mixed with KBr at a concentration of about wt 1%. Brunauer−Emmett−Teller (BET) specific surface areas of initially treated samples at 453 K for 8 h were calculated from nitrogen adsorption−desorption isotherms obtained at 77 K with Micromeritics ASAP 2020 equipment.

Photocatalytic Test. Detailed information on the raw materials is provided in the Supporting Information. The photocatalytic test was performed in a Schlenk flask (80 mL) under an atmospheric pressure of CO_2. In the Schlenk flask, the photocatalytic CO_2 reduction reaction was carried out by dispersing 50 mg catalyst powder in a solution containing solvent (4 mL), triethanolamine (2 mL), $CoCl_2$ (1 μmol), and bipyridine (15 mg). This mixture system was subjected to vacuum degassing and then backfilling with pure CO_2 gas. This process was repeated three times, and after the last cycle, the flask was backfilled with CO_2 (1 bar). The temperature of the reaction solution was maintained at 60 °C controlled by a flow of warming water during the reaction. Then, the system was irradiated with a nonfocus 300 W Xe lamp with a 420 nm cutoff filter under vigorous stirring. The produced gases (CO and H_2) were detected using a gas chromatography equipped with a packed molecular sieve column (TDX-1 mesh 42/10). Argon wass used as the carrier gas.

An isotopic experiment was carried out under the identical photocatalytic reaction conditions using $^{13}CO_2$ (98% in purity, 1 bar) as the carbon source. The photocatalytic evolution of CO was analyzed by gas chromatography−mass spectrometry (GC-MS).

RESULTS AND DISCUSSION

The photocatalytic CO_2 reduction was performed using a catalyst combination of g-CN as a photocatalyst and $Co(bpy)_3Cl_2$ as a reductive catalyst, using triethanolamine (TEOA) as the electron donor and hydrogen source. The reaction was carried out in acetonitrile under atmospheric CO_2 and visible light (λ > 420 nm). Upon visible light irradiation for 2 h, the system evolved CO (3.7 μmol) and H_2 (0.6 μmol) gases (entry 1, Table 1) as the main reaction products. There is only a trace amount of formic acid (HCOOH) determined by a NMR spectrometer even when $^{13}CO_2$ was imported into the reactive system (Figure S1, Supporting Information). The catalytic turnover number was calculated to be 4.3 with respect to the amount of cobalt ions added.

Table 1. Variation of Reaction Conditions[a]

runs	CO (μmol)	H_2 (μmol)	CO + H_2 (μmol)	Sel. (%)[b]	TON[c]
1	3.7	0.6	4.3	86.0	4.3
2[d]	n.d.[e]	n.d.	–	–	–
3[f]	n.d.	n.d.	–	–	–
4[g]	n.d.	0.5	0.5	–	0.5
5[h]	n.d.	0.6	–	–	–
6[i]	3.8	0.5	4.3	88.4	4.3
7[j]	n.d.	<0.1	<0.1	–	<0.1
8[k]	n.d.	<0.1	<0.1	–	<0.1
9[l]	n.d.	<0.1	<0.1	–	<0.1
10[m]	3.6	1.7	5.3	67.9	5.3
11[n]	n.d.	1.1	1.1	–	1.1

[a] Reaction conditions: MeCN (4 mL), TEOA (2 mL), CO_2 (1 bar), g-CN (50 mg), $CoCl_2$ (1 μmol), bpy(15 mg), 60 °C, 2 h, and λ > 420 nm. [b] Selectivity = $n_{CO}/n_{(CO+H2)} \times 100$. [c] Turn over number (mol amount of CO and H_2)/(mol amount of cobalt ion). [d] Without g-CN. [e] Not determined. [f] In dark. [g] Using Ar instead of CO_2. [h] Without TEOA. [i] Using triethylamine to replace TEOA. [j] Without bpy. [k] Without $CoCl_2$. [l] Without bpy and $CoCl_2$. [m] $CoCl_2$(10 μmol) and bpy. [n] Using Cp_2Co instead of both $CoCl_2$ and bpy.

A series of reference experiments were performed, and the results are summarized in Table 1. In the absence of either g-CN or light, there is no detectable production of H_2 and CO (entries 2 and 3, Table 1). The result revealed that the cobalt ions (together with the organic ligand) alone cannot induce the CO_2 conversion, reflecting the light-to-charge pair conversion effect of g-CN. The relationship between catalytic selectivity and Co^{2+} was further revealed by the formation of H_2 and CO when altering the Co^{2+} concentration (Figure S2, Supporting Information). Initially, both H_2 and CO productions increase along with the increase in the Co^{2+} concentration. With further increase Co^{2+} concentration, the H_2 production increases, but the CO production reaches a platform and remains unchanged later. This result revealed that low Co^{2+} concentration in the carbon nitride photocatalytic system is favorable for selective reductive production of CO, consistent with the literature where Ru-based dye was applied as light-absorbing materials.[32] Once CO_2 was replaced with argon gas, the evolution of CO was also not observed, thus excluding degradation effects of both polymeric carbon nitride photocatalysts and organic additives like TEOA and bpy.

To further confirm the source of the produced CO, we carried out an isotopic experiment using $^{13}CO_2$ under the identical photocatalytic reaction conditions. The photocatalytic evolution of CO was analyzed by gas chromatography mass (GC-MS). After 2 h visible light irradiation, the peak at 3.97 min and m/z 29 was assigned to ^{13}CO as shown in Figure 1. This provides solid experimental proof that the polymeric graphitic carbon nitride semiconductors can indeed catalyze the deoxygenative reduction of CO_2 to CO at mild conditions with visible light.

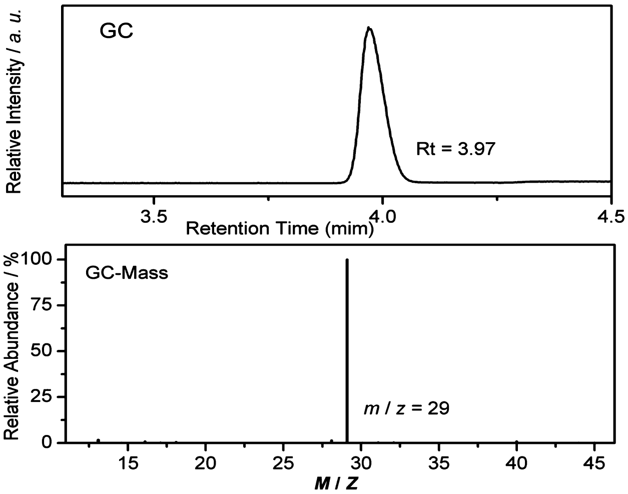


Figure 1. Gas chromatogram and mass spectra (m/z = 29) analyses of the carbon source of the evolved CO in the photocatalytic reduction of $^{13}CO_2$ by a carbon nitride semiconductor.

A further reference reaction showed that the photocatalytic reduction of CO_2 to CO stopped in the absence of cobalt ions or bpy ligands or both (entries 7, 8, and 9, Table 1). This result suggests the cooperative effect of cobalt ions and bpy ligands in supporting CO_2 reduction.[16] To shed light on the function of electron mediator $[Co(bpy)_3{}^{2+}]$ during the photoreductive process, photoluminescence (PL) analysis of the system was performed. The g-CN sample presented a strong PL signal peaking at about 500 nm due to the charge recombination.[27,33] After the addition of either $CoCl_2$ or bpy, there is only a slight quenching of the PL signal. However, almost a 35% intensity drop in the PL peak was observed when the g-CN suspension contained both cobalt ion and bpy ligand (Figure S3, Supporting Information).

Obviously electron−hole recombination was inhibited by the synergistic effect of Co^{2+} and bpy that share the responsibilities to establish a solution-based electron transfer complex for redox catalysis.[16] Similar promotional effects were also observed for Fe^{3+}, Mn^{2+}, and Ni^{2+} when chelated by bpy, but Co^{2+} was found to be the optimum cofactor among various metal ions examined (Table S1, Supporting Information). Further investigations on the optimization of organic ligands with different coordinating environments (e.g., chemical and electronic structures) are useful.

The photocatalytic performance of the current system can also be triggered by the reaction medium (Table S2, Supporting Information). MeCN, DMF, or THF were found to be favorable reaction media for the CO_2 reduction reaction because they possess nitrogen or/and oxygen atoms that can interact with and solubilize CO_2 via Lewis acid−base interactions.[34,35] No reaction occurred when using water or chloroform as the solvent that possesses a weak chemical affinity toward CO_2 molecules.

To confirm that the reaction was indeed induced by light excitation of g-CN, CO evolution as a function of the incident light wavelength was investigated. As shown in Figure 2, the trend of CO production matches well with the optical absorption spectrum of the CN polymer. This result reveals that CO_2 reduction is associated with charge generation, separation, and subsequent tandem electron transfer catalysis. Note that the longest active wavelength of the g-CN is still in the deep blue visible light range. By modification of g-CN by copolymerization,[36] the active wavelength can be extended to as long as about 550 nm (data no shown). Indeed, only such a system would be really useful for artificial photosynthesis, but the current first proof-of-concept report is for simplicity focusing on the pristine g-CN photocatalysts.

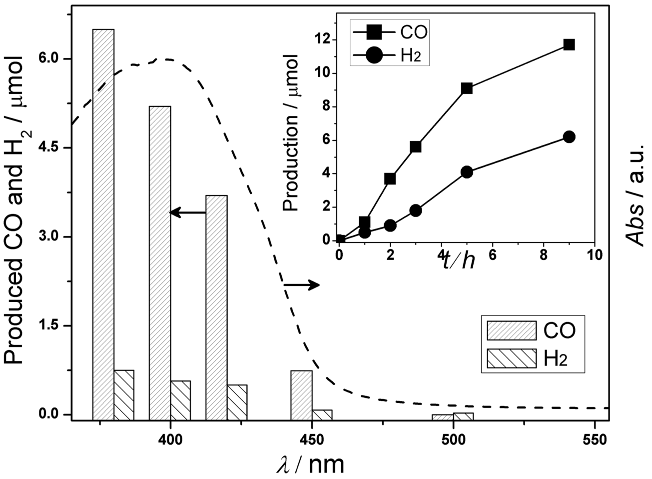


Figure 2. UV−vis diffuse reflectance spectrum of g-CN (dash line). The histogram represents the production of CO and H_2 photocatalyzed by g-CN. The insert in the figure is the time−conversion plot for photocatalytic CO_2 reduction.

A prolonged operation of the photochemical system gave a gradual increase in both CO and H_2 evolutions in a nonlinear fashion (Figure 2 insert). Cycle experiments were also conducted to examine the system stability, and results revealed a slight activity loss after the first run but thereafter remained virtually unchanged for CO production (Figure 3).

The used g-CN was subjected to physical characterizations by X-ray diffraction and infrared-reflection (Figures S4 and S5, Supporting Information). No alternation in the spatial and chemical structures was observed, reflecting the high structural stability of g-CN in photocatalytic applications that is however consistent with the literature on water splitting by g-CN.[27]

In the next set of experiments, the surface of g-CN was loaded with reductive and oxidative cocatalysts, respectively. It was found that the modification of Pd and Ru nanoparticles led

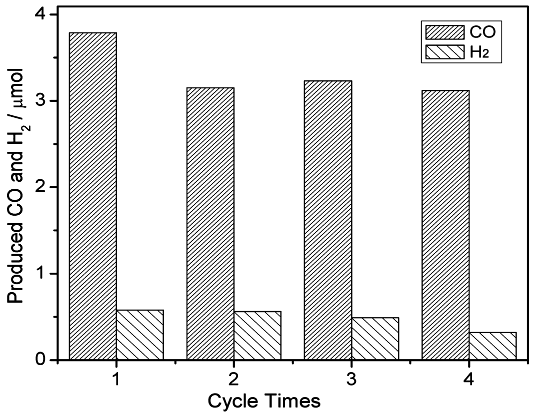


Figure 3. Stability study of the catalytic evolution of CO and H_2 over the g-CN photocatalyst.

to a significant improvement in H_2 evolution; however, the CO evolution was almost completely suppressed (Table 2). This can be interpreted as competing catalytic kinetics on the surface of g-CN. It has already been demonstrated that g-CN can function as a metal-free coordinating substrate for the chemical activation of CO_2, and it is also known that Pd or Ru can act as an effective electron sink to lower the overpotential of H_2 evolution.[36] Thus, the addition of Pd or Ru on the surface of g-CN promotes hydrogen evolution catalysis. It is however remarkable that the photochemical splitting of CO_2 by g-CN can be achieved also without any noble metal catalysts, presumably due to the activation of CO_2 by g-CN with basic functionalities that reduces the reaction barrier of CO_2 reduction.

Table 2. Reductive and Oxidative Promotions of g-CN and MCN Photocatalysts for CO_2 Reduction[a]

	catalyst	CO (μmol)	H_2 (μmol)	Sel. (%)	TON
1	Ru/g-CN	n.d.	35.1	–	35.1
2	Pd/g-CN	n.d.	34.9	–	34.9
3	CoO_x/g-CN	7.6	2.3	76.7	9.9
4	MCN	6.3	0.6	91.3	6.9
5	CoO_x/MCN	10.2	2.8	78.5	13

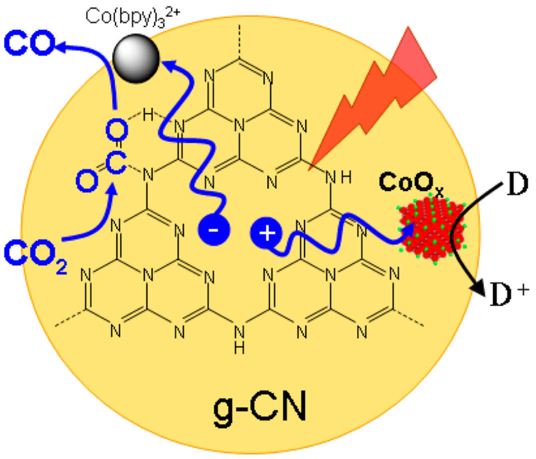
[a]Reaction condition: the same as those in Table 1.

The oxidative promotion of the g-CN-mediated CO_2 reduction reaction was achieved by using cobalt oxide (CoO_x) nanoparticles as a third component that were dispersed onto g-CN by a simple thermal treatment in air atmosphere at 350 °C.[37] As shown in Table 2, CoO_x/g-CN hybrids showed a significant improvement in photocatalytic activity over the parental binary system toward CO_2-to-CO conversion due to the acceleration in the oxidative partner reaction by promoting the transfer of light-stimulated holes from the surface/interface of g-CN to the cobalt oxide phase.

To maximize the photocatalytic performance, nanopores were imparted into the g-CN network by a hard-templated approach using SiO_2 nanoparticles according to our previous synthetic approaches.[28,38,39] A mesoporous carbon nitride (MCN) with an enlarged surface area of 135 m^2/g (Figure S6, Supporting Information), together with CoO_x/MCN, was therefore applied for the CO_2 photoreduction reaction. Both samples again feature an enhanced photocatalytic performance over the corresponding g-CN and CoO_x/g-CN samples for the reduction of CO_2 to CO under visible light irradiation.

The photocatalytic processes of the reduction of CO_2 to CO by g-CN, in cooperation with both an electron mediator (Co^{2+} and bpy) and oxidative catalyst (cobalt oxide), can be depicted in Scheme 1. The excitation of g-CN with the visible light induces the generation, separation, and interfacial transfer of charge carriers. The presence of the electron mediator and oxidative cocatalyst significantly accelerates the transfer processes by the formation of surface heterostructures and the establishment of electron transport chains. High-energy electrons and holes are thus generated for tandem chemical conversion of CO_2 and an oxidizable organic substrate. The activated CO_2 was then photocatalytically split into CO and [O], accompanied with H_2 evolution from the oxidative dehydrogenation of TEOA as a side reaction. The sum reaction is $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$, where both protons and electrons still come from the organic substrate TEOA. Here, biomass or even water can in principle be envisaged to act as a sustainable source of electrons and protons for this hybrid photochemical system.[39,40]

Scheme 1. Cooperative Effect of Cobalt Redox Catalysis and g-CN Photocatalysis for Activation and Reduction of CO_2 to CO Under Visible Light Irradiation



In summary, we have successfully activated polymeric g-CN with cobalt species for CO photosynthesis from CO_2 with visible light by using g-CN semiconductors as both CO_2 activator and photocatalyst and cobalt species as redox promoters. The thus constructed photosystem splits CO_2 to CO via carboxyl anion radical intermediates, here with an apparent quantum yield of 0.25% at 420 nm. The photocatalyst was stable throughout the reaction, without noticeable alteration in the chemical and X-ray structures. The work puts an important step forward for artificial photochemical CO_2 splitting with cheap and all-sustainable systems. Continuing the work on optimization of the system, coupled with already known tools of carbon nitride chemistry (e.g., engineering of band gap and surface[35] and texture properties[29]), will certainly allow for developing an even more efficient CO_2 reduction system, free of rare noble metal catalysts.

ASSOCIATED CONTENT

Supporting Information

Detailed experimental description and extra characterization and activity results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is financially supported by the National Basic Research Program of China (2013CB632405), National Natural Science Foundation of China (21033003 and 21173043), State Key Laboratory of NBC Protection for Civilian (SKLNBC2013-04K), and Specialized Research Fund for the Doctoral Program of Higher Education (20133514110003).

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