

PCCP

Accepted Manuscript



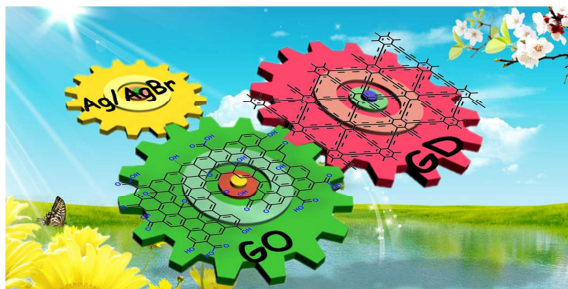
This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Graphic Abstract



Pristine graphdiyne has been hybridized with Ag/AgBr using graphene oxide as coupling reagent, and enhanced photocatalytic performances has been realized.

Pristine Graphdiyne–Hybridized Photocatalysts using Graphene Oxide as Dual–Functional Coupling Reagent†

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2014,
Accepted 00th January 2014

DOI: 10.1039/x0xx00000x

www.rsc.org/

Xiao Zhang,^{‡a} Mingshan Zhu,^{‡a} Penglei Chen,^{a*} Yongjun Li,^b Huibiao Liu,^b Yuliang Li,^b and Minghua Liu^a

Advanced functional hybrids based on carbon materials (CMs) represent one of the main achievements of scientific communities. To achieve the hybridization, pristine CMs have to be chemically modified, or surfactants, which are nonfunctional for the performances of the hybrids, have to be employed as cross-linkage. It is strongly desired to construct pristine CMs-based hybrids using dual-functional coupling reagents, which work not only as a glue for hybridization but also as functional component for an enhanced performance. Here, we report that pristine graphdiyne (GD), a recently synthesized new carbon allotrope, could be facilely hybridized with Ag/AgBr using graphene oxide (GO) as cross-linkage. We demonstrate that compared to Ag/AgBr, Ag/AgBr/GO, and Ag/AgBr/GD, our Ag/AgBr/GO/GD exhibits boosted photocatalytic performances toward the degradation of methyl orange (MO) pollutant under visible-light irradiation. In our Ag/AgBr/GO/GD, GO serves not only as glue for a successful hybridization but also as functional component for the enhanced catalytic performances. Beyond GD, our work likely paves new avenue for the fabrication of advanced functional hybrids based on pristine carbon allotropes, wherein desired functions or properties might be achieved by choosing desired CMs and desired hybridized components.

1. Introduction

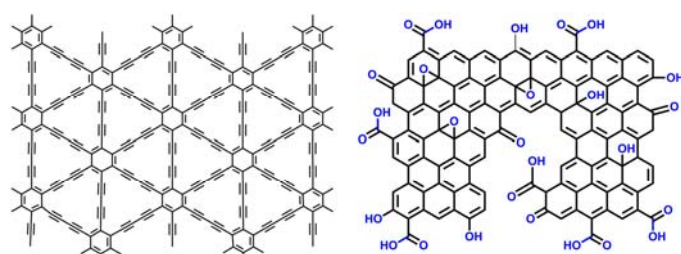
Allotropes of carbon materials (CMs), including fullerene, carbon nanotube, graphene *etc.*, have recently received numerous expectations from scientific communities. This is owing to their unique π -conjugated systems and skeleton characters, which confer them with prominent electrochemical, photophysical, and biological properties.^{1–7} These natures render them promising scaffold for advanced functional hybrids in a variety of fields, such as energy harvesting/storage/conversion, catalysts, *etc.*^{4–7} Currently, CMs-based hybrids represent one of the main achievements of scientific communities in the search for new advanced functional materials.^{1–7} To fabricate their hybrids, it generally is necessary that the pristine CMs, which have no anchoring sites on their skeleton, have to be modified.^{1–7} On one hand, chemical modification would break the intrinsic properties of the pristine CMs to some extent. On the other hand, the hybridization could also be achieved *via* noncovalent modifications, for example, using surfactant as integrative reagent.^{1, 3–6} Nevertheless, in most of the cases, the used surfactants work only as glue reagent other than the functional

component of the formulated hybrids. It is strongly desired to construct pristine CMs-based hybrids using dual-functional coupling reagents, which work not only as glue for hybridization but also as functional components for an enhanced performance of the fabricated composites.

On another front, while fullerenes, carbon nanotubes, and graphene *etc.* have witnessed a tremendous development in the area of CMs-based hybrids,^{4–7} the launch of new carbon allotropes is considered to be an important issue for emergent advanced functional materials of new physicochemical properties and application possibilities. In this direction, graphdiyne (GD), a new carbon allotrope (Scheme 1, left), has gained particular attention.^{8–22} Electronically, GD is constructed by sp - and sp^2 -hybridized periodic carbon networks, while it is structurally composed of repeating pattern of hexagonal carbon rings with the nearest-neighbored hexagons cross-linked by diacetylene ($-C\equiv C-C\equiv C-$). These features endow GD with a rich variety of emergent electronic, mechanical and optical properties, which are different from other carbon variants. It is predicted that GD could work as promising advanced functional

materials in a wide range of fields, including nonlinear optics, catalysts, *etc.*^{8, 9, 13–22}

Like other carbon allotropes, the interest in GD has traced a similar trajectory, that is, after investigations on the theoretical and synthetic aspects of the bare GD, hybrid materials based on GD have consequentially become a focused issue, although this topic is currently in its infancy stage.^{9, 13, 14} For example, it has recently been reported that the photocatalytic performances of TiO₂ toward the photodegradation of organic pollutants could be enhanced upon the formation of GD–hybridized species, TiO₂/GD.^{13, 14} It is verified that this could be owing to the high electron mobility of GD, which works as an acceptor of the photogenerated electrons, suppressing the recombination of the electron–hole pairs. Nevertheless, the TiO₂/GD therein was fabricated under high temperature and pressure in terms of a hydrothermal reaction to promote the formation of Ti–O–C and Ti–C bonds. Meanwhile, only a limited enhancement in the catalytic reactivity could be achieved. It still remains a formidable challenge to construct pristine GD–based high performance hybrids under ambient conditions.



Scheme 1. Chemical structure of GD (left) and GO (right).

To address this tough challenge, we herein report that pristine GD could be facilely hybridized with Ag/AgBr photocatalysts using graphene oxide (GO, Scheme 1, right), a hotly investigated graphene derivative with its plane and edge decorated with various oxygen functionalities,^{23–28} as dual–functional coupling reagent under ambient conditions. Significantly, we show that compared to the Ag/AgBr, Ag/AgBr/GO, and Ag/AgBr/GD, the catalytic performances of our Ag/AgBr/GO/GD hybrids, toward the degradation of methyl orange (MO) pollutant under visible light irradiation, are 8.9, 4.3 and 2.9 times enhanced, respectively. The boosted catalytic reactivity is owing to the synergistic effect of GO and GD sheets, which promotes an efficient charge separation/transfer, and suppresses the recombination of the electron–hole pairs. In our Ag/AgBr/GO/GD hybrid, GO works not only as glue reagent for hybridization but also as functional component for the boosted catalytic performances.

The significance of our new protocol is twofold. First, beyond GD, it likely opens new horizons for the construction of advanced functional materials based on other pristine CMs. Second, but not least, other than the addressed high–efficient photocatalysts, advanced materials of desired functions and properties might be constructed by choosing desired hybridized components.

2. Experimental Section

2.1. Materials

Graphite powder (Alfa Aesar, 325 mesh, 99.9995%), silver nitrate (AgNO₃, Sigma–Aldrich, >99%), cetyltrimethylammonium bromide (CTAB, Alfa Aesar, 95%) and methyl orange (MO, Alfa Aesar, >98%) were used as received without additional purification or treatment. Ultrapure Milli–Q water (18.2 MΩ) was used as solvent for the preparation of various aqueous dispersions.

2.2. Synthesis of graphdiyne (GD) and graphene oxide (GO)

Our GD sheets were synthesized *via* a cross–coupling reaction of hexaethynylbenzene by some of our coauthors. The synthesis was achieved according to the methods reported previously.¹⁰ GO nanosheets were fabricated through a chemical exfoliation of graphite powder by using a modified Hummers' method. The detailed synthesis was carried out according to the procedures described previously.²⁷ The specific procedures for the synthesis of GD and GO were described in ESI.

2.3. Preparation of GO/GD suspension

In a typical process, 10 mg GD sheets were added into a 20 mL aqueous dispersion of GO nanosheets (1 mg mL^{–1}). The mixture was treated with an ultrasonic homogenizer (Ningbo Scientz Biotechnology Co., Ltd., Scientz–II D, frequency = 20 kHz, output power = 400 W) for 1 hour, after which an aqueous dispersion of GO/GD was obtained. The products were collected and washed thoroughly with ultrapure Milli–Q water *via* repeating centrifugations (2000 rpm, 5 minutes), after which they were submitted to various characterizations.

2.4. Synthesis of Ag/AgBr/GO/GD, Ag/AgBr/GD, Ag/AgBr and Ag/AgBr/GO *via* an oil–in–water microemulsion medium

For the fabrication of Ag/AgBr/GO/GD, 500 μL of the above prepared GO/GD suspension was injected into a 10 mL aqueous solution of AgNO₃ (5 × 10^{–3} mol L^{–1}) under magnetic stirring. The mixture was stirring for 10 minutes, and then a 500 μL chloroform solution of CATB (6 × 10⁴ mg L^{–1}) was added dropwise to the dispersion within about 5 minutes at room temperature. The stirring was continuously maintained for another 20 minutes for the evaporation of chloroform. The resultant dispersion was subsequently treated by centrifugation (10000 rpm, 10 minutes) and the produced solids were collected and washed thoroughly with ultrapure Milli–Q water by repeating centrifugations. After the fabrication, the as–formulated Ag/AgBr/GO/GD species were subjected to various characterizations or to photocatalytic performances.

For the synthesis of Ag/AgBr/GD species, almost similar processes were carried out except that an aqueous dispersion of GD (500 μL, 1 mg mL^{–1}) instead of the suspension of GO/GD was added to the AgNO₃ aqueous solution. Moreover, the synthesis of Ag/AgBr and Ag/AgBr/GO, which was also realized *via* an oil–in–water microemulsion system, was performed according to the procedure described elsewhere.²⁹

2.5. Photocatalytic performances

For catalytic experiments, 9 mg Ag/AgBr-based photocatalysts were dispersed in an aqueous solution of methyl orange (MO, 60 mg L⁻¹, 9 mL). A quartz cuvette was used as the reactor. A 500 W xenon arc lamp installed in a laboratory lamp housing system (CHF-XM35-500 W, Beijing Trusttech Co. Ltd., China) was employed as the light source. The light passed through a 10 cm water filter and a UV cutoff filter (>400 nm) before entering the reactor. The reaction system was kept for 30 minutes in a dark room to achieve an equilibrium adsorption state before visible-light irradiation. Aliquots of the dispersion (0.3 mL) were taken out from the reaction system for real-time sampling. The photodegradation of MO was investigated by measuring the real-time UV-vis absorption of MO at 463 nm. For catalytic reactivity evaluation, C is the concentration of MO at a real-time t , and C_0 that in the MO solution immediately before it was kept in dark.

2.6. Fabrication of Electrodes and Photoelectrochemical Measurements

First, indium tin oxide (ITO) glass electrodes were modified by our Ag/AgBr-based composites. To achieve this, 5 mg Ag/AgBr-based materials were dispersed in 2 mL ethanol, which was then coated onto a 2 cm × 4 cm ITO electrode and dried under ambient conditions. The photocurrent experiments were carried out in a three-electrode system using ITO electrodes, which were modified by our Ag/AgBr-based composite, as the working electrode, a platinum wire and a saturated calomel electrode (SCE) as the counter electrodes and the reference electrode, respectively. An aqueous solution of NaCl (0.1 M) was used as the electrolyte. The working electrode was irradiated with visible-light during the measurement. Photocurrent-time characteristics were recorded with a CHI 660B electrochemical analyzer (Shanghai Chenhua Instrumental Co., Ltd., China).

The electrochemical impedance spectral (EIS) measurements were carried out on a conventional three-electrode cell using an electrochemical workstation (CHI 660B) at room temperature. The modified ITO electrode served as the working electrode, a platinum wire worked as the counter electrode, and a SCE electrode worked as the reference electrodes. The measurement was performed in a 0.1 M NaCl solution with a 2.5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1) mixture as a redox probe. The impedance spectra were recorded with the help of ZPlot/ZView software under an ac perturbation signal of 5 mV over a frequency range of 0.05 Hz to 100 kHz at a potential of 0.1 V.

2.7. Apparatus and measurements

The scanning electron microscopy (SEM) measurements were carried out using a Hitachi S-4800 system. The energy dispersive X-ray spectroscopy (EDX) was measured with a Horiba EMAX X-act energy dispersive spectroscopy that was attached to the Hitachi S-4800 system. X-ray diffraction (XRD) measurements were performed on a PANalytical X'Pert PRO

instrument with Cu K α radiation. UV-vis diffuse reflectance spectra of the samples were obtained on an UV-vis spectrophotometer (Hitachi U-3010) using BaSO₄ as the reference. The photodegradation of the MO pollutant was monitored by measuring the real-time UV-vis spectra of the catalytic systems using a Hitachi U-3010 spectrometer. The Raman spectra were recorded on a Renishaw inVia plus Raman microscope using a 514.5 nm argon ion laser. All the measurements were carried out under ambient conditions.

3. Results and discussion

3.1. Fabrication and characterization

The GD sheets were synthesized by some of our coauthors.¹⁰ As indicated by the SEM images (Fig. 1A and Fig. S1), the average size and thickness of our GD sheets were *ca.* 80 and 2 μ m, respectively. First, we attempted to synthesize Ag/AgBr/GD hybrids *via* a microemulsion medium, wherein cetyltrimethylammonium bromide (CTAB) and AgNO₃ served as Br and Ag sources,^{27, 29} respectively. To achieve this, an aqueous dispersion of GD sheets was added into a AgNO₃ aqueous solution at room temperature under vigorous stirring. Subsequently, a chloroform solution of CTAB was added into the system. After the evaporation of chloroform, the products were collected and washed thoroughly with ultrapure water *via* repeating centrifugation. As shown in Fig. 1B and S2, both GD sheets and Ag/AgBr nanospecies could be observed from the SEM image of the as-synthesized products. Note that most of the Ag/AgBr nanospecies stand away from the GD sheets. On the other hand, most of the GD surface manifests itself with almost similar feature as that of the bare GD shown in Fig. 1A and S1, except that only a small fraction of the surface is decorated with Ag/AgBr nanospecies. This indicates that our pristine GD sheets could not be well hybridized with Ag/AgBr species. This could be owing to the lack of anchoring sites on the surface of the bare GD sheets, which disfavors a good hybridization.

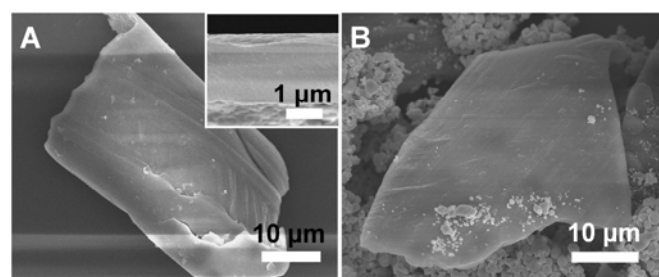


Fig. 1 Typical SEM image of the bare GD (A), and Ag/AgBr/GD (B). The insert in panel A is the cross section SEM image of our GD.

Currently, GO has received much attention as a novel cousin of graphene. The decoration of various oxygen functionalities on its basal plane and edge, and the existence of locally distributed π -system (polyaromatic graphene fragment) on its framework (Scheme 1, right panel) provide it with fertile opportunities for the construction of GO-based advanced

functional hybrids *via* various noncovalent forces, such as electrostatic, coordination, dipole, or π - π interactions.^{6, 23–25} On the other hand, it has recently been demonstrated that in the unique π -conjugated system of GD, the sp^2 and sp hybridized carbon atoms of GD are negatively and positively charged, respectively. This is owing to the occurrence of an electron transfer from the latter to former.^{21, 22} These issues might provide new opportunities for the construction of π - π interactions and electrostatic interactions assisted GD-based hybrids using GO as an integrative component.

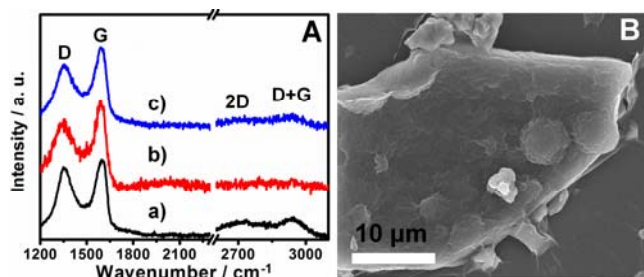


Fig. 2 Panel A: Raman spectra of GO (a), GD (b) and GO/GD (c). Panel B: Typical SEM image of the as-formulated GO/GD species.

Inspired by these basic understandings, we attempted to fabricate Ag/AgBr/GO/GD hybrids using GO nanosheets as the glue reagent. To realize this, GD sheets were added into an aqueous dispersion of GO under vigorous stirring. The obtained dispersion was treated with an ultrasonic homogenizer. Then, the products were collected and washed thoroughly with water *via* repeating centrifugation. Fig. 2A shows the Raman spectra of the as-formulated products. Those of our GO and GD sheets are also presented for comparison. It can be seen that GO displays typical D- and G-bands maximum at *ca.* 1354 and 1601 cm^{-1} , respectively. Besides, a weakly smeared 2D-band around 2694 cm^{-1} together with a combination of the D- and G-bands around 2940 cm^{-1} , could also be discerned. These are well-documented Raman spectra of GO.^{30, 31} For GD sheets, characteristic D- and G-bands maximum around 1354 and 1586 cm^{-1} , respectively, but no distinct overtone 2D-band and D+G combination band, could be observed.¹⁰ Meanwhile, a broad yet weak band around 2000 cm^{-1} , which can be attributed to the vibration of conjugated diene links $-C\equiv C-C\equiv C-$, could also be observed.¹⁰ In contrast, for the as-formulated products, D-, G-, overtone 2D, and combination of D+G bands could be observed. These observations preliminarily indicate the formation of GO/GD species, which might be assisted by the π - π interactions between GO and GD.³² Similar proposal has been reported for the formation of GO/carbon nanotube and GO/fullerene composites.³² On the other hand, it has been proved that as a result of an electron transfer from the sp to the sp^2 hybridized carbon atoms, the former and latter carbon atoms in the GD sheets are positively and negatively charged, respectively.^{21, 22} Moreover, it has been verified that owing to the ionization of the carboxylic acid and phenolic hydroxy groups, GO nanosheets are negatively charged.²⁵ These issues suggest that the electrostatic interactions between GD and GO

sheets might also contribute partially to the formation of the GO/GD species.

The SEM images of the products were also investigated. As shown in Fig. 2B, it can be seen that GD species, whose surface are distinctly wrapped with gauze-like GO nanosheets, could be observed. In addition, except those covered on the surface of the GD species, almost no free GO nanosheets separated from GD could be observed. It should be noted that the as-formulated samples were collected and washed thoroughly with ultrapure water *via* repeating centrifugation. The results showed that when the aqueous dispersion of GO nanosheets was treated under the similar conditions, no sediment could be found from the bottom or the wall of the centrifuge tubes. These experimental facts further indicate the formation of GO/GD composites.

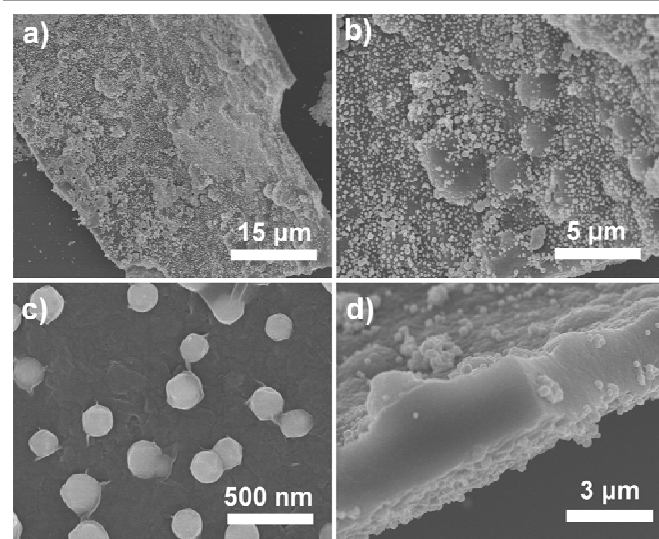


Fig. 3 Typical low-magnification (a), high-magnification (b, c), and cross section (d) SEM images of the as-fabricated Ag/AgBr/GO/GD hybrids.

To fabricate Ag/AgBr/GO/GD hybrids, almost similar procedures as those in the case of Ag/AgBr/GD were carried out, except that an aqueous dispersion of GO/GD instead of the bare GD sheets was employed. The SEM images of thus-manufactured products were investigated. As shown in Fig. 3, Ag/AgBr nanospecies, which are homogeneously anchored on the surface of GO/GD could be observed. A close observation of the SEM images (Fig. 3d) further reveals that the Ag/AgBr nanospecies are distributed both on the top, bottom and side of the GO/GD sheets. More significantly, almost no free Ag/AgBr nanospecies could be observed outside the GO/GD species. Together with the results observed from the Ag/AgBr/GD systems (Fig. 1B, and S2), which are formulated without the participation of GO nanosheets, these observations indicate that GD sheets could be well hybridized with Ag/AgBr species *via* GO nanosheets. The capping of Ag/AgBr by the carboxylic acid groups of GO nanosheets leads to the formation of the Ag/AgBr/GO/GD composites.^{28, 29}

This could be further verified by the Fourier transform infrared spectra (FT-IR) of the samples, as shown in Fig. S3. It

can be seen that the typical FT-IR spectrum of GD displays a distinct band at *ca.* 1587 cm^{-1} , which could be assigned the skeletal vibrations of the aromatic rings.¹⁰ For GO, the characterized C=O carbonyl stretching band at 1731 cm^{-1} , and the vibrations of the adsorbed water molecules at *ca.* 1625 cm^{-1} , could be observed distinctly.^{27, 33, 34} In the cases of the GO/GD, the C=O carbonyl stretching band of GO at 1731 cm^{-1} could still be observed evidently, while the skeletal vibrations of the aromatic rings of GD at 1587 cm^{-1} , could not be discerned, since it is covered up by the broad band of the vibrations of the adsorbed water molecules of GO. Significantly, in the cases of the Ag/AgBr/GO and Ag/AgBr/GO/GD species, the C=O carbonyl stretching band shifts to a lower wavenumber of *ca.* 1709 cm^{-1} . Together with the results of SEM (Fig. 3), Raman spectra (Fig. 2), these results verify a successful hybridization between Ag/AgBr and GO or GO/GD.^{27, 35} Experimentally, we have also attempted to disclose the structure of our samples by transmission electron microscopy (TEM). Unfortunately, we found that our samples suffered a fast decomposition soon after the focusing. Similar phenomenon has been reported previously,^{36–38} where it has been found that the silver halide species could be destroyed rapidly by the high-energy electron beam of TEM. Nevertheless, the results of Raman spectra (Fig. 2), SEM (Fig. 3), and FT-IR spectra (Fig. S3) verify that GO nanosheets could work as glue reagent for a successful hybridization between GD sheets and Ag/AgBr nanospecies.

Besides Ag/AgBr/GD and Ag/AgBr/GO/GD, Ag/AgBr and Ag/AgBr/GO species were also prepared *via* our oil-in-water microemulsion medium according to the methods reported previously.²⁹ As described in the aftermentioned paragraphs, these structures were fabricated to make a comparative investigation on their catalytic performances in relation to the effects of GO, GD, and GO/GD species.

The components of our Ag/AgBr, Ag/AgBr/GO and Ag/AgBr/GO/GD hybrids were estimated by energy dispersive X-ray spectroscopy (EDX) analysis. As shown in Fig. S4, for Ag/AgBr/GO and Ag/AgBr/GO/GD species, in addition to the signals ascribed to Si (note that the Si slice was used as solid support for the EDX measurements), those attributed to C, O, Br, and Ag could also be detected evidently. For Ag/AgBr/GO/GD hybrids, the atomic ratio between C and O is *ca.* 5.6. This value is larger than that of the Ag/AgBr/GO species, which is *ca.* 2.6. This is reasonable, since only C but no O exists in the skeleton of our pristine GD sheets. This decreases and increases the relative content of O and C, respectively. Furthermore, the atomic ratio between Br and Ag is *ca.* 1:1.1 for all the samples. This value is larger than the theoretic stoichiometric atomic ratio between Br and Ag in AgBr, which should be 1:1. This could be owing to the ambient light-induced generation of metallic Ag species, leading to the formation of Ag/AgBr species.^{28, 39} For the bare Ag/AgBr nanospecies, almost similar results are obtained, except that no C and O elements could be detected. The EDX analysis of our Ag/AgBr/GD species is not shown herein, because their poor hybridization does not permit us to carry out the corresponding

measurements, wherein a homogeneous hybridization is generally required.

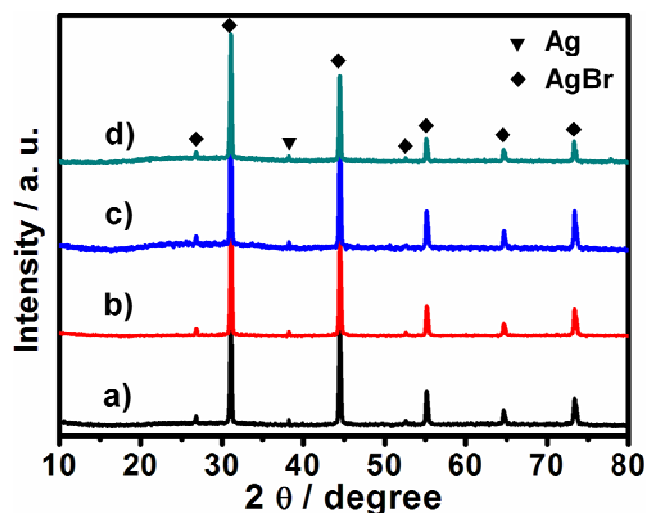


Fig. 4 XRD pattern of our Ag/AgBr (a), Ag/AgBr/GO (b), Ag/AgBr/GD (c), and Ag/AgBr/GO/GD (d) species. The diffraction peaks ascribing to Ag and AgBr are marked with ▼ and ◆, respectively.

The XRD patterns of our products were investigated to identify the formation of Ag/AgBr-based composites. As shown in Fig. 4, all of our samples display distinct diffraction peaks (2θ) at *ca.* 26.7° (111), 30.9° (200), 44.3° (220), 52.5° (311), 55.0° (222), 64.5° (400), 71.1° (331) and 73.2° (420), which could be ascribed to the typical diffractions of cubic phase AgBr (JCPDS file: 6-438).^{29, 39, 40} Meanwhile, weak diffraction peak at *ca.* 38.2°, which could be indexed to the (111) facet of cubic phase metallic Ag (JCPDS file: 65-2871),^{29, 39, 40} could also be observed. These facts confirm the formation of Ag/AgBr species in these samples. It is noted that negligible diffraction peaks attributing to GO or GD sheets could be detected from these samples. Similar phenomenon has been reported for the GO or GD-involved hybrids, wherein it is suggested that the absence of the diffraction peaks of GO or GD sheets might be owing to their low diffraction intensity.^{13, 28, 41}

To further disclose the existence of the metallic Ag species in our samples, their UV-visible diffuse reflectance spectra were also investigated. As shown in Fig. S5, besides the strong absorptions located in the UV region, all of the samples exhibit broad yet distinct absorptions in visible region between *ca.* 475–700 nm. As it is known, the bare AgBr species could only show apparent absorptions in UV region and in visible region with a wavelength shorter than *ca.* 475 nm.^{39, 42} Accompanied by the experimental facts of XRD pattern (Fig. 4) and EDX analysis (Fig. S4), these results further verify the formation of Ag/AgBr species in our samples. The existence of metallic Ag species evokes surface plasmon resonance (SPR) absorptions in the visible region.

3.2. Catalytic performances

Recently, Ag/AgX-based photocatalysts (X= Cl, Br, I) have become an issue of particular concern.^{27–29, 40, 43–45} This is owing to their outstanding visible-light-driven catalytic performances, although AgX species are conventionally used as the primary source materials in photographic film and are unstable upon photo illumination. Despite numerous efforts in achieving high-quality Ag/AgX-based photocatalysts, it is still highly desirable to initiate new opportunities for a substantial enhancement in their catalytic reactivity to meet the demands of future environmental issues.⁴³

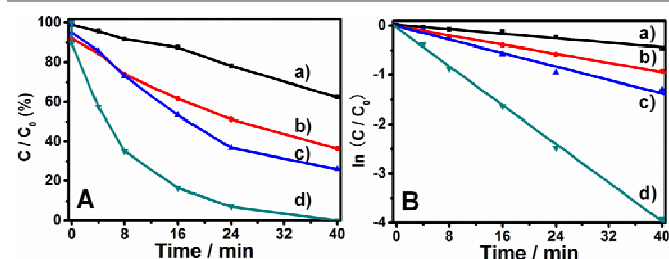


Fig. 5 Photocatalytic performances (A) and the corresponding kinetic linear simulation curves (B) of the investigated photocatalysts toward the photodegradation of MO pollutant under visible-light irradiation. The employed photocatalysts are Ag/AgBr (a), Ag/AgBr/GO (b), Ag/AgBr/GD (c), and Ag/AgBr/GO/GD (d) species, respectively.

Motivated by the aforementioned results and together with these brief backgrounds, the catalytic performances of our Ag/AgBr-involved materials toward the photodegradation of MO pollutant under visible light irradiations were investigated. As shown in Fig. 5A and Table 1, when our bare Ag/AgBr species is employed as the catalysts, *ca.* 37.6% MO molecules are decomposed within 40 minutes. In contrast, when our Ag/AgBr/GO and Ag/AgBr/GD composites are used as the catalysts, *ca.* 63.7% and 74.1% MO molecules are eliminated under the similar experimental conditions, respectively. Significantly, nearly 100% MO molecules are decomposed, when our Ag/AgBr/GO/GD hybrid is employed. As plotted in Fig. 5B, there is a nice linear correlation between $\ln(C/C_0)$ and reaction time (*t*). This indicates that the MO photodegradation reaction over our catalysts follows the first-order kinetics: $-dC/dt = kC$. Herein, *C* stands for the real-time concentration of MO molecules, *t* represents reaction time, and *k* stands for rate constant.

As shown in Fig. 5B and summarized in Table 1, compared to that over Ag/AgBr (0.011 min^{-1}), the rate constant of the photocatalytic reaction over our Ag/AgBr/GO (0.023 min^{-1}) and Ag/AgBr/GD (0.034 min^{-1}) species are distinctly increased by a factor of *ca.* 2.1 and 3.1, respectively. However, there is only *ca.* 1.5 times difference when the later two cases, Ag/AgBr/GO and Ag/AgBr/GD, are compared. This indicates that our Ag/AgBr/GO and Ag/AgBr/GD have comparable catalytic reactivity, although there exists somewhat differences. This could be reflected in the aftermentioned transient photocurrent response curves (Fig. 6) and the EIS curves (Fig. 7) of the ITO electrodes modified by our Ag/AgBr/GO and Ag/AgBr/GD, where comparable results with small differences could be observed. On the other hand, it can be seen that the

rate constant of the MO photodegradation reaction over our Ag/AgBr/GO/GD hybrids is estimated to be *ca.* 0.098 min^{-1} . This value is evidently larger than that over the bare Ag/AgBr, Ag/AgBr/GO and Ag/AgBr/GD species, which is *ca.* 0.011, 0.023 and 0.034 min^{-1} , respectively. It can be seen that compared to the Ag/AgBr, Ag/AgBr/GO, and Ag/AgBr/GD composites, the catalytic reactivity of our Ag/AgBr/GO/GD species is *ca.* 8.9, 4.3, and 2.9 times enhanced, respectively. These facts indicate that upon the hybridization of GO/GD, the resultant Ag/AgBr/GO/GD hybrids could work as high-performance catalysts for the elimination of organic pollutants under visible-light illumination.

Table 1. Summary of the catalytic performances of our Ag/AgBr-based photocatalysts for the photodegradation of MO pollutant under visible-light irradiations.

Catalysts	Degradation percentage (%)	Kinetic constant (min^{-1})	Determination coefficient (R^2)
Ag/AgBr	37.6	0.011	0.99
Ag/AgBr/GO	63.7	0.023	0.998
Ag/AgBr/GD	74.1	0.034	0.991
Ag/AgBr/GO/GD	~100	0.098	0.999

As known, an efficient electron separation/transfer is one of the most crucial issues that affect the catalytic performances of a photocatalyst.^{35, 41, 42, 46} It has recently been verified that GD could work as one of promising catalyst supports or promoters in terms of facilitating an electron separation/transfer.^{8, 9, 13, 14} This is owing to their unique π -conjugated system, which endows GD with a high electron mobility,^{11, 20} and renders them capable of promoting an efficient charge separation/transfer.^{9, 13, 14} To verify this in our present photocatalysts, their transient photocurrent responses under intermittent visible-light illumination were investigated in terms of photocurrent-time response (*I*-*t*) curves by means of three-electrode photoelectrochemical measurements. The indium tin oxide (ITO) glass, which was modified by our Ag/AgBr-based composite, was used as the working electrode. As shown in Fig. 6, it can be seen that for all the investigated samples the photocurrent increases immediately when the light irradiation is switched on, while a dramatic decrease in the photocurrent is observed when the light irradiation is switched off. Such expeditious, steady, and reversible photocurrent responses could be operated repeatedly and reproducibly several times during each switch-on and switch-off cycle. These results indicate the separation and transportation of the photogenerated electron-hole pairs in our samples upon illumination.

For ITO photoelectrodes modified by our bare Ag/AgBr species, only discernible photocurrent responses with weak current intensity could be observed. In contrast, those modified by our Ag/AgBr/GO hybrids exhibit an evident enhancement in the photocurrent intensity. These results are in good agreement with the fact that compared to the bare Ag/AgBr species, our Ag/AgBr/GO hybrids could display an enhanced catalytic performance (Fig. 5 and Table 1), indicating that the

hybridization of GO nanosheets could promote the charge separation/transfer and thus suppress the charge recombination of electron-hole pairs. This is owing to the unique locally distributed polyaromatic π -conjugated system of GO species, which makes them capable of working as electron reservoir and transporter to trap and transfer the photoinduced electrons from Ag/AgBr nanospecies, and accordingly enhance the separation efficiency of the electron-hole pairs.²⁷

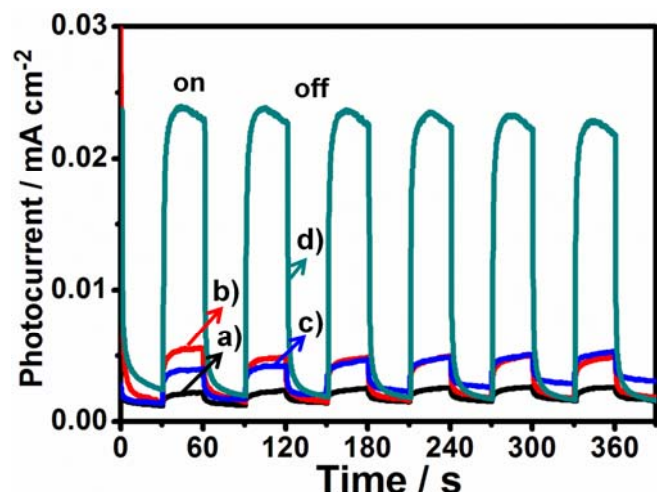


Fig. 6 Transient photocurrent responses of the ITO electrodes modified by our Ag/AgBr (a), Ag/AgBr/GO (b), Ag/AgBr/GD (c), and Ag/AgBr/GO/GD (d) species. The illumination was periodically interrupted every 30 seconds during the measurements.

On the other hand, in the case of the photoelectrodes modified by our Ag/AgBr/GD species, comparable photocurrent responses as those of the Ag/AgBr/GO-modified electrodes are detected. These observations are in accordance with the photocatalytic results shown in Fig. 5 and Table 1, wherein our Ag/AgBr/GO and Ag/AgBr/GD hybrids show very close catalytic performances. Similar to the case of Ag/AgBr/GO species, this indicates that the introduction of GD species to Ag/AgBr could also favor the separation and transfer of the photogenerated charge carriers.^{13, 14} In terms of density functional theory (DFT) calculations, it has been demonstrated that, the in-plane intrinsic electron mobility of a GD sheet could reach an order of *ca.* $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, which is nearly as high as that of the pristine graphene.¹¹ This unique feature render GD species promising electron collector in photocatalysts to trap and transport the photoinduced electrons, facilitating an enhancement in catalytic reactivity,^{13, 14} although the lack of active anchoring sites on the surface of the pristine GD does not favor a good hybridization (Fig. 1B and S2).

Geometrically, GO could be figured as polyaromatic fragments of the pristine graphene, whose edge and basal plane are functionalized with various oxygen-containing groups. On one hand, the existence of the oxygen-containing groups on their skeleton could destroy their π -conjugated system, leading to a substantial decrease in the electron transport properties of GO. On the other hand, it has been widely recognized that the catalytic performances of semiconductor photocatalysts could

be essentially enhanced upon hybridization with GO.^{4, 47, 48} The boosted catalytic reactivity could basically be understood with regard to the GO-promoted photo-induced charge separation/transfer *etc.*^{4, 47, 48} Although compared to the pristine graphene, GO displays significantly decreased electron transport properties, the polyaromatic graphene fragments of GO, which could serve as an electron relay mediator, are suggested to play an important role for the facilitated charge separation/transfer, leading to an enhancement in the photocatalytic performance.^{49–51} Together with the outstanding electron transport properties of GD,^{13, 14} it thus could be expected that a more efficient separation of the photogenerated electron-hole pairs might be realized in our Ag/AgBr/GO/GD composites, since the Ag/AgBr nanospecies therein is in a good hybridization with GD *via* GO nanosheets (Fig. 3). This could be verified by the distinctly boosted photocurrent of the ITO photoelectrodes modified by our Ag/AgBr/GO/GD composites. As shown in Fig. 6, compared to that of the electrodes modified by the Ag/AgBr ($1.0 \mu\text{A cm}^{-2}$), Ag/AgBr/GO ($3.2 \mu\text{A cm}^{-2}$), and Ag/AgBr/GD ($2.4 \mu\text{A cm}^{-2}$) species, the responsive photocurrent intensity of the Ag/AgBr/GO/GD-modified ITO electrodes ($21.8 \mu\text{A cm}^{-2}$) is approximately 22, 7 and 9 times increased, respectively. These results confirm that the synergistic effect of GO and GD sheets contributes much to the distinctly promoted separation of the photogenerated electron-hole pairs, leading to a substantially boosted photocatalytic reactivity.

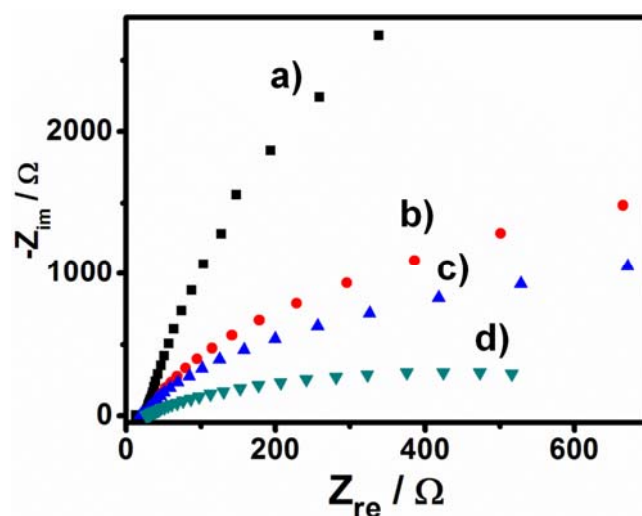


Fig. 7 The EIS changes of the ITO electrodes modified by our Ag/AgBr (a), Ag/AgBr/GO (b), Ag/AgBr/GD (c), and Ag/AgBr/GO/GD (d) species.

To provide more evidence for our proposals, EIS of our samples were examined as Nyquist plots. As shown in Fig. 7, the measured semicircular arcs of the electrodes modified by our Ag/AgBr/GO and Ag/AgBr/GD composites display comparable radius, which is evidently smaller than that of the electrodes modified by the bare Ag/AgBr nanospecies. In general, a smaller semicircular arc in the EIS indicates a faster interfacial charge transfer and a more effective separation of the

photogenerated electron–hole pairs.^{41, 52, 53} These observations suggest a decrease in the solid state interface layer resistance and the charge transfer resistance on the surface of our Ag/AgBr/GO and Ag/AgBr/GD species.⁵² Together with the above–mentioned results of transient photocurrent responses of the samples (Fig. 6), this further indicates that the GO and GD sheets could indeed serve as electron reservoirs to promote the charge separation and thus suppress the recombination of the photogenerated electron–hole pairs, leading to an enhance catalytic performance. More importantly, it can be seen that compared to that of the electrodes modified by Ag/AgBr/GO and Ag/AgBr/GD species, the arc radius of the electrodes modified by our Ag/AgBr/GO/GD hybrids displays a further decrease. These results further confirm the occurrence of a more efficient charge separation in the Ag/AgBr/GO/GD hybrids, where the Ag/AgBr nanospecies are well hybridized with GD *via* GO nanosheets.

4. Conclusions

In summary, using GO nanosheets as coupling reagent, we have demonstrated that the pristine GD species could be facilely hybridized with Ag/AgBr nanospecies at room temperature under ambient conditions. The as–formulated Ag/AgBr/GO/GD hybrids could work as highly efficient visible–light–driven photocatalysts toward the photodegradation of MO pollutant. Compared to the Ag/AgBr, Ag/AgBr/GO, and Ag/AgBr/GD species, our Ag/AgBr/GO/GD composites display distinctly boosted catalytic reactivity. The synergistic effect of GO and GD sheets, which could promote an efficient charge separation/transfer, plays an important role. In our new strategy, GO nanosheets work not only as glue reagent for a successfully hybridization but also as a functional component for an enhanced catalytic performance. We envision that our new protocol, using GO nanosheets as a dual–functional coupling reagent, might be extended to some other CMs–based hybrids,⁵⁴ where advanced functional materials of desirable functions or properties might be constructed by selecting desired carbon allotropes and desired hybridization components.

Acknowledgments

This work was supported financially by the National Natural Science Foundation of China (21372225, 21021003, and 91027042), the National Key Basic Research Project of China (2011CB932301 and 2013CB834504), and the Chinese Academy of Sciences (XDA09030200, and 1731300500015). The authors also thank Dr. Chuncheng Chen, and Wanhong Ma from Institute of Chemistry, Chinese Academy of Sciences, for their helpful revision on English.

Notes and references

- ^a Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Colloid, Interface and Chemical Thermodynamics, Chinese Academy of Sciences, Beijing 100190, P. R. China; E–mail: chenpl@iccas.ac.cn
^b CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

† Electronic Supplementary Information (ESI) available: Low–magnification SEM image of our GD sheets, and the as–formulated Ag/AgBr/GD species. EDX elemental analysis of our Ag/AgBr, Ag/AgBr/GO, and Ag/AgBr/GO/GD hybrids. UV–vis diffuse reflectance spectra of our photocatalysts. See DOI: 10.1039/b000000x/

‡ These authors contributed equally to this work.

- E. Nakamura and H. Isobe, *Acc. Chem. Res.*, 2003, **36**, 807–815.
- D. M. Guldi, G. M. A. Rahman, V. Sgobba and C. Ehli, *Chem. Soc. Rev.*, 2006, **35**, 471–487.
- N. Karousis, N. Tagmatarchis and D. Tasis, *Chem. Rev.*, 2010, **110**, 5366–5397.
- H. Bai, C. Li and G. Shi, *Adv. Mater.*, 2011, **23**, 1089–1115.
- D. Eder, *Chem. Rev.*, 2010, **110**, 1348–1385.
- V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim, *Chem. Rev.*, 2012, **112**, 6156–6214.
- C. J. Shearer, A. Cherevan and D. Eder, *Adv. Mater.*, 2014, **26**, 2295–2318.
- A. L. Ivanovskii, *Prog. Solid State Chem.*, 2013, **41**, 1–19.
- Y. Li, L. Xu, H. Liu and Y. Li, *Chem. Soc. Rev.*, 2014, **43**, 2572–2586.
- G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, *Chem. Commun.*, 2010, **46**, 3256–3258.
- M. Long, L. Tang, D. Wang, Y. Li and Z. Shuai, *ACS Nano*, 2011, **5**, 2593–2600.
- J. Chen, J. Xi, D. Wang and Z. Shuai, *J. Phys. Chem. Lett.*, 2013, **4**, 1443–1448.
- S. Wang, L. Yi, J. E. Halpert, X. Lai, Y. Liu, H. Cao, R. Yu, D. Wang and Y. Li, *Small*, 2012, **8**, 265–271.
- N. Yang, Y. Liu, H. Wen, Z. Tang, H. Zhao, Y. Li and D. Wang, *ACS Nano*, 2013, **7**, 1504–1512.
- Y.–X. Yu, *J. Mater. Chem. A*, 2013, **1**, 13559–13566.
- K. Srinivasu and S. K. Ghosh, *J. Phys. Chem. C*, 2012, **116**, 5951–5956.
- Y. Jiao, A. Du, M. Hankel, Z. Zhu, V. Rudolph and S. C. Smith, *Chem. Commun.*, 2011, **47**, 11843–11845.
- H.–J. Cui, X.–L. Sheng, Q.–B. Yan, Q.–R. Zheng and G. Su, *Phys. Chem. Chem. Phys.*, 2013, **15**, 8179–8185.
- S. W. Cranford and M. J. Buehler, *Nanoscale*, 2012, **4**, 4587–4593.
- X. Qian, Z. Ning, Y. Li, H. Liu, C. Ouyang, Q. Chen and Y. Li, *Dalton Transactions*, 2012, **41**, 730–733.
- P. Wu, P. Du, H. Zhang and C. Cai, *Phys. Chem. Chem. Phys.*, 2014, **16**, 5640–5648.
- P. Wu, P. Du, H. Zhang and C. Cai, *J. Phys. Chem. C*, 2012, **116**, 20472–20479.
- J. Kim, L. J. Cote and J. Huang, *Acc. Chem. Res.*, 2012, **45**, 1356–1364.
- D. Chen, H. Feng and J. Li, *Chem. Rev.*, 2012, **112**, 6027–6053.
- H. Yin, H. Tang, D. Wang, Y. Gao and Z. Tang, *ACS Nano*, 2012, **6**, 8288–8297.
- H.–P. Cong, P. Wang and S.–H. Yu, *Chem. Mater.*, 2013, **25**, 3357–3362.
- M. Zhu, P. Chen and M. Liu, *ACS Nano*, 2011, **5**, 4529–4536.
- M. Zhu, P. Chen and M. Liu, *Langmuir*, 2013, **29**, 9259–9268.
- M. Zhu, P. Chen and M. Liu, *Langmuir*, 2012, **28**, 3385–3390.
- B. K. Gupta, P. Thanikaivelan, T. N. Narayanan, L. Song, W. Gao, T. Hayashi, A. Leela Mohana Reddy, A. Saha, V. Shanker, M. Endo, A. A. Martí and P. M. Ajayan, *Nano Letters*, 2011, **11**, 5227–5233.
- S. Wang, S. Dong, J. Wang, L. Zhang, P. Han, C. Zhang, X. Wang, K. Zhang, Z. Lan and G. Cui, *J. Mater. Chem.*, 2012, **22**, 21051–21056.
- V. C. Tung, J.–H. Huang, I. Tevis, F. Kim, J. Kim, C.–W. Chu, S. I. Stupp and J. Huang, *J. Am. Chem. Soc.*, 2011, **133**, 4940–4947.
- X. Ou, L. Jiang, P. Chen, M. Zhu, W. Hu, M. Liu, J. Zhu and H. Ju, *Adv. Funct. Mater.*, 2013, **23**, 2422–2435.
- X. Ou, P. Chen, L. Jiang, Y. Shen, W. Hu and M. Liu, *Adv. Funct. Mater.*, 2014, **24**, 543–554.
- M. Zhu, P. Chen and M. Liu, *J. Mater. Chem.*, 2012, **22**, 21487–21494.
- J. Jiang and L. Zhang, *Chem. Eur. J.*, 2011, **17**, 3710–3717.
- M. Zhu, P. Chen, W. Ma, B. Lei and M. Liu, *ACS Appl. Mater. Interfaces*, 2012, **4**, 6386–6392.
- M. Zhu, P. Chen and M. Liu, *J. Mater. Chem.*, 2011, **21**, 16413–16419.

- 39 M. Zhu, C. Chen, P. Chen, B. Lei, W. Ma and M. Liu, *Phys. Chem. Chem. Phys.*, 2013, **15**, 12709–12716.
- 40 P. Wang, B. Huang, X. Zhang, X. Qin, H. Jin, Y. Dai, Z. Wang, J. Wei, J. Zhan, S. Wang, J. Wang and M.–H. Whangbo, *Chem. Eur. J.*, 2009, **15**, 1821–1824.
- 41 H. Zhang, X. Lv, Y. Li, Y. Wang and J. Li, *ACS Nano*, 2009, **4**, 380–386.
- 42 H. Cheng, B. Huang, P. Wang, Z. Wang, Z. Lou, J. Wang, X. Qin, X. Zhang and Y. Dai, *Chem. Commun.*, 2011, **47**, 7054–7056.
- 43 P. Wang, B. Huang, Y. Dai and M.–H. Whangbo, *Phys. Chem. Chem. Phys.*, 2012, **14**, 9813–9825.
- 44 P. Wang, B. Huang, X. Qin, X. Zhang, Y. Dai, J. Wei and M.–H. Whangbo, *Angew. Chem. Int. Ed.*, 2008, **47**, 7931–7933.
- 45 B. Li, H. Wang, B. Zhang, P. Hu, C. Chen and L. Guo, *ACS Appl. Mater. Interfaces*, 2013, **5**, 12283–12287.
- 46 P. V. Kamat, *J. Phys. Chem. Lett.*, 2012, **3**, 663–672.
- 47 Q. Xiang, J. Yu and M. Jaroniec, *Chem. Soc. Rev.*, 2012, **41**, 782–796.
- 48 N. Zhang, Y. Zhang and Y.–J. Xu, *Nanoscale*, 2012, **4**, 5792–5813.
- 49 S. Min and G. Lu, *J. Phys. Chem. C*, 2011, **115**, 13938–13945.
- 50 A. Iwase, Y. H. Ng, Y. Ishiguro, A. Kudo and R. Amal, *J. Am. Chem. Soc.*, 2011, **133**, 11054–11057.
- 51 C. Su and K. P. Loh, *Acc. Chem. Res.*, 2013, **46**, 2275–2285.
- 52 M. Adachi, M. Sakamoto, J. Jiu, Y. Ogata and S. Isoda, *J. Phys. Chem. B*, 2006, **110**, 13872–13880.
- 53 C. Zhai, M. Zhu, F. Ren, Z. Yao, Y. Du and P. Yang, *J. Hazardous Mater.*, 2013, **263**, 291–298.
- 54 Instead of using GD, we have recently tried to prepare our hybrids using pristine graphite (G) powders and investigated their photocatalytic performances. The preliminary results indicated that similar as in the cases of GD, enhanced photocatalytic performances could also be observed from the produced Ag/AgBr/GO/G species. The further detailed study concerning this interesting issue is underway.