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ARTICLE TYPE

Graphene Oxide-Palladium Modified Ag-AgBr: A Visible- Light-Responsive Photocatalyst for the Suzuki Coupling Reaction

Shutao Gao, Ningzhao Shang, Cheng Feng, Chun Wang*, Zhi Wang

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The efficient utilization of the abundant and economical solar energy has received tremendous attention due to increased environmental and energy concerns. In this report, a plasmonic Ag-AgBr photocatalyst functionalized with graphene oxide-Pd was successfully fabricated and used as an efficient visible-light-responsive photocatalyst for the Suzuki coupling reaction. The integration of plasmonic Ag-AgBr with Pd nanoparticles supported on graphene oxide enabled efficient visible light harvesting for the catalytic reaction on the heterojunction structure. A possible catalytic mechanism for the highly efficient photocatalyst is proposed. This work provides a convenient means for the design of the efficient catalysts that are composed of a photocatalyst and a catalytically active transition metal for various organic transformations driven by visible light.

Introduction

With increased consumption of energy and growing environmental contaminations, the development of clean and sustainable energy utilizations and environmentally friendly technologies has become the research focus of world-wide scientific researchers. Solar energy from sunlight is widely believed to be the key to solving the future problems of the environment and energy resource because of its clean, sustainable, abundant and economical characteristics[1]. To efficient harvest of solar energy, various kinds of photocatalysts have been explored for applications in splitting water into hydrogen, photocatalytic degradation of organic pollutants, preparing dye sensitized solar cells and so on[2].

Recently, the use of sunlight to drive chemical reactions has received much attention and has been studied as an important way to pursue environmentally benign and green synthetic process[3]. However, most of the photocatalysts were used only under irradiation by ultraviolet (UV) light. Consequently, only 3–5% of the solar energy reaching the earth can be utilized. So the development of an efficient system for visible light energy conversion into chemical energy is one of the urgent subjects for research because sunlight is mostly composed of visible light[4]. To date, visible light-driven chemical reactions, such as photocatalytic oxidation[5], reduction[6], C–H bond activation, C–C and C–N bond formation[7], dechlorination[8], and so on, have been realized by using different visible light photocatalysts including metal oxide, polymeric graphitic carbon nitride, plasmonic and dye sensitized photocatalysts. However, the available visible light photocatalysts suitable for selective organic transformations are still very few[4b]. The scope and efficiency of the reactions catalyzed by visible light photocatalysts need to be enlarged and enhanced significantly. Great challenges still exist and need to be resolved before sunlight becomes a viable source of energy for organic synthesis.

The palladium-catalyzed C-C cross-coupling reaction plays a key role in the synthesis of many important chemicals including pharmaceuticals, herbicides, and polymers. Up to now, only a few visible light photocatalysts have been developed for the C-C cross-coupling[4b]. More recently, Au–Pd/ZrO_2 was prepared by Zhu et al and used as photocatalyst for Suzuki coupling of iodobenzenes and aromatic boronic acids under visible light irradiation[7b]. The results indicated that the Au/Pd molar ratio of the alloy nanoparticles has an important impact on the performance of the catalysts. Huang et al developed an efficient one-pot strategy for the fabrication of Au–Pd core–shell nanowheels, which were successfully used as photocatalyst for the Suzuki coupling reaction of iodobenzene and phenylboronic acid at 50 ^{o}C[9]. The unique structure of the AuPd nanowheels significantly enhanced not only their catalytic activity but also their ability to exploit the light. Plasmonic Au-Pd nanostructures could harvest visible-to near-infrared light for Suzuki coupling of bromobenzenes and aromatic boronic acids under the irradiation of 809 nm laser or sunlight[10]. The plasmonic Au nanorods absorb visible light while the Pd shell acts as the direct catalyst for the coupling reaction. Differently sized Au–Pd nanostructures were prepared and mixed together to make the mixture light-responsive over the visible to near infrared region. However, the above-mentioned photocatalysts are expensive. Mesoporous polymeric graphitic carbon nitride (mpg-C_3N_4) is a graphene-like layered material and can function as a photocatalyst for selective organic reactions[2d]. In 2013, Antonietti et al reported that Pd nanoparticles supported on mpg-C_3N_4 could catalyze the Suzuki coupling reaction at room temperature[11], in which mpg-C_3N_4 acts as the photocatalyst whilst Pd acts as the coupling catalyst. However, this reaction was driven by the direct irradiation with a 150 W Xe lamp which contains UV light rather than visible light only. By filtering off the UV part of the xenon lamp (<420 nm), the yield of the product decreased to 49% after reaction for 12 hours. So exploring more efficient visible light phototcatalysts to facilitate the coupling reaction under mild conditions is still a challenge.

Silver halides decorated with silver (Ag@AgX), which exhibit high absorption in the visible region due to the surface plasmon resonance (SPR) of silver nanoparticles, represent a class of highly efficient visible-light-driven photocatalyst[12]. Current applications of Ag@AgX photocatalysts are mainly focused on the decomposition of organic pollutants and the evolution of H_2[13], whilst catalytic organic transformations (including Suzuki coupling reaction) involving Ag@AgX under light irradiations stay essentially untouched.

Graphene, a novel carbon nanomaterial, has attracted extensive attention in recent years due to its excellent electronic and optical properties, great mechanical strength, and extreme large specific surface area, which make graphene-related materials attractive for many potential applications including energy storage, catalysis, biosensors, molecular imaging and drug delivery[14]. Especially, graphene-based photocatalysts have attracted a lot of attention due to their high electron and hole transport ability, good electron conductivity, large specific surface area and high adsorption ability for organic molecules[13b,15].

In this report, a plasmonic Ag-AgBr photocatalyst functionalized with graphene oxide-Pd (GO-Pd@Ag-AgBr) was successfully fabricated and used as an efficient visible-light-responsive photocatalyst for the Suzuki coupling reaction. The integration of plasmonic Ag-AgBr with catalytic Pd nanoparticles in one nanostructure significantly enhanced not only their ability to exploit the light, but also the intrinsic catalytic activity of Pd.

Results and discussions

Material characterizations

The components of the obtained GO-Pd@Ag-AgBr (for the preparation details, see Supporting Information) were investigated by X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX).

Figure S1 showed the XRD patterns of (a) Ag-AgBr, (b) AgBr, and (c) GO-Pd@Ag-AgBr. All the samples of AgBr, Ag-AgBr, and GO-Pd@Ag-AgBr exhibited characteristic diffraction peaks of AgBr (JCPDS file: 06-438). The peaks at 26.6^o, 31.0^o, 44.2^o, 52.4^o, 55.0^o, 64.4^o and 73.1^o (marked with"•") are attributed to (111), (200), (220), (311), (222), (400) and (420) crystal planes of AgBr, respectively. No diffraction peak attributed to GO was observed in the XRD pattern due to the relatively low amount and low diffraction intensity of GO, which is consistent with the reported works about other GO-involved nanocomposites[16]. For the Ag-AgBr and GO-Pd@Ag-AgBr composites, the peak at 38.1^o (marked with "♦") corresponding to the (111) crystal plane of Ag clearly represents the formation of Ag (JCPDS No. 04-0783), which could be ascribed to partial conversion of AgBr to elemental Ag through the reduction with hot glycerol during the high-temperature incubation process.

X-ray photoelectron spectroscopy was used to obtain information on surface of GO-Pd@Ag-AgBr sample. Ag 3d, Br 3d, Pd 3d and C 1s XPS are spectra were shown in Figure S2. Two specific peaks of Ag 3d located at ca. 368 and 374 eV could be attributed to Ag $3d_{5/2}$ and Ag $3d_{3/2}$ binding energies, respectively[17]. The XPS of Ag $3d_{5/2}$ showed that the fitted peaks at 367.60 and 368.2 eV corresponded to Ag(I) and Ag(0), respectively, while the Ag $3d_{3/2}$ peaks at 373.6 and 374.3 eV corresponded to Ag(I) and Ag(0), respectively. Figure S2b shows the peaks of Br $3d_{5/2}$ and Br $3d_{3/2}$ with the binding energy of 68.2 eV and 69.4 eV, which could be assigned to Br(I). The XPS of Pd $3d_{5/2}$ showed that the fitted peaks at 337.6 and 335.3 eV corresponded to Pd(II) and Pd(0), respectively, while the Pd $3d_{3/2}$ peaks at 342.8 and 340.5 eV corresponded to Pd(II) and Pd(0), respectively[8]. Figure S2d showed C 1s XPS spectra of GO-Pd@Ag-AgBr. The deconvoluted peak at a binding energy of 284.6 eV is attributed to C-C, C=C, and C-H bonds. The peaks at the binding energy of 286.7, and 288.9 eV were attributed to the C-O bands (expoxy and hydroxyl) and carboxylate C=O from carboxylic acid, respectively[18].

The EDX spectrum of GO-Pd@Ag-AgBr was shown in Figure S3. Oxygen and carbon element were detected distinctly, which suggests the existence of GO species in the sample. Moreover, quantitative analysis shows that the atomic ratio between Ag and Br is about 1.33:1. This value is larger than the theoretic stoichiometric atomic ratio between Ag and Br in AgBr, which should be 1:1. The results suggests the possible generation of metallic Ag during the synthesis process. The quantitative amount of components in the sample can be approximately estimated from the elemental composition obtained from the EDX analysis. The weight percentage of Ag^0 in the GO-Pd@Ag-AgBr was about 12.1%.

The above facts strongly confirm the existence of metallic Ag species in the photocatalyst, which could arouse surface plasmon resonance absorptions in the visible region.

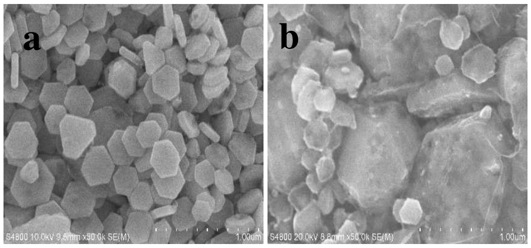


Figure 1. SEM image of (a) Ag-AgBr and (b) GO-Pd@Ag-AgBr.

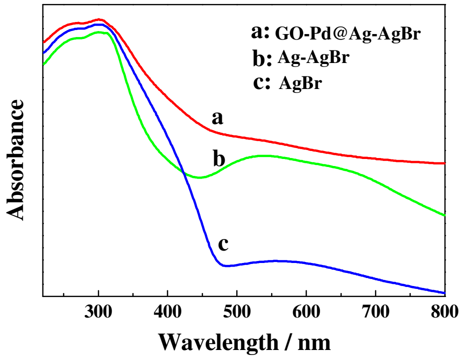


Figure 2. UV–vis DRS spectra of (a) GO-Pd@Ag-AgBr, (b) Ag-AgBr, and (c) AgBr.

Figure 1 showed the typical scanning electron microscopy (SEM) images of the as-prepared Ag-AgBr and GO-Pd@Ag-AgBr nanocomposites. It clearly showed the AgBr as a polyhedron (Figure 1a). As shown in Figure 1b, the Ag-AgBr nanoparticles were well dispersed and encapsulated by the GO nanosheets, indicating the well coupling between the Ag-AgBr nanoparticles and the GO nanosheets.

The UV-visible diffuse reflectance spectra (DRS) of AgBr, Ag-AgBr, and GO-Pd@Ag-AgBr are shown in Figure 2. Compared with AgBr, the much stronger absorption of Ag-AgBr in the visible-light region can be attributed to the surface plasmon resonance of silver nanoparticles. After modified with GO-Pd, GO-Pd@Ag-AgBr has a large number of different shapes and diameter, the surrounding environment of Ag-AgBr is also changed, so that the plasmon oscillations cover a wide range of frequencies. Hence GO-Pd@Ag-AgBr can absorb a wide range of visible light, which makes the photocatalyst use the visible light more efficiently.

Results of SEM observation, absorption, EDX, and XPS revealed that Ag-AgBr nanoparticles were successfully covered with GO-Pd, indicating that the Ag-AgBr plasmonic photocatalyst was facilely functionalized with Pd.

The photo catalytic activity of GO-Pd@Ag-AgBr was investigated using the Suzuki reaction of phenyl bromide and phenyl boronic acid as the model reaction. Considering that photothermal effect could contribute to the conversion reaction in principle, the reactor was carefully thermostatted to exclude the possibility of thermal reaction and thus investigate the photocatalytic nature of the process. As shown in Table S1, GO-Pd@Ag-AgBr gives an excellent yield (99%) of the coupled product with visible light irradiation at 25 ^{o}C for 1 h. For comparison, we also conducted a similar catalytic reaction under the same conditions but without visible light irradiations (reacted in the dark). As a result, only a yield of 9% was obtained (Table S1, entry 2). These results clearly demonstrated that light irradiation can smoothly trigger the coupling reaction under mild conditions. However, no product was generated with either Ag-AgBr or GO-Pd under light irradiation, which verified the importance of combining the photocatalyst with the intrinsic palladium catalyst for driving the Suzuki coupling reaction. To demonstrate the structural advantage of the GO-Pd@Ag-AgBr, we also used Pd@Ag-AgBr as the catalyst for comparison, and only a yield of 88% was obtained. GO usually exhibits a higher adsorption capacity for the organic molecules[16b], which is beneficial for the enhancement of the photocatalytic activity of GO-Pd@Ag-AgBr. The synergistic effects of the coupling of Ag-AgBr and GO enhanced the electrons transfer from Ag-AgBr to GO, which could suppress the electron–hole recombination and thus lead to the enhancement of the photocatalytic performance of the GO-Pd@Ag-AgBr photocatalyst.

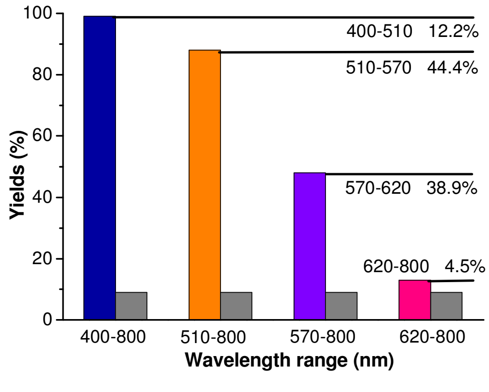


Figure 3. Influence of cut-off threshold wavelength on the Suzuki coupling reaction. Gray column: the yields of the thermal reaction (reacted in the dark).

When the reaction of phenyl bromide and phenyl boronic acid was carried out with visible light irradiation at 25 ^{o}C for 20 min and then reacted in the dark (light off) for 40 min, the yield of the reaction is 67%. While the yields of the coupled product with visible light irradiation at 25 ^{o}C for 20 min and 1 h were 64% and 99%, respectively. The results indicate that light is indeed the driving force in this system.

The dependence of the photocatalytic activity on light wavelength is a characteristic of plasmon resonance photocatalysts, which differs from semiconductor photocatalysts[3b,19]. For semiconductor photocatalyst, the wavelength of absorption is fixed, or limited to a certain wavelength range in which the photons have an energy larger than the semiconductor band gap. The photocatalytic activity of semiconductor photocatalyst does not vary with the change of irradiation wavelength[19]. The effects of light wavelengths on the photocatalytic activity of GO-Pd@Ag-AgBr were investigated. The wavelength range was tuned by using various glass filters to cut off the irradiation below a certain value of wavelength. As shown in Figure 3, when the reactor was illuminated with different wavelength ranges of light, 400–800, 510–800, 570–800 and 620–800 nm, the yields of biphenyl decreased significantly. From the results obtained from the irradiation of different wavelengths, the contribution of the light in a narrow wavelength range could be estimated. Since the reaction temperature was held constant, the yields of the thermal reaction (reacted in the dark) remain unchanged regardless of the filter used, which is 9% in this case (gray column in Figure 3). So the total light irradiation enhancement (the contribution of light irradiation in the wavelength range of 400–800 nm) is 90% (= 99%–9%). This figure also shows that light irradiation in the wavelength range of 510-620 nm contributed the main part of driving the Suzuki reaction, accounting for 83.3% of the total light irradiation enhancement, of which, 44.4% came from the light irradiation with wavelengths between 510 nm and 570 nm and 38.9% from the light between 570 nm and 620 nm. The remaining 16.7% contribution of the total light irradiation enhancement resulted from the light with wavelengths between 400–510 nm and 620–800 nm account for. Given that the strong plasmon resonance absorption of Ag-AgBr is in the wavelength range of about 500 nm to 650 nm (Figure 2), the above results indicated that the silver nanostructures' SPR plays an important role in enhancing the reaction yield.

Additional control experiments were conducted to further investigate the catalytic mechanism of GO-Pd@Ag-AgBr for the coupling reaction. Under visible light irradiation, both AgBr and Ag nanoparticles can produce photo-generated electrons and holes. In principle, the energetic electrons and holes could activate the electron-deficient and electron-rich intermediates respectively, to facilitate various organocatalytic reactions, including C-C coupling reactions[11]. The role of the photo-generated holes in promoting the Suzuki coupling reaction was investigated by adding hole scavenger. As a result, after the addition of hole scavenger, i.e. triethanolamine, no product was obtained under light irradiation (Table S1, Entry 6), However, in the presence of triethanolamine, the reaction could proceed at 80 ^{o}C without light irradiations (Table S1, Entry 7). The above results clearly demonstrated that the light induced Suzuki coupling reaction can only be realized with the involvement of photo-generated holes, which could be ascribed to that the holes could activate arylboronic acids by cleaving the C-B bonds, and this is in agreement with the results of literature[11]. According to the activation mechanism of Pd-containing catalysts, the activity of Pd-based catalysts would be enhanced by increasing their electron density[20]. The photo-generated electrons transferred to the Pd sites might enhance the catalytic activity of Pd.

Without inert atmosphere, the yield of the product decreased to 87% (Table S1, Entry 8). The result could be explained as follows: The photo-generated electrons coming from AgBr and Ag nanoparticles can be transferred to GO, and subsequently combined with the dissolved oxygen to produce superoxide anion radicals ($\cdot O_2^-$). The active species, $\cdot O_2^-$, can decompose the adsorbed organic molecules and induce the formation of undesired products. And the consumption of photo-generated electrons by oxygen is unfavorable for increasing the electron density of Pd.

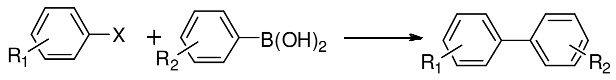
Although a more precise reaction mechanism for the photo-induced coupling reaction is still under investigation, a plausible reaction mechanism can be depicted as Figure S4 on the basis of the above investigations and previous reports. Under light illumination, the metal Ag could effectively act as miniature antennae to absorb light. The SPR-excited electrons would be generated and enriched at the surface of Ag nanoparticles. Since the Fermi energy level of AgBr is lower than that of Ag, so the transfer of SPR electrons from Ag to the conduction band of AgBr is energetically favorable. Apart from the plasmonic photocatalysis process, the conventional AgBr-based semiconductor photocatalysis simultaneously proceeded because AgBr can be directly photo-excited under light illumination, to generate electrons/holes pairs (e^-/h^+) in AgBr. For the coupling reaction between bromobenzene and boronic acid, the rate-determining step is the breaking of the C–Br bond[21], in which the electron transfer from the Pd atom to the Br and C atoms exists. These photo-generated electrons in the conduction band, together with the injected SPR electrons from Ag NPs, could transfer to Pd nanoparticles located on the surface of GO nanosheets and then initiate the catalytic reaction. The energetic electrons at the surface Pd sites increase the electron density and thus could enhance the intrinsic catalytic activity of Pd in promoting the coupling reaction.

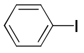
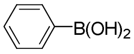
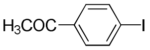
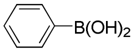
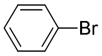
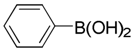
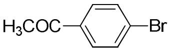
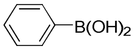
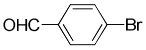
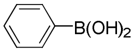
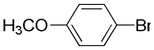
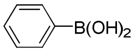
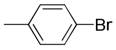
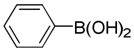
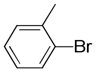
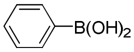
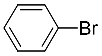
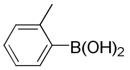
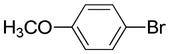
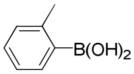
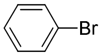
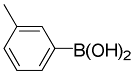
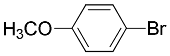
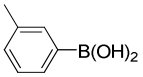
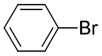
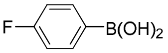
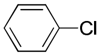
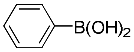
To examine the efficacy of the visible light responsive photocatalyst, the coupling reactions of a series of substituted aryl halides and phenylboronic acids were carried out under visible light irradiations (Table 1). It is known that the yields of the Suzuki coupling reactions depend on the type of halide element, the positions of the substitutional groups and their electron withdrawing/donating capabilities. When the active substrates, iodobenzenes, were used, the coupling reaction can be completed within 30 min with yields of 96%-97% (Table 1, entries 1 and 2). For the less reactive bromobenzene, the photocatalytic coupling reactions could also proceeded well and the reactions could be completed in 1-2 hours with a good to excellent yields. Bromobenzenes with electron-donating groups (CH_3, and OCH_3) and electron-withdraw groups (CHO and CH_3CO) were examined to investigate the electronic influence on the catalytic performance of the photocatalyst. It was observed that the electron-donating groups had a negative effect on the conversions of the corresponding coupled products. Moreover, yields of 78% and 90% were obtained even when inactive substrates, such as *o*-tolylboronic acid, were supplied (Table 1, entries 9 and 10). In contrast, only a yield of 6% was obtained for the coupling reaction of inactive chlorobenzene and phenylboronic acid, which indicated that the photocatalyst can not activate the chlorobenzene substrates.

The recyclability and reusability of a heterogeneous catalyst is a very important aspect for its practical applications. After the photocatalytic reaction, GO-Pd@Ag-AgBr can be recycled by centrifugation and washing with water and ethanol, respectively. The XRD pattern of the used photocatalyst (see Figure S5) demonstrated that the structure has not been changed except for the amount of metallic Ag increased slightly, which could be ascribed to the photoreduction of AgBr when it endured prolonged light irradiation. The photocatalytic activity of the used GO-Pd@Ag-AgBr did not have a significant loss after three runs. However, the catalyst was gradually deactivated from the fourth run on. The cause for that might be attributed to the leaching of Pd. In fact 18% of Pd was leached after four runs. Further experiments are required to tackle the issue of the Pd leaching problem to maintain the stability of the catalyst. It is worth noting that bare Pd nanostructures or even supported Pd NPs in conventional Suzuki coupling reactions also usually suffer from significant loss in the activity due to Pd leaching[22].

In conclusion, a plasmonic Ag-AgBr photocatalyst functionalized with graphene oxide-Pd was successfully fabricated and used as an efficient visible-light-responsive photocatalyst for the Suzuki coupling reactions. Pd-free Ag-AgBr and Ag-AgBr-free GO-Pd were inactive, whereas the GO-Pd@Ag-AgBr sample was active in the photocatalytic coupling reaction. These results demonstrated that the intrinsic catalytic activity of Pd can be significantly enhanced at ambient temperatures by visible light irradiation of Ag-AgBr, which can be ascribed to the photo-induced energetic electrons located at the surface of Pd sites. Moreover, the photo-induced holes could activate benzeneboronic acid. These results clearly show that the unique structure of the GO-Pd@Ag-AgBr could significantly enhance not only their catalytic activity but also their ability to exploit the light. This ability was vital to the development of a new catalyst system that could effectively drive chemical conversion under mild conditions. The findings in the current study revealed that the combination of a photocatalyst and a metal with an intrinsic catalytic activity could be a class of potential photocatalysts for driving chemical reactions. The findings in the current work could provide a general guiding line for designing new catalyst structures to catalyze specific reactions where the light, instead of heat is used as the energy source. The knowledge acquired in this study may inspire further studies in searching for the new efficient visible-light-responsive photocatalysts for a wider range of organic synthesis.

Table 1. Suzuki-Miyaura coupling reactions catalyzed by GO-Pd@Ag-AgBr



Entry	Aryl halides	Arylboronic acids	Time / h	Yield / %
1			0.5	97
2			0.5	96
3			1	99
4			1	99
5			1	99
6			2	99
7			2	84
8			2	82
9			1	78
10			2	90
11			1	79
12			2	95
13			2	89
14			2	6

[a] Reaction conditions: 2 mL of water, 2 mL of ethanol, 1.5 mmol K_2CO_3, 0.6 mmol benzeneboronic acid, 0.5 mmol bromobenzene, 25 mg of catalyst, N_2 atmosphere, 300 W Xe lamp with UV cutoff filter (providing visible light with >400 nm), 25 °C.

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Notes and references

College of Science, Agricultural University of Hebei, Baoding 071001, Hebei, China; Tel: +86-312-7528291; Fax: +86-312-7528292; E-mail: chunwang69@126.com.

† Electronic Supplementary Information (ESI) available: Characterization data of all products. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Graphene Oxide-Palladium Modified Ag-AgBr: A Novel Visible- Light-Responsive Photocatalyst for the Suzuki Coupling Reaction

Shutao Gao, Ningzhao Shang, Cheng Feng, Chun Wang, Zhi Wang*

College of Science, Agricultural University of Hebei, Baoding 071001, China

Graphical Abstract:

In this paper, a plasmonic Ag-AgBr photocatalyst functionalized with graphene oxide-Pd was successfully fabricated and used as an efficient visible-light-responsive photocatalyst for the Suzuki coupling reaction. A possible catalytic mechanism for the highly efficient photocatalyst is proposed.