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Multifunctional core-shell Pd@Cu on MoS₂ as a visible light-harvesting photocatalyst for synthesis of disulfide by S—S coupling



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ABSTRACT

Visible light harvesting materials are considered promising cost-effective heterogenous catalysts for organic synthesis. A novel and efficient synthesis of multifunctional core-shell Pd@Cu/MoS₂ nanostructures is utilized for synthesis of disulfides by S—S Coupling. The Pd@Cu core-shell was obtained by one-pot hydrothermal synthesis, and a simple method was used to load it onto the MoS₂. The as-prepared materials were characterized by scanning electron microscopy, transmission electron microscopy, X-ray powder diffraction, X-ray photo-electron spectroscopy, UV–vis diffuse reflectance spectroscopy, and photoluminescence spectroscopy. The Pd@Cu/MoS₂ nanostructures revealed excellent photocatalytic activity, reusability, and stability towards the oxidative coupling of mercaptans to disulfanes. The outstanding photocatalytic activity of Pd@Cu/MoS₂ will enhance interest in the field of multifunctional core-shell nanomaterials as photocatalysts for a wide variety of applications.

1. Introduction

Metal nanoparticles (NPs) have been utilized since the last decades as catalysts for numerous organic reactions. One of the promising aspects of metal NPs catalyst is the synergetic effect of the catalysis [1-3]. Synergistic catalysis can be obtained by highlighting the benefit from bi-, trimetallic, and multifunctional hybrid catalyst simultaneously. Multifunctional hybrid catalysts represent an effective strategy in which two or more different active sites concurrently activate the reactants to achieve a chemical transformation. The strategy is also able to increase the efficiency and selectivity of the desired product. However, to acquire a best-designed catalyst structure, further studies are still needed. The well-defined multifunctional structures such as core-shell nanostructures represent three-dimensional models that were widely implemented for organic reactions. A core-shell structure can protect the core from the outside environment to increase the stability and recyclability of the catalyst. Other advantages of this nanostructure are sintering prevention, selective percolation of molecules, and the addition of new physical or chemical properties [4-7]. Transition metals such as Au, Pt, Pd, Ni, Fe, and Cu have been mostly fabricated to achieve the multifunctional core-shell structures [1-3,5,6,8,9].

Furthermore, catalysts with a multi-structure design Pd and Cu based

have been effectively used for organic transformation to expand on hybrid or core-shell structured catalysts [5,10–12]. However, increasing the catalytic activity of these materials still requires an addition of hazardous agent as co-catalyst, which introduces additional complexity to the system. Another limitation is still use high temperatures to complete the reactions [2,7–9]. However, one possible way to achieve high catalytic activity in mild conditions, that is energy suitable, and has a simple chemical work-up is to employ light harvesting materials. Heterogeneous visible light photocatalysts have recently received significant attention owing to their unique properties. However, the selective organic synthesis of these photocatalysts currently results in unsatisfying conversion and selectivity. Thus, a photo-induced active material for organic synthesis still needs to be developed by modifying the composition and structures of the photocatalysts [13–16].

In the last decade, layered molybdenum disulfide (MoS₂) has attracted notable attention, and various photocatalytic behaviors have been reported, such as the high mobility of charge carriers, excellent optical absorptivity, and narrow bandgap (1.3–1.8 eV), in addition to its low cost and non-toxicity [17–20]. The improved performance of MoS₂ has been driven by a limited set of properties, such as the recombination of photogenerated electron-hole pairs, photocorrosion, and the edge activity effect [20,21]. Efforts to expand the photocatalytic properties of

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MoS₂ have included control of the morphology, modulation of the energy band via doping, band alignment via the formation of heterojunctions with other semiconductors, modification with excess sulfur or carbon nanostructures, and assembly by surface plasmon resonance (SPR) [22].

Modifying MoS₂ photocatalysts by SPR can widen the absorption spectrum from ultraviolet to the visible (UV-vis) area or even Near-Infrared Spectroscopy (NIR) because of an increase in charge transfer and the local electric field [22-25]. Metal nanomaterials, such as Au, Pt, Ag, Pd, and Cu, have been investigated as plasmonic photocatalysts that strongly absorb visible light and produce SPR depending on the shape, size, material, and whether it encloses another nanostructure [26-29]. Therefore, the metals/semiconductors with their unique properties have been studied in environmental, selective organic transformation, disinfection, and energy production areas [24,30]. In the organic transformation field nanocomposites such as Pt/TiO₂ [31-33], Au/TiO₂ [32-34], Pd/TiO₂ [33], Rh/TiO₂ [32], Ag/TiO₂ [33], Au/CeO₂ [35], Au-Pd/ZrO₂ [36], Pd/SiC [37], and Pt-Cu/TiO₂ [38], have been selectively processed to create a valuable product. However, noble metals remain the state-of-the-art materials used to combine with the semiconductor photocatalysts. In addition, they primarily use the conventional structure. Therefore, a challenge remains to develop a photocatalyst by reducing or substituting the noble metal combination with non-noble metal. Bimetallic systems, such as Pd and Cu nanomaterials, have also been proven as an active material in many organic reactions [39,40]. Moreover, multifunctional structures, such as hybrid or core-shell nanostructures, can be an alternative way to enhance the photocatalytic activity for organic synthesis, because core-shell nanostructures using different materials improve the light absorption, photostability, and charge-carrier dynamic ability comped to the conventional structure, which remains primarily focused on the H₂ production and degradation reaction [24,30,41].

In the other hands, Organosulfur compounds with S—S bonds, are important structures for synthetic and medicinal chemistry, from the laboratory to industrial-scale production. Disulfides have a unique structure that provides various promising biological activities, including antitumor, antibiotic, and enzyme-inhibitory activities [42–44]. Because of the versatile importance of organic disulfides, there has been a large effort to synthesize symmetric and asymmetric disulfides.

Based on the above considerations, the development of a multifunctional core-shell nanostructure containing Pd and Cu for loading onto MoS_2 could be a promising strategy for organic transformation of thiols to disulfide (Scheme 1). A simple core-shell nanostructure (Pd@Cu) that is synthesized through a one-pot hydrothermal method is presented. In addition, the Pd@Cu core-shell structures result in SPR on MoS_2 semiconductors, which increases the photocatalytic activity. The results reveal the efficiency of $Pd@Cu/MoS_2$ as an oxidative coupling photocatalyst.

2. Materials and methods

2.1. General remarks

All chemicals were used as received without additional purification. The morphology of the catalysts was characterized using a SUPRA 40 V P (ZEISS) microscope for field emission scanning electron microscopy (SEM) and a TALOS F200X (200 keV, FEI) microscope for field emission transmission electron microscopy (TEM). Then, X-ray diffraction (XRD) patterns were collected using an X'Pert³ MRD (Malvern Panalytical) diffractometer. X-ray photoelectron spectroscopy (XPS) data were obtained by an AXIS Supra (Kratos Analytical Ltd) instrument. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed by an Optima 8300 (PerkinElmer) instrument. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was performed by a V-770 UV–vis/NIR (JASCO) spectrophotometer. Photoluminescence (PL) spectroscopy was performed by a FluoroMate FS-2 spectrofluorometer. Lastly, the product of organic conversion was analyzed using a gas chromatography-mass spectrometry (GC–MS), QP2010 SE (SHIMADZU) gas chromatograph.

2.2. Synthesis of core-shell Pd@Cu nanocatalyst

Copper (II) nitrate hemi(pentahydrate) (0.15 g) and polyvinylpyrrolidone (MW \sim 55,000, 0.03 g) were dissolved in a dimethylformamide (DMF) solution (30 mL) under stirring. Then, palladium (II) nitrate hydrate (0.3 M, 0.3 mL) was added to the solution while continuously stirring for 15 min. The reaction mixture was transferred into a Teflon-lined autoclave (100 mL capacity), sealed, and maintained at 180 °C for 24 h. Lastly, the well-grown core-shell Pd@Cu nanocatalysts were gathered and washed with ethanol and water, and then dried. For comparison, the single Pd and Cu catalyst was also prepared.

2.3. Synthesis of core-shell Pd@Cu loaded on MoS₂ (Pd@Cu/MoS₂)

First, MoS_2 nanoflowers were synthesized using a hydrothermal method. Sodium molybdate dihydrate (5 mmol) and thiourea (21 mmol) were mixed in a water solution. After stirring for 30 min, oxalic acid (6 mmol) was added to the solution. The product was obtained by heating in a Teflon-lined autoclave at 200 °C for 24 h and then washing it several times with deionized water and ethanol. Before loading the core-shell Pd@Cu, MoS_2 (1 wt.%, 150 mL) was functionalized using a poly



Scheme 1. Schematic illustration of step-by-step synthetic procedure for photocatalyst Pd@Cu/MoS₂ nanostructures and its application for oxidative coupling of thiol to disulfides.

(ethyleneimine) (PEI) solution (0.37 wt.%) in water under reflux conditions for 12 h. Then, core-shell Pd@Cu dissolved in ethanol and MoS₂ dissolved in water were mixed, and the reaction continued at 60 °C. The weight ratio of Pd@Cu and MoS₂ was 1:2, respectively. After stirring for 3 h, the product was collected by centrifugation, washed with water, and dried. The weight ratio of Pd@Cu and MoS₂ 1:4 and 1:1 was also prepared for comparison.

2.4. Photocatalytic activity of $Pd@Cu/MoS_2$ for the oxidative coupling of thiols

The reaction mixture consisted of thiol (0.1 mol), a catalyst based on Pd (0.5 mol%), and solvent (3 mL). Following the reaction, the catalyst was removed by centrifugation. Afterward, the disulfide product was obtained by adding ethyl acetate, separating the catalyst by centrifugation, dehydrating with MgSO₄, and concentrating with a rotary evaporator. Then, the conversion of the product was measured by the GC–MS technique. Photocatalytic reactions were conducted under irradiation from a Xenon (Xe) lamp (300 W) with a 400–800 nm cut-off and an intensity of 0.1 W/cm². The lamp is equipped with liquid filter (reduce heat), IR cut-off (block wavelength >800 nm), and specific long pass filter (cut-on 400, 455, 515, 610 nm) to block the transmission below specific wavelength.

3. Results and discussion

The core-shell nanostructure containing Pd and Cu was synthesized by a one-pot hydrothermal method. The fabrication of one-pot (singlestep) process for core-shell nanomaterials is a considerable challenge in the development of robust, low cost, and efficient methodology compared to a multiple step process [45]. Here, the core-shell Pd@Cu was fabricated by the *in situ* co-reduction and seeding-growth due to the difference in reduction potentials of the two soluble metal salts (Pd and Cu). The higher standard redox potential of Pd²⁺/Pd (+0.99 eV) compared to Cu²⁺/Cu (+0.34 eV) can be advantageous for the formation of a Pd core because the reduction process occurs more rapidly in Pd than in Cu in the presence of a suitable reduction agent. In this method, DMF can act both as a reaction medium and a reduction agent in the

presence of PVP as the capping agent. In addition, a high thermal condition will make all the reduction processes complete more rapidly [46-48]. The morphology of core-shell Pd@Cu was studied using SEM and TEM. The spherical shape of Pd@Cu was confirmed (Fig. 1a) with a size distribution centered around 64.5 nm (Fig. S1a,b). For comparison, the bare Pd and Cu was synthesized using same method (Fig. S2c-f). High-angle annular dark-field (HAADF) and energy dispersive X-ray spectroscopy (EDX) analysis also indicated that the core was composed of Pd NPs, while the shell was composed of Cu NPs (Fig. 1b-e). The fabricated Pd@Cu was loaded onto MoS2 nanoflowers by a simple reflux condition to obtain the multifunctional Pd@Cu/MoS2 structure. Prior to loading, the MoS₂ was functionalized using PEI to more easily distribute the Pd@Cu onto the MoS₂ [49]. The quality of the loading of Pd@Cu on MoS₂ was determined by SEM analysis, as shown in Fig. 1f and S1c. The thickness of the MoS_2 petal was confirmed to be <15 nm. The layer of MoS₂ and the core-shell nanostructure of Pd@Cu is clearly shown in the TEM analysis in Fig. 1g-i, as well as the HADFF and EDX elemental mapping in Fig. 1i-0.

Next, the Pd@Cu, MoS₂, and Pd@Cu/MoS₂ photocatalysts were analyzed by XRD to further confirm the crystalline structure. As shown in Fig. 2, the XRD pattern of Pd@Cu was indexed to Pd PDF#87-0645 and Cu PDF#04-0836. The peaks located at 40.58, 47.00, and 68.60° for Pd and 43.30, 50.45, and 74.10° for Cu were indexed to the reflections of the (111), (200), and (220) crystalline planes of cubic Pd and cubic Cu, respectively. The XRD profile showed highly crystalline structures of both Pd and Cu without alloying or oxide phases of either metal. The comparison of XRD pattern for single Pd and Cu was shown on Fig. S3. The MoS₂ peak matched the MoS₂ reference, PDF#76-1539, with the (100), (100), (102), and (110) crystalline planes at 14.22, 33.15, 36.00, and 58,9°. There were no significant changes in the peaks after loading the core-shell nanostructure onto the MoS₂ support, which indicates the successfully grafting of the Pd@Cu onto the MoS₂ without any damage.

XPS analysis was used to evaluate the surface chemical state of the prepared catalyst, as shown in Fig. 3. From the survey scan spectrum (Fig. S4), Mo, S, Cu, Pd, and O were present in the sample. All spectrums were calibrated as 284.5 eV of C-C binding energy came from the surface contamination. Furthermore, the XPS spectrum of Pd, as shown in



Fig. 1. (a) TEM images; (b-e) HAADF and EDX elemental mapping of core-shell Pd@Cu; (f) SEM image; (g-i) TEM images; (j-o) HAADF and EDX elemental mapping of Pd@Cu/MoS₂ nanostructures.



Fig. 2. XRD patterns of core-shell Pd@Cu, MoS_2 , and $Pd@Cu/MoS_2$ nano-structures with the references.

Fig. 3a, reveals two main peaks at binding energies (BEs) of 335.2 and 340.0 eV, which were assigned to Pd $3d_{5/2}$ and Pd $3d_{3/2}$, respectively. The Pd NPs were affirmed as well, without any additional characteristic peaks. The Cu 2p XPS spectrum was deconvolved to determine the presence of Cu°, Cu⁺, and Cu²⁺ in the prepared catalyst (Fig. 3b). The main peak of the spectrum was at 931.6 eV, which confirmed the formation of Cu NPs. However, another peak at 933.7 eV, which indicated

the existence of Cu^{2+} , was present because of the oxidation of Cu° during sampling or unreacted Cu^{2+} from the synthesis process. The satellite peak was relatively low, suggesting that the sample was primarily Cu NPs. The deconvolution of the Mo 3*d* and S 2*s* XPS spectra at BEs from 234.0 to 225.0 eV indicated a peak from MoS₂ and some impurities (MoO_x) (Fig. 3c). In addition, the main peak from S 2*p* was found at BEs of 161.3 eV and 262.5 eV, which correspond to S 2*p*_{1/2} and S 2*p*_{3/2}, respectively (Fig. 3d).

The optical properties of the photocatalyst were investigated by UV-vis DRS and PL spectroscopy. Fig. 4a shows the UV-vis DRS images of as-prepared bare Pd@Cu, MoS₂, and Pd@Cu/MoS₂ nanocatalysts. The as-prepared Pd@Cu nanocatalyst shows a broad visible absorption in the 350-600 nm region. The main peak at 540-580 nm corresponds to the plasmon resonance band of Cu° NPs [50]. The absorbance of MoS₂ was large in most of the visible region [51]. After introducing Pd@Cu onto the MoS₂, the UV-vis DRS peak was similar, but with a slightly higher intensity at 540–650 nm and a red shift. The band gaps of Pd@Cu, MoS₂, and Pd@Cu/MoS₂ are 1.40, 1.76, and 1.53 eV, respectively. The loaded of SPR Pd and Cu to MoS₂ narrowed the band gap. The PL spectrum for MoS₂ showed emission at 675 nm with an excitation at 488 nm (Fig. 4b). After loading with Pd@Cu, a red shift was also identified. In addition, PL entirely depends on electron-hole pair recombination. A lower intensity was observed for Pd@Cu/MoS2 compared to the bare MoS2, implying that the electron-hole pair recombination was effectively reduced and the lifetimes of the photogenerated carriers were prolonged owing to the synergistic effect of Pd@Cu and MoS₂ [52,53].

The photocatalytic activity of the multifunctional core-shell $Pd@Cu/MoS_2$ nanostructure was applied to oxidative coupling of thiols to



Fig. 3. XPS spectra of Pd@Cu/MoS₂ nanostructures (a) Pd 3d lines, (b) Cu 2p lines, (c) Mo 3d + S 2 s lines, and (d) S 2p lines.



Fig. 4. (a) UV-vis DRS and band gap (inset), and (b) PL spectra of prepared samples.

disulfides. The introduction of core-shell nanostructures can enhance catalytic activity and stability in various organic reactions [11,12,54, 55]. However, light active heterogenous catalysts for organic transformations still mostly rely on conventional structures [24]. Therefore, multifunctional core-shell nanostructures need to be developed for these applications. Core-shell nanostructures can improve light absorption compared to conventional structures, primarily because they allow incident light with multiple light scatterings and reflections within the core-shell structure [41]. In addition, the MoS₂ flower-like shape has been reported can improve light absorption efficiency owing to the increase of light paths compared to spherical and coil-like structures [17]; an illustration of incident light is shown in Fig. 5. Thus, the use of the core-shell Pd@Cu/MoS₂ as a photocatalyst for the oxidative coupling of thiols could be an excellent strategy to improve the photocatalytic activity.

The selective oxidation coupling of 4-chlorobenzenethiol to bis(4chlorophenyl) disulfide was chosen as a model to identify the optimum conditions. As shown in Table 1, the optimum conditions (entry 3) were obtained using 0.1 mmol of the substrate, CH_3CN and water in a 3:1 ratio as the solvent, and 0.5 mol% of a photocatalyst based on Pd. The metal loading was calculated by ICP-OES to be 5.61 wt.% for Pd and 25.05 wt.% for Cu, which does not differ greatly from the theoretical values (6 wt.% Pd, 27 wt.% Cu, and MoS₂ for the balance). In addition, the solvent has a significant role in this photocatalytic oxidative coupling of thiol. A mixture of an aprotic solvent (CH₃CN) and H₂O (3:1) efficiently obtained a high conversion and the desired product with the Pd@Cu/MoS₂ catalyst under light irradiation compared to using a single solvent. However, in the presence of a protic solvent (CH₃CH₂OH) barely any conversion was achieved. The 3:1 ratio of CH₃CN: water had better conversion than other ratios because of the poor solubility of thiol in water. These result are consistent with a previous report [56,57]. Moreover, the conversion of thiols to disulfides was insignificantly different using a strict oxygen-free environment (entry 9) and increased with adding external O₂ as an oxidant (entry 10). The high conversion in open to air (entry 3) provides a convenient operating protocol. The ratio of synthesized Pd@Cu particles on MoS2 was also applied for comparison (entry 11-12).

As explained in the above results, the optimized oxidative coupling reaction of mercaptan to disulfane catalyzed by $Pd@Cu/MoS_2$ used a $CH_3CN:H_2O$ (3:1) solution at room temperature (r.t) for 3 h in air. The



Fig. 5. Schematic diagrams of light pathways in (a) nanoparticles, (b) core-shell spheres, and (e) flower-like.

Table 1

The photocatalytic activity of Pd@Cu/MoS2 nanostructures for oxidative coupling of thiol reactions.

					CI
2	SH	Pd@Cu/MoS ₂		<> ^S ∖s	
CI		r.t, air, <i>hv</i>	CI /		
Entry	Cat. (mol %)	Solvent	Time (h)	Conv. ^a (%)	Selec. ^a (%)
1	Pd@Cu/MoS ₂ (0.5)	CH ₃ CN:H ₂ O (1:1)	3	69.5	98.5
2	Pd@Cu/MoS ₂ (0.5)	CH ₃ CN:H ₂ O (1:3)	3	40.0	99.6
3	Pd@Cu/MoS ₂ (0.5)	CH ₃ CN:H ₂ O (3:1)	3	99.8	99.6
4	Pd@Cu/MoS ₂ (0.5)	CH ₃ CN:H ₂ O (3:1)	1	47.2	99.2
5	Pd@Cu/MoS ₂ (0.5)	CH ₃ CH ₂ OH:H ₂ O (3:1)	3	54.4	99.0
6	Pd@Cu/MoS ₂ (0.25)	CH ₃ CN:H ₂ O (3:1)	3	65.5	99.0
7	Pd@Cu/MoS ₂ (0.5)	CH ₃ CN	3	44.5	98.4
8	Pd@Cu/MoS ₂ (0.5)	H ₂ O	3	38.7	99.5
9 ^b	Pd@Cu/MoS ₂ (0.5)	CH ₃ CN:H ₂ O (3:1)	3	96.0	98.7
10 ^c	Pd@Cu/MoS ₂ (0.5)	CH ₃ CN:H ₂ O (3:1)	3	100	99.6
11 ^d	Pd@Cu/MoS ₂ (0.5)	CH ₃ CN:H ₂ O (3:1)	3	96.8	99.2
12 ^e	Pd@Cu/MoS ₂ (0.5)	CH ₃ CN:H ₂ O (3:1)	3	78.8	99.4

Reaction conditions: 0.1 mmol 4-chlorobenzenethiol, 3 ml solvent, 0.5 mol% photocatalyst base on Pd. The reactions were conducted in air at r.t (25 °C) under Xe-lamp irradiation (400-800 nm) with light intensity of 0.10 W/cm². ^a Conversions and selectivity determined by GC-MS analysis.

^b under N₂ atmosphere.

^d ratio Pd@Cu:MoS₂ (1:1).

e ratio Pd@Cu:MoS₂ (1:4).

optimized photocatalytic condition was then implemented with a diverse range of thiols into their relevant disulfanes product (Table 2). The scope of this reaction was explored by using a variety of aromatic, heteroaromatic, and aliphatic thiols. Aromatic thiols were transformed to their corresponding products with high selectivity (>90 %), regardless of the presence of either electron-withdrawing substituents or electron-donating substituents, such as halide, methyl, and methoxy groups (entries 1–5). Heteroatomic thiols, such as nitrogen-containing heteroaromatic thiols (entry 6-7) and benzylic thiol (entry 8), were also converted under the optimized reaction conditions, with excellent conversion and selectivity as well as the aromatic thiols. Additionally, the variety of thiols with excellent photocatalytic activity also included aliphatic thiols (entry 9-11). Furthermore, because asymmetric disulfides are also essential bioactive compounds [58,59], asymmetric aryl-alkyl disulfides (entry 12) were produced with high selectivity by combining 1 equivalent of an aryl thiol and 1.5 equivalent of an aliphatic thiol.

The excellent catalytic activity of the oxidative homocoupling of thiols is closely related to the light harvesting ability of $Pd@Cu/MoS_2$ and the synergic effect of Pd, Cu and MoS2 in the multifunctional coreshell nanostructure. To demonstrate how much the light harvesting ability improved the catalytic activity, the comparison of results in Fig. 6 are given. Fig. 6a show that the irradiation of Xe light with a 400-800 nm wavelength enhanced the catalytic activity only using a small amount intensity (0.1 W/cm²). For comparison, the reactions using Pd/ ${\rm MoS}_2,\ {\rm Cu}/{\rm MoS}_2$ under light irradiation and in the dark were also

collected. Therefore, the core-shell Pd@Cu nanostructure on MoS₂ is more likely the cause of the high catalytic activity compared to bare Pd@Cu, MoS₂, or a mixture of both without any preparation. Since the light intensity (0.1 W/cm^2) is used in this study, the temperature after the reaction was measured to be ± 31 °C. Thus, the effect of temperature was evaluated to identify the material as thermo-catalyst, photocatalyst, or both. To obtain the completed reaction (99 % conversion) needs high temperature (100 °C) without irradiation of light (Fig. 6b) indicates that Pd@Cu/MoS2 is a more photoactive catalyst. In addition, the action spectrum for the photocatalytic activity Pd@Cu/MoS2 was identified by dependency of wavelength (Fig. 6c). The optical long-pass filter cut-on was used to block the region transmission below the chosen wavelength (i.e., 400 nm cut-on, block transmission <400 nm). The conversion was obtained to be 99 % under irradiation wavelength of 400-800 nm. The conversion reduced to 90 %, 80 %, and 49 % under irradiation of 455-800, 515-800, and 610-800 nm, respectively. Because the conversion of thiol in dark condition was 33 %, the amount contribution of 400-455 nm was 13 % calculated by ((99-90)/(99-33) × 100 %) in the total of light-irradiated conversion. Analog to other wavelengths are 15 %, 47 %, and 24 % for 455-515, 515-610, and 610-800 nm lightinduced, respectively. These results are in good accordance with the UV-vis DRS pattern shown in Fig. 4a.

From these results, the mechanism of the oxidative coupling of thiol by Pd@Cu/MoS₂ can be proposed (Fig. 7). Based on previously reported research [60,61], the S and H moieties of thiol are adsorbed on the surface of the catalyst. During the photoreaction under visible light, electron-hole pairs are generated. The holes in the valence band of the MoS₂ semiconductor move to the thiol group, generating a thiyl radical and a hydrogen protons (H^+). In the presence of air, O_2 can be reduced by accepting electrons from a combination of MoS₂ conduction band and electron-rich Pd@Cu to provide a superoxide $(O_2^{\cdot-})$. By this synergic system, the thiyl radical supposedly reacts with another thiyl radical to produce disulfide. In addition, the superoxide transforms to hydrogen peroxide, which decomposes into water and oxygen, and encloses the catalytic cycle. In the absence of air, the electron-hole transfer of the catalyst by incident of light leading the formation of thiyl radical and hydrogen radical, then disulfide product was generated by radical coupling of thiyl radical (Fig. S5). The addition of 2,2,6,6-tetramethylpiperidine-1-oxyl as a radical scavenger, the desired product was not detected implying the radical is involved in the reactions. Here, the role of electron-hole pairs in the photocatalytic reaction can also be probed by disturbing the reaction with electron and hole scavengers. P-benzoquinone is well-known as an electron and superoxide radical scavenger, and ethylenediaminetetraacetic acid is well-known as a hole scavenger. The result in Fig. 6b shows a decrease in the amount of disulfide product produced, indicating the importance of the electron-hole system in multifunctional core-shell Pd@Cu/MoS2 photocatalyst.

Along with photocatalytic activity, recyclability is also a critical factor for heterogenous catalyst in organic applications. To demonstrate the reusability of Pd@Cu/MoS2, the photocatalyst was reused five times with 4-chlorobenzenethiol using the optimized protocol. After each completed reaction, the catalyst was easily recovered for reuse by centrifugation and washing with ethanol. As shown in Fig. 8, the photocatalytic activity of Pd@Cu/MoS2 remained high over the five uses without any significant loss. The stability of the catalyst was also examined by identifying the morphology and structure before and after rescue. The morphology of the catalyst was analyzed by SEM (Fig. S6), and the structure of catalyst was analyzed by XRD (Fig. 8b), after five sequential cycles. Despite slight changes in the morphology, the structure of the catalyst was well maintained.

There have been many reports on the oxidative coupling of thiol to disulfide reactions catalyzed via heterogeneous conventional structures or multifunctional structures, but most need to be performed in harsh conditions, such as in the presence of an oxidation agent or at an elevated temperature. The high photocatalytic activity of the Pd@Cu/ MoS₂ used in this study is compared with previously reported catalyst is

^c O₂ atmosphere.

Table 2

The photocatalytic activity of Pd@Cu/MoS₂ nanostructures for oxidative coupling of various thiols.

$2 \text{ RSH} \xrightarrow{\text{Pd}@Cu/MoS_2} \text{RS-SR}$						
Entry	Substrate	Product	Conv. ^a (%)	Selec. ^a (%)		
1	SH	s's	>99	90		
2	CI	S S CI	>99	>99		
3	Br	CI ⁻ S S Br	90	>99		
4	H ₃ C SH	Br' CH	>99	98		
5	H ₃ CO SH	H ₃ C OCH ₃	93	>99		
6	SH SH		>99	>99		
7	N SH N		>99	>99		
8	SH	S-S	95	>99		
9	SH	s's	>99	92		
10	H3COSH	H ₃ CO S S OCH ₃	94	>99		
11	SH	H_S_S_H_	>99	>99		
12	SH +	S-S-OCH3	87	75 ^b		
	н₃со ^Ŭ ѕн					

Reaction conditions: 0.1 mmol thiol, 3 ml CH₃CN:H₂O (3:1) solvent, in air at r.t for 3 h, 0.5 mol% photocatalyst base on Pd, Xe-lamp irradiation (400–800 nm) with light intensity of 0.10 W/cm². ^a Conversions and selectivity determined by GC–MS analysis. ^b 0.1 mmol Ar-SH and 0.15 mmol alkyl-SH, Ar-S-S-Ar 24 %.



Fig. 6. (a) Comparison of various catalyst under irradiation of light and in the dark condition, (b) temperature dependence using $Pd@Cu/MoS_2$ without light, (c) wavelength dependence (irradiation of light) using $Pd@Cu/MoS_2$, (d) Additional various condition. N.R is no reaction.



Fig. 7. Plausible mechanism for the visible light induced photocatalytic oxidative coupling of thiol reaction using Pd@Cu/MoS2 nanostructures in the presence of air.



Fig. 8. (a) Reusability study of photocatalytic activity by Pd@Cu/MoS₂ nanostructures catalyst for oxidative coupling of thiol reaction (b) XRD analysis of Pd@Cu/MoS₂ nanostructures catalyst before and after reaction.

shown in the supporting information (Table S1). This demonstrates that visible light harvesting material, especially multifunctional core-shell nanostructures, can efficiently generate disulfide products and achieve excellent recyclability and stability. Moreover, the reaction was conducted in mild condition, and the products were obtained by easy work up.

4. Conclusions

A multifunctional core-shell nanostructure, Pd@Cu/MoS₂, was synthesized by an efficient method. The Pd@Cu core-shell was synthesized by a one-pot hydrothermal method, which is a novel, low cost, and efficient methodology compared to a multiple step process. The coreshell Pd@Cu was loaded to a MoS₂ semiconductor support using a simple reflux condition. The synergetic combination of Pd@Cu and MoS₂ enhanced the catalytic activity for synthesis of disulfide by S—S coupling. The photogenerated hole-electrons between the MoS₂ and Pd@Cu played a crucial role in the light harvesting material for photocatalytic reactions. Moreover, in addition to the high photocatalytic activity, good recyclability, and stability were accomplished. This multifunctional core-shell nanostructure can provide a direction for further modification of other heterogenous photocatalysts for cost-effective organic synthesis, among other applications.

CRediT authorship contribution statement

Mohammad Yusuf: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing - original draft. Sehwan Song: Formal analysis. Sungkyun Park: Funding acquisition. Kang Hyun Park: Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118025.

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