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Mesoporous SiO₂/BiVO₄/CuO_x Nanospheres for Z-Scheme, Visible Light Aerobic C-N Coupling and Dehydrogenation

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ABSTRACT

In light of the growing demand to use renewable energy, we have synthesized a mesoporous bismuth vanadate-copper oxide-silica photocatalyst ($\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$) to act as a chromophore in a Z-scheme system. These photocatalysts are intended for effective light harvesting and charge separation in the synthesis of solar chemicals, using air as an environmentally benign oxidant. Full characterization of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ was conducted, including X-ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS), and scanning transmission electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), which confirm the presence of CuO_x at the heterojunction of the nanostructures. The other characterization methods that were employed included powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), elemental mapping, UV-vis diffuse reflectance spectroscopy (UV-vis DRS), N_2 sorption experiments, photoluminescence spectroscopy (PL), electrochemical impedance spectroscopy (EIS), and photocurrent measurements. Notably, the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres perform seven times faster than bulk BiVO_4 and provide higher yields for the oxidative coupling of amines to imines, which are valuable precursors for agrochemicals and active pharmaceutical ingredients. The superior photocatalysis of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ is attributed to the surface CuO_x nanoparticles that increase the average PL lifetime from 2.3 to 4.5 ns, which improved the charge separation and decreased the unproductive recombinations of electron-hole pairs. In addition, the photocurrent density of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ electrode was about 3.5 times higher than that of $\text{SiO}_2/\text{BiVO}_4$, while lower charge transfer resistance was observed by EIS. Meanwhile, chemical scavenging experiments revealed that holes and superoxide radicals were the main reactive oxygen species in the photocatalytic reaction. The nanospheres also show broad functional group tolerance, good recyclability with high conversions, and high to moderate yields for the oxidatively coupled imine products after eight runs. Thus, we demonstrate that an effective and green approach in artificial photosynthesis is applicable for organic synthesis as well.

Keywords: Artificial photosynthesis; bismuth vanadate-copper oxide composite; C-N coupling; heterogeneous catalysis; mesoporous nanospheres

1. Introduction

The exploitation of solar energy in the production of fuels and chemicals has taken on greater urgency lately due to the increasingly palpable environmental and economic effects of global climate change. To address this challenge, several groups, including ours [1-9], have been inspired by the effectiveness of natural photosynthesis in capturing sunlight and coupling the separated charges for multielectron redox catalysis. A fundamental feature of the light harvesting mechanism among green plants is the integration of two visible light absorbers in Photosystems I and II to create a “Z-scheme”. The two chromophores, chlorophylls P680 and P700, are organized so that electrons flow from P680 to P700 with high fidelity by interfacing with both thermodynamically and kinetically favorable intermediates. This essentially creates a “molecular photodiode” for effective light absorption and charge separation, allowing P680 to build up four holes to oxidize water, while P700 acquires two electrons to reduce NADP^+ [9].

To mimic this vital capability of photosynthesis, the groups of Domen, Li, Nocera, Yang, and others have assembled visible light absorbing, Z-scheme semiconductor systems to harvest solar energy for the production of solar fuels *via* water splitting or CO_2 reduction, as well as to mitigate the environmental impact of water pollution [10-28]. Complementary to these pioneering studies, a number of research teams have started to focus on the production of solar chemicals to broaden the scope of light utilization applications. For instance, T. J. Meyer, G. J. Meyer, and their co-workers have used dye-sensitized photoelectrochemical cells to simultaneously oxidize halides to halogens and hypohalites as solar chemicals while producing H_2 as well [29-32]. Likewise, Reisner and his team have employed alcohols and lignocellulosic biomass in photodriven oxidative processes [33, 34], while Sun and co-workers utilized biomass-derived furfuryl alcohol and 5-hydroxymethylfurfural (HMF) as the substrates in cadmium sulfide/nickel (CdS/Ni) photocatalyzed water splitting [35, 36]. Z. Li and his co-workers have also used metal organic frameworks (MOFs) [37, 38] and ZnIn_2S_4 [39] in the oxidation of amines to imines, which are important building blocks for the synthesis of fine chemicals. In the same vein, our team has been developing alternative approaches to harness sunlight in the production of solar chemicals and fuels, while using exclusively earth abundant elements

[9]. We have developed molecular complexes and metal oxide semiconductors as chromophores [40, 41], molecular Ni electrocatalysts capable of H₂ evolution from seawater [42], and molecular V photocatalysts that mediate C-C bond cleavage in biomass lignin model compounds, with the intention of integrating them into one unit for solar chemicals production [9, 43, 44].

Some candidates that have emerged for solar to chemical energy conversion are Bi-based materials, due to their efficient photocatalytic performance, high stability, low cost, and modest toxicity [45]. Bi-based nanomaterials have been introduced for photoinduced water splitting and environmental remediation, among other applications [46]. One example is BiVO₄, which commonly exists in three phases: tetragonal zircon, monoclinic scheelite, and tetragonal scheelite [47]. Among these, monoclinic BiVO₄ has the best reported photocatalytic performance, with a narrow band gap of about 2.4 eV for visible light absorption [46, 48], and a moderate charge diffusion length of 100 nm [49]. Furthermore, the valence band potential is around +2.5 V vs. normal hydrogen electrode (NHE), ample to oxidize many organic compounds [50-54]. Consequently, BiVO₄ has been employed in the partial oxidation of secondary amines to imines [52] and methane to methanol in the presence of O₂ [55], underscoring its value in harvesting light for solar chemicals production.

Here, we have developed mesoporous SiO₂/BiVO₄/CuO_x nanospheres as chromophores in a Z-scheme system for effective light harvesting and charge separation in the synthesis of solar chemicals. Mesoporous nanomaterials are attractive due to their large surface areas, open pore systems, controllable pore sizes and morphologies, and high chemical and thermal stability [56, 57]. Previous reports on the poor photocatalytic activity of BiVO₄ when in nanoparticulate form were attributed to the poor crystallinity, for the generation of O₂ from aqueous solutions for instance [58]. Heat treatment did not improve the activity due to severe sintering, which reduced the nanoparticles' surface areas [59]. In contrast, we have overcome these problems by preparing dispersible SiO₂/BiVO₄/CuO_x nanospheres and established that they are efficient visible light photocatalysts for the aerobic oxidative coupling of amines and dehydrogenation of indolines in the presence of

molecular O₂ in air as a green oxidant under ambient conditions. Moreover, loading BiVO₄/CuO_x in the mesoporous SiO₂ nanoparticles could potentially inhibit the aggregation that often occurs for photocatalytic reactions using dispersed materials; such agglomeration is known to be a major factor in the loss of catalytic activity among nanomaterials over time [60-62]. The staggered type II heterojunction between BiVO₄ and CuO_x facilitated concurrent absorption of two photons over a broader visible spectrum and also more effective charge separation. Notably, the mesoporous SiO₂/BiVO₄/CuO_x nanospheres can be recycled, and perform seven times faster than BiVO₄ nanospheres alone, providing higher yields for imine products and a greener synthetic method to valuable precursors for fine chemicals, agrochemicals, and active pharmaceutical ingredients [63-65].

2. Results and discussion

2.1. Synthesis and structural characterization

Fig. 1 illustrates the synthesis of mesoporous SiO₂/BiVO₄/CuO_x nanospheres. The DMSN were synthesized via a soft templating approach from tetraethyl orthosilicate [66], and then used to load the metal oxides [56]. Surface modification of the DMSN with *n*-propyltriethoxysilane to give propyl-DMSN was necessary to ensure effective BiVO₄ precursor loading in the next step. Four samples of DMSN, with increasing amounts of Bi(NO₃)₃•5H₂O and NH₄VO₃ loaded (45, 56, 59, and 63 wt% of BiVO₄ relative to SiO₂), were prepared *via* an incipient wetness impregnation procedure [56]. The samples were annealed in air at 500 °C for 2 h, and the amount of BiVO₄ loaded was found to be 12, 14, 19, and 22 mol% with scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), corresponding to the increasing loadings of the BiVO₄ (Fig. S1, Supplementary material). Finally, CuO_x was incorporated on the mesoporous SiO₂/BiVO₄ nanospheres by a polyol process. After evaluating the samples, we identified 59 wt% SiO₂/BiVO₄ with 20 mol% CuO_x (relative to BiVO₄) as the optimal catalyst (*vide infra*) and characterized it rigorously.

Fig. 1. Synthetic route to the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres.

PXRD measurements were conducted to verify the crystalline properties of the nanospheres. Fig. 2a-c and S2 (Supplementary material) reveal discernible peak splitting at 2θ of 35° , diagnostic of a monoclinic scheelite phase for all samples (JCPDS 00-044-0081) [67]. The crystalline domain sizes of the as-prepared BiVO_4 samples based on the PXRD were calculated using the Scherrer Eq. (1) [68]:

$$\tau = K\lambda/(\beta \cos\theta) \quad \text{Eq. (1)}$$

In the Scherrer equation: τ is the mean crystalline domain size, $K = 0.94$ is a dimensionless shape factor, $\lambda = 1.54178 \text{ \AA}$ is the $\text{Cu } K_\alpha$ X-ray wavelength, β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle. Although no diffraction peaks corresponding to CuO_x could be observed due to the low CuO_x loading levels, their presence was confirmed by electron microscopy.

Fig. 2. PXRD pattern of (a) $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$, (b) 59 wt% $\text{SiO}_2/\text{BiVO}_4$, and (c) bulk BiVO_4 crystals. The red boxes highlight the diagnostic peak splitting of monoclinic scheelite BiVO_4 . (d) HRTEM and (e) lattice fringes with d-spacings of 0.309 nm corresponding to the (112) plane of BiVO_4 in the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres. HAADF-STEM image (f), and elemental mapping images of Bi (g, magenta), Cu (h, yellow), and V (i, cyan).

The TEM images of the DMSN (Fig. S3, Supplementary material) and $\text{SiO}_2/\text{BiVO}_4$ samples (Fig. 2d and S4, Supplementary material) show defined, non-aggregated, mesoporous dendritic nanospheres. The SiO_2 scaffold has thus effectively prevented the BiVO_4 nanocrystals from sintering during the thermal treatment and the BiVO_4 particles retained their nano-sized structure in the composite [59, 69]. The average particle sizes for all the $\text{SiO}_2/\text{BiVO}_4$ samples are about 150 nm, with the exception of the 63 wt% loading, which had aggregated particles outside the nanospheres due to overloading. The HRTEM images of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres (Fig. 2e and S5a-b, Supplementary material) further demonstrate that the dendritic particles are composed of BiVO_4 nanocrystals, with the lattice d-spacing of 0.309 nm corresponding to the (112) plane of monoclinic BiVO_4 (Fig. 2e). Moreover, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) together with elemental mapping evidently verify the uniform distribution of Bi, V, and Cu within the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres (Fig. 2f-i and S5c). In addition, the morphology of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres was examined as illustrated in Fig. S6a,b (Supplementary material), and reveals that the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres have porous and rough surfaces with average sizes of 150 nm, in accordance with the TEM results (Fig. 2 and S4, Supplementary material).

The EDS experiments with SEM also confirm that 19 mol% (relative to BiVO_4) of Cu has been incorporated on the surface of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres (Fig. S6c-i, Supplementary material). The surface area and pore structure of the $\text{SiO}_2/\text{BiVO}_4$ samples were analyzed by the Brunauer-Emmett-Teller (BET) method. The N_2 sorption data of the samples each display a type IV isotherm (Fig. S7, Supplementary material), indicating the presence of mesoporosity [70].

2.2. Redox and optical properties

XPS was then performed to investigate the oxidation states of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres. As shown in the survey spectra (Fig. S8a, Supplementary material), Bi, O, V, and C are observed in $\text{SiO}_2/\text{BiVO}_4$, while Cu was detected only in the

SiO₂/BiVO₄/CuO_x sample. The Cu 2p core level spectrum of SiO₂/BiVO₄/CuO_x can be fitted to four components (Fig. 3a).

Fig. 3. XPS of SiO₂/BiVO₄/CuO_x nanospheres for (a) Cu 2p and (b) V 2p. (c) UV-vis DRS and (d) Tauc plots of the BiVO₄ samples. (e) Work function and (f) UPS of SiO₂/BiVO₄/CuO_x nanospheres.

The two major peaks at 932.5 and 952.4 eV are characteristic of Cu^+ $2p_{3/2}$ and $2p_{1/2}$, respectively. The peaks at 933.8 and 954.1 eV and the two shake-up satellites at about 942.2 and 961.9 eV correspond to the Cu^{2+} $2p_{3/2}$ and $2p_{1/2}$ signals, which are characteristic of a $3d^9$ ground state configuration for CuO [71, 72]. It is noteworthy that the intensity of Cu^+ is stronger than Cu^{2+} on the surface, implying that CuO_x is predominantly Cu_2O . By comparing the spectral area intensities of the peaks in Fig. 3a, it was found that the ratio between $\text{Cu}_2\text{O}:\text{CuO}$ in $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ was 7:2.

The presence of V and the other elements were also observed in the composite samples (Fig. 3b and S8, Supplementary material). For both $\text{SiO}_2/\text{BiVO}_4$ and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres, the binding energies at 516.5-516.6 and 524.0-524.1 eV, correspond to the V $2p_{3/2}$ and V $2p_{1/2}$ bands, respectively (Fig. 3b and S8b, Supplementary material). The binding energies of the Bi 4f band, in which two peaks are located at about 158.8 and 164.1-164.2 eV, can be indexed to the Bi $4f_{7/2}$ and Bi $4f_{5/2}$ bands, respectively (Fig. S8c,e, Supplementary material). Two O 1s bands for both $\text{SiO}_2/\text{BiVO}_4$ and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres (Fig. S8d,f, Supplementary material) were fitted and the binding energies at 529.3-529.4 and 530.2-530.4 eV are ascribed to lattice oxygen of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ and adsorbed H_2O or surface hydroxyl groups, respectively. The O 1s bands at 532.7-532.9 eV correspond to the lattice oxygen in SiO_2 . Based on the HRTEM and XPS results, we believe that there is mixed valent CuO_x on the surface of the heterojunction of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanostructures.

We then evaluated the optical properties of the nanospheres and bulk BiVO_4 (Fig. 3 and S9, Supplementary material) with UV-vis DRS. The E_g of the samples were calculated from the UV-vis spectra by using a Tauc plot following Eq. (2) [73],

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \quad \text{Eq. (2)}$$

where α , h , A , and ν are the absorption coefficient, Planck's constant, proportionality constant, and photon frequency, respectively. The coefficient, n , was found to be 4, consistent with the direct band gap properties of BiVO_4 [74]. E_g was estimated to be 2.42,

2.60, and 2.60 eV for bulk BiVO₄, SiO₂/BiVO₄, and SiO₂/BiVO₄/CuO_x respectively. The absorption edge of SiO₂/BiVO₄ and SiO₂/BiVO₄/CuO_x were slightly blue-shifted compared to bulk BiVO₄. Such a blue shift in the absorption edge of SiO₂/BiVO₄ relative to bulk BiVO₄ concurs with a report by Iwase and Kudo, which explained that it was likely due to quantum confinement effects in the BiVO₄ nanocrystals [58]. Despite the additional absorption around the NIR region, the SiO₂/BiVO₄/CuO_x nanospheres have similar band gaps (E_g) as their corresponding SiO₂/BiVO₄ samples, likely due to the low CuO_x loading.

The valence band energies (E_{VB}) of SiO₂/BiVO₄/CuO_x, SiO₂/BiVO₄, and bulk BiVO₄ were determined by the addition of the work function (Φ relative to vacuum) and the valence band maxima (VBM) measured using UPS (Fig. 3 and S10, Supplementary material). The E_{VB} of SiO₂/BiVO₄/CuO_x, SiO₂/BiVO₄, and bulk BiVO₄ were found to be -6.86, -7.20, and -6.54 eV, respectively (Fig. 3 and S10, Supplementary material). The conduction band maxima (CBM) of SiO₂/BiVO₄/CuO_x can be estimated by subtracting the band gap ($E_g = 2.60$ eV) from the VBM, giving a CBM of -4.26 eV. The corresponding relative VB and CB levels are thus 2.42 V and -0.18 V versus the normal hydrogen electrode (NHE), respectively, by assuming that the reference of 0 V versus NHE corresponds to 4.44 eV versus the vacuum level [75]. From these results, the highly positive valence band implies a high oxidation ability of BiVO₄ [76], which favors the oxidation of benzylamine [77].

In addition, the UPS results support the staggered type II heterojunction upon incorporating CuO_x onto SiO₂/BiVO₄, with the VBM position at 3.13 ± 0.05 shifted to 2.89 ± 0.05 eV (or -7.20 shifted to -6.86 eV when normalized to vacuum) after band alignment (Fig. S11, Supplementary material). This shift favors the transfer of photogenerated electrons in the CB of BiVO₄ to the holes in the VB of Cu₂O upon visible light irradiation. This promotes the charge separation efficiency of the SiO₂/BiVO₄/CuO_x, which resulted in the superior photocatalytic oxidation from amine to imines.

2.3. Optimization of photocatalytic conditions

With the SiO₂/BiVO₄/CuO_x nanospheres in hand, we applied them for the visible light-driven photocatalytic oxidative coupling of 4-methoxybenzylamine using molecular O₂ in air as the terminal oxidant, with bulk BiVO₄ as a reference for comparison (Table 1).

Table 1

Evaluation of the optimized photocatalyst for the oxidative coupling of 4-methoxybenzylamine.^a

Entry	Photocatalyst	t (h)	Conv (%) ^b	Yield (%) ^b	TOF/SA ^c (h ⁻¹ m ⁻² g)	TOF (h ⁻¹)
1	Bulk BiVO ₄	24	100	98	0.16	0.41
2	SiO ₂ /BiVO ₄ (45 wt%)	12	66	65	0.0031	0.54
3	SiO ₂ /BiVO ₄ (56 wt%)	12	98	97	0.0066	0.81
4	SiO₂/BiVO₄ (59 wt%)	12	100	99	0.0070	0.83
5	SiO ₂ /BiVO ₄ (63 wt%)	12	87	87	0.0083	0.73
6 ^d	SiO ₂ /BiVO ₄ (59 wt%)	12	57	52	0.0036	0.43
7 ^e	SiO ₂ /BiVO ₄ (59 wt%)	12	46	40	0.0028	0.33
8 ^f	SiO ₂ /BiVO ₄ /CuO _x (10 mol%)	3.5	60	58	0.014	1.66
9^f	SiO₂/BiVO₄/CuO_x (20 mol%)	3.5	100	99	0.023	2.83
10 ^f	SiO ₂ /BiVO ₄ /CuO _x (50 mol%)	3.5	100	99	0.023	2.83

^a Reaction conditions: 0.10 mmol of 4-methoxybenzylamine, 10 mol% “BiVO₄” photocatalyst, 0.80 mL of CD₃CN in air, 48 W white LED lamp, 30 °C; ^b Determined by ¹H NMR yield with 3,5-dimethylanisole as an internal standard; ^c TOF normalized by the BET surface area (SA, Table S2); ^d Conducted in acetone; ^e Conducted in ethyl acetate; ^f Copper loading (mol% relative to BiVO₄) based on SiO₂/BiVO₄ (59 wt%).

In each experiment, a 10 mol% loading level of BiVO₄ relative to the substrate was used. Although the bulk BiVO₄ sample apparently exhibited the highest turnover frequency per unit surface area (TOF/SA), all the SiO₂/BiVO₄ samples showed faster overall photocatalytic activity due to the substantially higher surface areas. Among the different loadings of BiVO₄, SiO₂/BiVO₄ (59 wt%), exhibited the optimal catalytic performance with 100% conversion only after 12 h. giving a turnover frequency (TOF) over twice as high as bulk BiVO₄, with 99% yield (Table 1 entry 4). We propose that the variation in the photocatalytic performance among the different loading levels was correlated with the size of the nanocrystallites according to the following trend: 59 wt% ≈ 56 wt% > 45 wt%.

A thicker depletion layer is typically found to induce greater band bending in larger crystals and promote charge separation [69], while small BiVO_4 nanocrystals contain higher surface defects with low crystallinity, resulting in lower activity (Table 1 entry 2). On the other hand, the highest loading level we examined (63 wt%) resulted in aggregation of the nanospheres as depicted in the TEM images (Fig. S4, Supplementary material). Negligible conversion and yield were observed in control experiments in the absence of any catalysts (Table S1, entry 1). Thus, we believe that the higher exposed surface area (Table S2) and shorter charge transport distances, attributable to the nano-sized mesostructure of the composite, ensure efficient charge extraction and improved photocatalytic activity in the nanospheres over bulk BiVO_4 .

After optimizing the BiVO_4 loading at 59 wt% (Table 1 entries 2-5), CuO_x was introduced as a co-catalyst to further improve the catalytic performance (entries 6-8). Furthermore, in order to investigate the effects of using more eco-friendly solvents, the reaction was performed in acetone and ethyl acetate (Table 1, entries 6 and 7). Alcohols and water are unsuitable solvents because they can interfere in the oxidative coupling as competing nucleophiles. Among the solvents we tested, acetonitrile was the greenest solvent for this organic transformation, although we expect the heterogeneous photocatalysts to be stable in alcohols and water for other catalytic processes. The staggered type II heterojunction formed between BiVO_4 and CuO_x could facilitate simultaneous absorption of two photons in a Z-scheme over a broader visible spectrum as well as more effective charge separation. The optimal Cu loading level is 20 mol% relative to BiVO_4 . Using this catalyst (Table 1 entry 9), the catalytic reaction showed quantitative conversion and yield after only 3.5 h, outperformed photocatalysts reported in similar organic transformation [37, 39, 52, 78], and gave a TOF around 7 times higher than bulk BiVO_4 . Low conversions and yields were recorded with just Cu_2O , CuO , or a mixture of Cu_2O and CuO with ratio of 7:2 (to mimic the surface composition determined by XPS studies above) in control experiments (Table S1, Supplementary material).

We then proceeded to expand the substrate scope of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ photocatalyst for a general oxidative coupling of benzylamines (Table 2). Electron-rich benzylamines

(methoxy, methyl, and *tert*-butyl derivatives) and electron- deficient ones (fluoro, chloro, bromo, and trifluoromethyl derivatives) were all compatible substrates. Also, the reaction rate of the regio-isomer increased in the order of ortho < meta < para, indicating the effect of steric hindrance on the rate (Table 2, entries 9-13), although the yields remained high regardless.

Table 2

Photocatalytic oxidative coupling of various substrates by SiO₂/BiVO₄/CuO_x nanospheres.^a

Entry	Products	t (h)	Yield (%) ^b	TOF (h ⁻¹)
1	R = phenyl	4	99	2.48
2	R = 4-fluorophenyl	6	99	1.65
3	R = 4-chlorophenyl	5	99	1.98
4	R = 2-chlorophenyl	7.5	99	1.32
5	R = 2,4-chlorophenyl	9	98	1.09
6	R = 4-bromophenyl	6	99	1.65
7	R = 4-(trifluoromethyl)phenyl	7	99	1.41
8	R = 3-(trifluoromethyl)phenyl	11	99	0.90
9	R = 4-methoxyphenyl	3.5	99	2.83
10	R = 3-methoxyphenyl	5	99	1.98
11	R = 2-methoxyphenyl	6.5	99	1.52
12	R = 4-methylphenyl	4	99	2.48
13	R = 2-methylphenyl	6.8	99	1.46
14	R = 4- <i>tert</i> -butylphenyl	6	96	1.60
15	R = 2,4,6-trimethylphenyl	11	96	0.87
16	R = 1-naphthyl	10	99	0.99
17	R = thiophene	7	99	1.41
8 ^c	R = 3,4-methylenedioxyphenyl	13	83	0.64
19		9	86	0.96
20 ^c		22	77	0.35
21 ^c		30	61	0.20

^a Reaction conditions: 0.10 mmol of substrate, 6.0 mg SiO₂/BiVO₄/CuO_x nanospheres, 0.80 mL of CD₃CN in air, 48 W white LED lamp, 30 °C. ^b Determined by ¹H NMR spectroscopy with 3,5-dimethylanisole as an internal standard; All reactions had quantitative conversion. ^c Conducted with 1 atm O₂.

The SiO₂/BiVO₄/CuO_x nanospheres are also tolerant to heterocycles such as 2-thiophenemethylamine, which is known to poison metal catalysts *via* the sulfur atom (Table 2, entry 17). In addition to the homocoupling reactions, an oxidative cross-coupling between benzylamine and heptylamine was also conducted, showing good yields (Table 2, entry 20). Benzaldehyde was formed as a minor by-product in all reactions (~1-4%), which was likely due to hydrolysis of the imines in the presence of water from the reduction of O₂. We further performed the oxidative dehydrogenation of 2-methylindoline and gratifyingly, the reaction proceeded with quantitative conversion and a yield of 61% (Table 2, Entry 21).

2.4. Mechanistic insights by radical scavenging

To derive insights into the photocatalytic mechanism of SiO₂/BiVO₄/CuO_x, the reaction rates have been compared for different *para*-substituted benzylamines and in the presence of disparate chemical scavengers. The Hammett plot for a series of benzylamine derivatives of increasing electron-deficiency (methoxy, methyl, hydrogen, chloro, and trifluoromethyl) evidently exhibit a negative slope ($\rho = -0.27$, $R^2 = 0.93$), implying the intermediacy of a carbocationic ArCH₂NH₂⁺⁺ formed due to oxidation by the SiO₂/BiVO₄/CuO_x nanospheres (Fig. 4a and Table S3) [79].

Scavenging experiments were then conducted to compare the rates for the oxidative coupling of 4-methoxybenzylamine (Fig. 4b). The scavengers include triethylamine (TEA) for holes, AgNO₃ for electrons, benzoquinone (BQ) for superoxide, and isopropanol (IPA) for hydroxyl radicals [52, 80, 81]. IPA had little effect, whereas TEA, and both AgNO₃ and BQ dramatically diminished the conversion after 7 h, indicating that holes and superoxide radicals were the main reactive species. Electronic paramagnetic resonance (EPR) spectroscopy was used to detect the superoxide radicals with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as the radical trap. We observed EPR signals that are characteristic of a superoxide adduct of DMPO [28, 82], confirming that superoxide radicals are generated during the photocatalytic reaction with SiO₂/BiVO₄/CuO_x (Fig. S12, Supplementary material). To detect an amine radical cation intermediate formed due to oxidation by the holes during the reaction, a stable radical (2,2,6,6-

tetramethylpiperidin-1-yl)oxy (TEMPO) was employed as a radical trap. We observed inhibition of the reaction by TEMPO, confirming that the reaction proceeded *via* a radical process (Fig. S41, Supplementary material). Subsequently, the amine radical cation intermediate was successfully trapped by diisopropyl azodicarboxylate, and the product from this trapping was confirmed by ^1H NMR spectroscopy and liquid chromatography-mass spectrometry (Fig. S42 and S43 respectively, Supplementary material). In addition, an “on-off” experiment indicated that this photocatalysis was probably not a radical chain reaction (Fig. 4c).

Fig. 4. Hammett plot for the photooxidative coupling of para-substituted benzylamines over $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ (b) Comparison of conversion rate after addition of different chemical scavengers. (c) Conversion rate against time for the oxidative coupling of 4-methoxybenzylamine with consecutive light and dark exposure. (d) Recycling performance of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ towards photooxidative coupling of 4-methoxybenzylamine.

There are at least two possible, commonly recognized mechanisms for the migration and separation of electron and hole pairs: a double charge transfer and a Z-scheme mechanism (Fig.

5). A mechanism via a double charge transfer mode [75] (Fig. 5a) is probably not operating since the more positive CB electrons of BiVO_4 (+0.2 V vs. NHE) [83] would not be able to reduce O_2 to superoxide radicals (-0.16 V vs. NHE) [84]. On the other hand, the more negative CB of CuO_x is able to reduce O_2 to superoxide radicals and hence, the Z-scheme mechanism (Fig. 5b) is likely to be energetically more feasible [27].

Fig. 5. Proposal for the photoexcited electron–hole separation processes: (a) a double charge transfer mechanism and (b) a Z-scheme mechanism.

On the basis of the type II heterojunction band alignment of BiVO_4 and CuO_x , we propose light absorption and charge separation *via* a Z-scheme (Fig. 6). The excited electrons are transferred to O_2 to produce superoxide radicals, while the holes oxidize the amine to amine radical cations. A reaction between the superoxide radical and the amine radical cation forms the intermediate iminium cation followed by the imine, which leads to the product after addition of a second amine and loss of NH_3 .

Fig. 6. Proposed mechanism for the oxidative coupling of benzylamine photocatalyzed by the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres.

2.5. Photoluminescence and photoelectrochemical studies

PL and TR-PL experiments were then performed on $\text{SiO}_2/\text{BiVO}_4$ and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ to determine the recombination efficiency of the charge carriers, both of which were found to exhibit emission with a maximum around 505 nm (Fig. 7a) [74]. TR-PL measurements were performed (Fig. 7a) to probe the origin of the charge recombination components. By fitting the TR-PL decay curves to exponential models, the average PL lifetime of $\text{SiO}_2/\text{BiVO}_4$ was found to increase from 2.3 to 4.5 ns with the addition of CuO_x on the surface, which corresponds to the recombination rate of photogenerated carriers under light excitation. Therefore, the longer PL lifetime indicates slower charge recombination rates for $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ after the introduction of CuO_x on the surface, which improves the charge separation lifetime and extraction of photogenerated electron-hole pairs, leading to the improved photocatalytic performance.

The photocatalytic activities of the prepared composites are closely related to the separation and transport ability of the photogenerated electron-hole pairs. EIS and photocurrent measurements were thus used to investigate the separation efficiency of the charge pairs. Typically, a Nyquist plot obtained from an EIS measurement gives an arc, where a smaller arc radius indicates a lower charge transfer resistance across the electrolyte/semiconductor, which correlates to more effective separation of the electron-hole pairs [27, 28]. Instead, we observed almost linear plots for both $\text{SiO}_2/\text{BiVO}_4$ and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$, which could be due to the high charge transfer resistance caused by the insulation of the SiO_2 . Similar observations had been made in reports by Zeng and co-workers [27, 28]. Nonetheless, the EIS “radius of the arc” of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ is smaller than that of $\text{SiO}_2/\text{BiVO}_4$, implying that the photoexcited charge carriers in $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ have lower recombination efficiency than in $\text{SiO}_2/\text{BiVO}_4$ (Fig. 7c) [27, 28]. Therefore, the EIS results indicated that the $\text{BiVO}_4/\text{CuO}_x$ heterojunction could facilitate the separation of photoinduced charge pairs, leading to the improved photocatalytic performance.

Transient photocurrent experiments were also performed to support the EIS studies and investigate the charge separation abilities [85] of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ and $\text{SiO}_2/\text{BiVO}_4$

electrodes (Fig. 7d). The photocurrent density of the electrodes were recorded for six “on-off” cycles with pulses of 10 seconds under visible light irradiation. The photocurrent density of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ electrode was about 3.5 times higher than that of $\text{SiO}_2/\text{BiVO}_4$ when taken at 0.50 V vs AgCl/Ag. This further highlighted that the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ photocatalyst was superior to $\text{SiO}_2/\text{BiVO}_4$ for more effective charge-pair separation and transfer *via* a Z-scheme system.

Fig. 7. (a) Time-integrated PL spectra, (b) time-resolved PL spectra, (c) EIS spectra, and (d) transient photocurrent response against time for $\text{SiO}_2/\text{BiVO}_4$ (black) and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ (red). In (b), the fits are the solid lines. PL and TR-PL experiments were performed on $\text{SiO}_2/\text{BiVO}_4$ and $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$, with photoexcitation at 400 nm and $\sim 30 \mu\text{J}/\text{cm}^2$ fluence.

2.6. Recyclability of the photocatalysts

To determine the stability and recyclability of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres, photooxidative coupling of 4-methoxybenzylamine was conducted for at least ten cycles with the catalyst recycled after each run (Fig. 4d). After each catalytic run, the heterogeneous catalysts could be recovered by centrifugation, and the residue was rinsed with solvent, dried, and recycled. It appeared that the BiVO_4 nanocrystals after multiple catalytic cycles did not aggregate when stabilized in the SiO_2 scaffold, as we anticipated (Fig. S13, Supplementary material). Consequently, high conversions of the substrate were maintained for the first three runs, after which a gradual decrease in the conversion was observed, although high yield for the oxidatively coupled imine product was maintained [60-62].

To investigate the chemical composition of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres after photocatalysis, we conducted XPS measurements on the recovered nanomaterials after the 2nd and 4th cycles (Fig. S14, Supplementary material). The XPS data of the $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ nanospheres after the 2nd and 4th cycles show the presence of Cu 2p, Si 1s and Bi 4f, and V 2p bands in the samples. The binding energies of Bi 4f and V 2p bands were found to be similar to those in Fig. 3 and Fig. S8, Supplementary material, thus confirming that no significant change in the oxidation states of Bi and V had occurred after the photocatalytic reaction. The Cu 2p core level spectra of $\text{SiO}_2/\text{BiVO}_4/\text{CuO}_x$ after the 2nd and 4th cycles can be fitted with two components each (Fig. S13a and d, Supplementary material). The two peaks at 931.7-932.9 and 951.7-952.8 eV are characteristic of Cu^+ 2p_{3/2} and 2p_{1/2}, respectively. The two weak shake-up satellites correspond to the Cu^{2+} species [71, 72]. It is noteworthy that the intensities of the Cu^{2+} signals became negligible after the reaction compared to before the reaction (Fig. 3), implying that the Cu^{2+} species in CuO_x was further reduced to Cu_2O . In addition, this observation provided more definitive evidence that the electrons from BiVO_4 were transferred to CuO_x , which reduced Cu^{2+} to Cu^+ *via* a Z-scheme mechanism instead of oxidation of CuO_x to generate more Cu^{2+} species *via* a double charge transfer mechanism (Fig. 5) [27].

To understand the decay in catalytic activity, we investigated the quantitative elemental composition of the catalysts after the 2nd, 4th, 8th, and 10th cycles by SEM-EDS (Fig. S15, Supplementary material). Apart from incomplete recovery of the photocatalyst, it was found that the levels of V decreased as the catalysts were recycled, with the V:Bi ratio deviating from a 1:1 ratio. This indicated that small amounts of V leached during the catalytic process. Furthermore, although the Bi and Cu contents remained stable up to the 8th cycle, by the 10th cycle, both Bi and Cu also started to deplete from the nanospheres. Consequently, we propose that the slow decay in performance is due to slight dissolution of V first, followed by Bi and Cu later.

3. Conclusions

In summary, we have prepared mesoporous SiO₂/BiVO₄/CuO_x nanospheres as chromophores for a Z-scheme system with effective light harvesting and charge separation. The SiO₂/BiVO₄/CuO_x nanospheres show efficient photocatalytic oxidative coupling of a broad range of benzylamines and are viable for the dehydrogenation of indolines using molecular O₂ in air as an environmentally benign oxidant under ambient temperatures. The superior photocatalysis of SiO₂/BiVO₄/CuO_x is attributed to the higher exposed surface area and shorter charge transport distances, as well as the surface CuO_x nanoparticles, which extend the light absorption and dramatically improve charge separation. To the best of our knowledge, this is the first instance of uniform nanoparticulate BiVO₄/CuO_x catalysts that absorb light *via* a Z-scheme, for photoredox organic synthesis. In addition, we demonstrate that the nanospheres are recyclable and can provide a greener approach for photocatalytic organic synthesis. We envision that this work will pave the way for the use of more concepts from artificial photosynthesis in the production of fine chemicals.

Conflicts of interest

The authors have no conflicts of interest.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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