#### Article

# Synergistic Electronic Effects in AuCo Nanoparticles Stabilized in a Triazine-Based Covalent Organic Framework: A Catalyst for Methyl **Orange and Methylene Blue Reduction**

Venkata Swaroopa Datta Devulapalli,<sup> $\perp$ </sup> Rinku Kushwaha,<sup> $\perp$ </sup> Edwin Ovalle, Himan Dev Singh, Pragalbh Shekhar, Debanjan Chakraborty, Chathakudath Prabhakaran Vinod, Ramanathan Vaidhyanathan,\* and Eric Borguet\*

Cite This: ACS	Appl. Nano Mater. 2022, 5, 4744–	-4753	Read Online		
ACCESS	III Metrics & More	💷 Article Re	commendations	5) Supportin	g Information
<b>ABSTRACT:</b> Dev desirable target. In with gold (Au) and their catalytic activi absorbance measur	eloping stable active catalysts this pursuit, we have functiona l cobalt (Co) nanoparticles via ity in reducing methyl orange a rements of methyl orange (an	for reducing water-so alized covalent organic a a one-step aqueous sy and methylene blue is a nionic dye) reduction	luble pollutants is a frameworks (COFs) nthesis process, and examined. Operando revealed AuCoCOF	Au Co <u>e<sup>-</sup>e<sup>-</sup>e<sup>-</sup></u> e <sup>-</sup> COF	e- Dye Reduction Colorless

(1.3 Au/1.0 Co) to have superior kinetics over many other catalysts, which typically require additional external stimuli (e.g., photons) and higher catalyst loadings. After confirming the homogeneous dispersion of the nanoparticles on the COF support using three-dimensional (3D) tomography and material stability through powder X-ray diffraction (PXRD), infrared (IR), and thermal studies, we investigated their redox activity. Cyclic voltammetry (CV)



confirmed the involvement of both metals in the redox process, while spectroelectrochemical measurements show that their activity and kinetics remain unaltered by an applied potential. Solid-state UV measurements reveal that the neat COF is a semiconductor with a large band gap (2.8 eV), which is substantially lowered when loaded with cobalt nanoparticles (2.2 eV for CoCOF). The electronic synergy between Au and Co nanoparticles further reduces the band gap of AuCoCOF (1.9 eV). Thus, there is a definite advantage in doping non-noble metal nanoparticles into a noble metal lattice and nanoconfining them into a porous COF support. Our study highlights the significance of bimetallic COF-supported nanocatalysts, wherein one can engage each component toward targeted applications that demand redox activity with favorable kinetics.

**KEYWORDS:** covalent organic framework, nanoparticles, methyl orange reduction, band gaps, AuCoCOF, UV-vis spectroscopy

# INTRODUCTION

Metal nanoparticles have enabled significant breakthroughs in catalysis,<sup>1</sup> biomedical applications,<sup>2</sup> and magnetism<sup>3</sup> and serve as catalysts exhibiting high surface areas.<sup>4-6</sup> The tunability of the physical attributes of metal nanoparticles and optical properties such as the surface plasmon resonance<sup>7</sup> have opened up new avenues in microscopy<sup>8</sup> and sensing.<sup>9</sup> Nanoparticles have a large surface area-to-volume ratio and surface energies, making them thermodynamically unstable and leading to their aggregation.<sup>10</sup> Traditionally, metal nanoparticles have been synthesized using protective capping agents, which anchor on their surface and ultimately stabilize them by preventing their aggregation. Unfortunately, many of these organic capping agents are not resistant toward pH and or temperature changes<sup>11</sup> and hence detach from the nanoparticles or degrade, causing agglomeration of the nanoparticles.<sup>10</sup> Ironically, at a molecular scale, these bulky capping agents can hinder the surface accessibility for reactants and in some cases interact too strongly with the nanoparticles and poison them, thereby diminishing their catalytic properties. Therefore, increasing the stability and retaining the

activity of the nanoparticles by dispersing them on support systems is a common approach.<sup>13,14</sup>

Three-dimensional (3D) porous materials such as silica, metal-organic frameworks (MOFs), and zeolites exhibit high surface areas and porosity.<sup>15–17</sup> The functional groups present in porous materials can stabilize the nanoparticles (NPs). NPzeolite and NP-MOF hybrids have shown promise in catalyzing several organic reactions,<sup>18</sup> hydrogen evolution reactions,<sup>19</sup> oxygen evolution reactions,<sup>20</sup> and applications such as separations,<sup>21</sup> surface-enhanced Raman scattering,<sup>22</sup> and also biomedical applications (e.g., drug delivery<sup>23</sup> and photodynamic therapy<sup>24</sup>). The crystalline nature of these support materials helps in obtaining a well-defined and tunable hybrid material suitable for niche applications such as

Received: December 7, 2021 Accepted: February 8, 2022 Published: March 17, 2022







Figure 1. Schematic representation of material synthesis. Top: synthesis of the triazine-based imine COF. Bottom: NP-COF hybrid synthesis using gold salt with CoCOF as the template and HEPES as the reducing buffer.

asymmetric catalysis<sup>25,26</sup> and chiral separations.<sup>27</sup> An ideal support system should have optimal interactions with the nanoparticles to prevent aggregation without altering the intrinsic properties of nanoparticles.

Covalent organic frameworks (COFs) are crystalline organic porous materials with high surface areas and tunable porosities.<sup>28</sup> Strong covalent bonding results in the formation of a robust structure stable under a variety of conditions. Triazine (trzn)-based imine COFs are reported to be stable in strong acidic and basic media and in boiling water, making them suitable candidates for various practical applications including gas storage,<sup>29</sup> photocatalysis,<sup>30</sup> and energy storage systems.<sup>31–33</sup> Facile functionalization and postsynthetic modifications act as handles to tune the chemistry and functions of COFs, without damaging their structure and stability. Postsynthetic modifications by nanoparticle deposition on COFs show promise in the field of heterogeneous catalysis.<sup>34,35</sup> Lodging catalytically active metals as welldispersed nanoparticles in a COF support facilitates superior efficiency and reactivity compared to their constituents. In a study reported by Mullangi et al., palladium nanoparticles on a trzn-COF exhibited high rates and yields for a multifold Heck reaction compared to individual constituents.<sup>36</sup> Similar systems were designed and tested for water splitting and were reported to display efficient kinetics and low overpotentials for the oxygen evolution reaction (OER).<sup>37</sup>

Though NP-COF hybrids exhibit several advantages over their respective components, their synthesis poses several challenges. For instance, the creation of AuCOF hybrids requires heating mixtures of metal salts and COFs at high temperatures for prolonged time scales or using harsh chemicals.<sup>38,39</sup> Hence, methods to generate NP-COF hybrids using benign techniques are of huge interest. Synthesizing combinations of noble metal and non-noble metal hybrids is attractive to reduce the overall cost of the catalyst, facilitate electron transfer in the catalyst, and enhance the stability and activity of the overall catalyst by exploiting synergistic interactions.

Based on the criteria discussed above, we herein present a facile room-temperature deposition of gold and cobalt nanoparticles on a triazine-based imine COF and test the catalytic activity of the hybrid for methyl orange reduction. Gold nanoparticles display a wide variety of optoelectronic properties. Cobalt,<sup>40,41</sup> a d-block non-noble metal, shows strong affinity toward nitrogen<sup>42</sup> in COFs and is reported to display strong  $\pi - \pi$  interactions with aromatic groups, which avoids aggregation and loss of nanoparticles via leaching.<sup>43,44</sup> In addition, cobalt nanoparticles<sup>45</sup> reportedly show strong affinity toward azo dyes<sup>46</sup> and exhibit magnetic properties, making them potential candidates for applications.<sup>47</sup> Hence, combining the properties of Au and Co into a single hybrid material is desirable. We hypothesized that imine COFs could be suitable support systems for nanoparticles preventing their aggregation, hence preserving their catalytic properties. Apart from being a support system, imine COFs with their conjugated framework can facilitate electron transfer from nanoparticles to the target molecule.

The majority of dyes are toxic to the environment and living organisms and are one of the key contributors to aquifer pollution.<sup>48</sup> In addition, some dyes are carcinogenic and interact and accumulate in water animals, thereby progressing up the food chain. Such high toxicity is attributed to their nonbiodegradable nature, which results in a high residence time in the environment. Therefore, materials that readily degrade these dyes are of high interest. Unlike other contaminants, azo dyes are highly stable and resistant to



Figure 2. COF characterization: (A) powder X-ray diffraction (PXRD) patterns and (B)  $N_2$  adsorption isotherms (at 77 K) of the as-made IISERP-COF1, CoCOF, and AuCoCOF. The indexed *hkl* reflections correspond to the gold fcc lattice with JCPDS file no. 04-0784.



**Figure 3.** COF structure characterization: (A) TEM image shows the aggregation of flaky crystallites with the cotton-like morphology of COF along with a homogeneous distribution of particles. (B, C) HRTEM images of AuCoCOF showing the lattice fringes of different facets. (D, E) The selective area electron diffraction (SAED) pattern of AuCoCOF. (F) Energy-dispersive X-ray analysis (EDAX) assisted with HRTEM elemental mapping reveals the presence of Co and Au in the sample.

visible-light-induced self-photolysis.<sup>49</sup> Hence, chemical degradation of dyes via breaking robust azo bonds requires the use of strong oxidizing agents, UV light, and expensive catalysts.<sup>50,51</sup> Previously reported catalysts, namely, twodimensional (2D) and 3D transition metal dichalcogenides<sup>52</sup> and MOFs,<sup>53</sup> have shown some promise for dye degradation but suffer from synthesis/stability issues or slow reaction rates, which motivated us to test our NP-COF hybrids for catalytic reduction of anionic methyl orange as a proof of concept.

# RESULTS AND DISCUSSION

Design and Synthesis of IISERP-COF1, CoCOF, and AuCoCOF. IISERP-COF1  $(COF)^{36}$  was synthesized by a

previously reported method where a solvothermal reaction was performed between 4,4',4''-(1,3,5-triazine-2,4,6-triyl)tris(oxy)tribenzaldehyde and benzene-1,4-diamine in 1,4 dioxane, mesitylene, and aqueous acetic acid by heating at 120 °C for 72 h in a sealable ACE glass pyrex tube (Figure 1). (The synthesis procedure of CoCOF can be found in the Supporting Information.) The product was isolated as a bluish brown powder by vacuum filtration and washed with different solvents including DMF, THF, DMSO, methanol, water, and acetone. Inductively coupled plasma-mass spectrometry (ICP-MS) revealed the Co content in CoCOF to be 11 wt %.

Synthesis of AuCoCOF. CoCOF (10 mg/mL) was dispersed in water and sonicated for 5 min. One milliliter of

a 10 mM AuCl<sub>4</sub>·3H<sub>2</sub>O solution and 1 mL of 10 mM HEPES buffer were dispensed to 1 mL of CoCOF solution and stirred for 30 min at room temperature. After stirring, the solution was allowed to stand for 30 min in ambient, the supernatant was carefully discarded and the precipitate was collected. The precipitate was re-suspended in DI water and centrifuged and the supernatant was removed. This process is repeated two times, and then DI water was added to the final precipitate to obtain 1 mL of the solution. The resulting AuCoCOF was stored under ambient conditions (Figure 1). Note: for the synthesis of CoCOF see the Supporting Information, Page S3. AuCoCOF (1.3 Au/1.0 Co).

Bulk Characterization. IISERP-COF1 has a layered hexagonal structure with uniform 27 Å sized 1D channels (not factoring the van der Waals radii). The bulk phase purity of the COF and the composites were verified using powder Xray diffraction (Figures 2A, S1, and S2). The X-ray diffraction (XRD) patterns of CoCOF and AuCoCOF match well with the as-made COF (Figures 2A and S3). The peaks corresponding to Co metal or its oxide were not seen, suggesting the presence of either a small quantity or a small size of Co nanoparticles in CoCOF or that the nanoparticles could be amorphous.<sup>54</sup> Hence, to characterize Co, we resorted to high-resolution transmission electron microscopy (HRTEM) and postcalcination XRD studies. However, the XRD pattern of AuCoCOF shows a few intense peaks corresponding to pure, crystalline Au nanoparticles (JCPDS file no. 04-0784) and the COF, in the whole spectrum of  $2\theta$ values ranging from 1.5 to 80°. Specifically, the strong peaks at 38.21, 44.44, 64.61, and 77.63° correspond to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) family of planes for fcc Au nanoparticles, thus confirming a successful deposition of crystalline Au nanoparticles.

N2 adsorption at 77 K of the as-made COF shows a reversible type-IV adsorption isotherm<sup>55,56</sup> (Figure 2B) with a Brunauer–Emmett–Teller (BET) surface area of 1289  $m^2/g^{36}$ A model-independent Barrett-Joyner-Halenda (BJH) fit to the desorption branch yielded a pore size of 25.0 Å and a pore volume of 0.21 cc/g, which matches extremely well with the modeled structure (Figure S1). $^{57-59}$  This high N<sub>2</sub> uptake confirms the porosity of the COF (Figure 2A). Drastic lowering of the N<sub>2</sub> uptake is witnessed upon loading the nanoparticles (Figure 2B). This could result from the lodging of the NPs into the pores or from the adherence of the nanoparticles onto the COF surface depending on their limiting size. We investigated these possibilities using microscopy methods, and the results are presented later in the text. Infrared (IR) spectra of the COF, CoCOF, and AuCoCOF show the characteristic stretching vibrations such as -C=N and C-O in all cases, which confirms their functional group integrity (Figure S7). The red shift in the -C=N- frequency of CoCOF and AuCoCOF in comparison to COF could most likely be due to the interactions of the nanoparticles and the COF.

The fluffy, cotton-like morphology of COF, CoCOF, and AuCoCOF was revealed by field emission scanning electron microscopy (FESEM, Figures S9–S11). EDAX-elemental mapping (Figures S12–S15) shows the successful loading of nanoparticles in the COF matrix. High-resolution transmission electron microscopy (HRTEM, Figure 3A–C) revealed a homogeneous distribution of Au and Co throughout the sample. A particle size distribution assessed from the HRTEM indicated an average size of 14 nm (Figure S18). In some cases,

when the nanoparticles had grown to relatively larger sizes (>30 nm), their hexagonal morphology with well-defined edges could be seen, which was further evident from the selected area electron diffraction (SAED) images, which could be indexed to Au planes. This suggests that the nanoparticles could be growing as nanocrystals. Notably, the presence of lattice fringes corresponding to Au and Co facets shows the ability of the COF to expose various facets of the nanoparticles (Figure 3D,E). Although peaks corresponding to Co nanoparticles are absent in the PXRD, their detection via elemental analysis, coupled with the drop in porosity upon loading of the nanoparticles (Figure 2A,B), suggest that the nanoparticles are not as crystalline as Au and are buried within the COF.<sup>26</sup> Importantly, the EDAX-elemental mapping from STEM measurements and HRTEM 3D tomography (Figure 4) suggests the presence of C, N, and O in the same region as



**Figure 4.** Scanning transmission electron microscopy (STEM)elemental mapping shows the uniform distribution of Au and Co in the nanoparticles (A, B). Notably, they share the same spatial position. (C-E) Tomographic images along *x-*, *y-*, and *z*-axes, respectively, which show the cotton-like morphology of COF, consistent with FESEM, along with a homogeneous distribution of Au and Co nanoparticles.

Au and Co (Figures 3F and S12, S13, S16, S17). The red regions in 3D tomography indicate the nanoparticles, while the yellow regions correspond to the organic support, i.e., the COF. Importantly, the red region is made up of small dots, which represent the nanoparticles. Though on a microscopic scale, they look aggregated, they are separated nanoparticles. Also, these red islands are observed along all three directions, indicating that they are uniformly distributed by the COF. The yellow regions contain randomly stacked flakes of the COF, and the nanoparticles (red) are concentrated along the edges of such flakes. However, these tomography images do not display the small nanoparticles buried inside the flaky COF.

X-ray photoelectron spectroscopy (XPS) was employed to identify the oxidation states of the constituents. XPS spectra of CoCOF display a peak at a binding energy (BE) of 778.1 eV, which corresponds to the Co metal. In addition, peaks were observed at 781.1 (Co  $2p_{3/2}$ ) and 797.3 eV (Co  $2p_{1/2}$ ), and their corresponding satellite peaks at 786.08 and 803.28 eV, respectively. These match the peaks observed for Co(OH)<sub>2</sub> nanoparticles (Figure S19).<sup>33,53</sup> This suggests that the surface of the Co metal is hydroxylated under the aqueous-phase synthesis. The XPS bands of Au  $4f_{7/2}$  and Au  $4f_{5/2}$  appear at 84.5 and 88.1 eV, respectively, as expected for Au(0) present in AuCoCOF (Figure S20).<sup>60</sup>

Determination of the Composition of AuCoCOF from Its Calcined Form. To further understand the composition of the Au–Co nanoparticles present in AuCoCOF, we carried out some thermal treatment studies. We calcined the AuCoCOF samples under  $N_2$  at 600 °C for 12 h, and a PXRD pattern was obtained by subjecting the resulting powder to X-ray in an airsensitive sample holder equipped with a Kapton window. Peaks corresponding to metallic Au and Co were observed and could be indexed to known phases (Figure S21). From STEMelemental mapping (Figure 4), cobalt and gold seem to occupy the same spatial position. This could mean that either they are alloys with exactly the same lattice parameter, or they could be just a composite solid solution.

To clarify this, the PXRD of the calcined AuCoCOF was fitted using Rietveld refinement methods (Figures S21 and S22). A three-phase refinement including Au (JCPDS: 04-0784), cobalt (cubic ICSD: 44989), and cobalt (hexagonal JCPDS: 05-0727) yielded an excellent fit with at least one individual peak corresponding to one of these phases ( $\chi^2$  = 1.013, w $R_p = 0.1270$ ). The phase fractions were Au (cubic) = 74.38(3), Co (cubic) = 23.73(4), and Co (hexagonal) = 1.87(2). No appreciable change in the unit cell was detected,  $^{61}$ nor was any phase change observed.<sup>62</sup> Thus, most likely what we have is a solid solution of metallic Au (cubic), Co (cubic), and some hexagonal cobalt.<sup>63</sup> Of course, it cannot be ruled out that cobalt could have phase-segregated during the calcination process. We carried out the synthesis of AuCoCOF three times and analyzed their calcined phases, and the observations were unchanged. Though the Au/Co ratio (2.9 Au/1 Co) from the Rietveld refinements agrees with the trend observed from the ICP results (1.3 Au/1 Co), the Au amount estimated for the calcined samples from the Rietveld refinement is notably higher, most likely due to the ability of gold nanoparticles to crystallize better under calcination conditions compared to the cobalt nanoparticles, which is expected considering the facile melting and crystallization of softer gold.<sup>61</sup> Notably, CoCOF calcined under N<sub>2</sub> had reflections for cobalt metal (JCPDS: 05-0727), and there was no sign of cobalt oxide.

**Catalytic Activity of Hybrid COF Nanoparticles toward Dye Reduction.** To evaluate the catalytic properties of the COF hybrids, dye reduction was studied using the dyes methyl orange and methylene blue, following the procedures reported in Section 2 and Figure S23 in the Supporting Information. Reaction progress was monitored via changes in the in situ UV–vis spectra in the 300–700 nm region (Figures S24 and S25), recorded at regular intervals of 1 s. The spectra of methyl orange before the addition of any catalyst displayed a broad band centered at 464 nm in the visible region, which is attributed to the  $n-\pi^*$  transitions.<sup>53</sup> Similarly, the initial UV– vis spectra of methylene blue displayed a peak at 664 nm<sup>64</sup> (Figure S26).

The reduction of methyl orange by AuCOF was faster compared to reported catalysts (which also demand an external stimulus such as photoirradiation to drive the reaction).<sup>65–68</sup> The intensity of the peak at 464 nm starts decreasing, and the reaction proceeds to completion within 3 min, at which time the dye solution was observed to be colorless (Figures 5 and



Figure 5. Plot of absorbance (at 464 nm) versus time tracking the kinetics of reduction of methyl orange catalyzed by COF hybrids.

S24b). As the concentration of  $BH_4^-$  is much higher compared to that of the dyes, the concentration of  $BH_4^-$  is assumed to remain constant during the course of the reaction. In this scenario, pseudo-first-order rate laws were followed to analyze the rates of the reactions.<sup>48,69</sup> Quantitative analysis was performed using eq 1, and the graph of  $\ln(A/A_0)$  versus time (*A*: absorbance at time *t*) is plotted and the value of the rate constant (*k*) was obtained as 1.62 min<sup>-1</sup> (Figures S27–S29).

Cobalt reportedly shows affinity toward azo groups and is used for the reduction of several contaminants.<sup>45</sup> In the case of CoCOF, the absorbance of methyl orange remained unchanged until 5 min, after which a gradual decrease in the intensity of methyl orange was observed. Although CoCOF completely reduced methyl orange in 10 min ( $k = 0.16 \text{ min}^{-1}$ ), the kinetics are slow in comparison to AuCOF (Figures S24 and S27).

$$-\ln\!\left(\frac{A}{A_0}\right) = kt \tag{1}$$

Among all of the COF catalysts, the highest rate constant and the fastest reduction kinetics were observed in the case of AuCoCOF ( $k = 3.60 \text{ min}^{-1}$ ). Methyl orange was completely reduced in less than 1 min, and the rapid kinetics can be



Figure 6. Cyclic voltammograms of hybrid materials: (A) CoCOF showing the  $Co^{2+/}Co^{3+}$  redox couple and (B) AuCoCOF showing the  $Au^{0/}Au^{3+}$  redox couple at 50 mV/s scan speed for five cycles, from 0 to 0.9 V.

attributed to the synergy between Au and Co nanoparticles (Figures S29 and S30). To test the versatility of AuCoCOF applications, cationic dye methylene blue reduction was also studied using AuCoCOF. Interestingly, 100% reduction was observed in under 10 min (Figure S30), revealing the potential of AuCoCOF for degrading a variety of dyes.

To check if the nanoparticles are leaching from the COF during the reaction, we stirred AuCoCOF in deionized water for 15 min and filtered the solid. Using the filtrate, we observed no reduction of methyl orange (Figure S31), which suggests that there is no appreciable leaching of nanoparticles from the COF. Also, the low amount of the catalyst (0.25 mg per 1 mL) used in our studies, compared to reported catalysts (Table S1), highlights the advantages AuCOF and AuCoCOF presented in this study over other COF-based catalysts.

Control experiments performed using unsupported Au NPs, i.e., without the COF, revealed little reduction of methyl orange over a time period of 1 h (Figure S32), highlighting the significance of the support system. To identify any contribution of the support system itself toward the reduction, catalysis experiments were performed in the presence of pristine COF, with no metal nanoparticles deposited, to the solution containing methyl orange and monitored for 1 h. A small initial decrease in intensity at 464 nm (Figure S24a) was observed, which is attributed to the reduction of methyl orange by BH<sub>4</sub><sup>-</sup>. However, after the initial decrease, the intensity at 464 nm remained constant over a period of 1 h, which suggests that the pristine COF, by itself, does not catalyze the reduction of methyl orange.

**Catalytic Activity of Metal Nanoparticles Investigated via Electro and Spectroelectrochemical Studies.** To understand the superiority of the composite catalyst and to elucidate the function of each metal during catalysis, we resorted to some electro and spectroelectrochemistry studies. Cyclic voltammetry (CV) was performed to understand the oxidation states of Au and Co in the COF. Spectroelectrochemical experiments were performed to find out if an applied potential can alter the rate/activation energy of methyl orange reduction.

CV was performed on a typical three-electrode setup, with a Hg/HgO reference electrode and a platinum flag counter electrode. The catalyst-coated glassy carbon electrode, dried under an IR lamp, was used as the working electrode. The catalyst mass loading was maintained to be 20  $\mu$ g for all of the electrochemical studies. In all of the cases, deaerated 0.1 M KOH was used as an electrolyte.<sup>70</sup>

Cyclic voltammetry of CoCOF and AuCoCOF exhibit clear redox couples as well as good cyclability, as indicated by overlapping traces (Figure 6). CoCOF has a CV quite comparable to the previously reported one from our group.<sup>54</sup> There are two distinct redox processes I/I' and II/II' for CoCOF, and both are reversible, whereas the sharp increase (at 0.7 V) belongs to the irreversible oxidation of water (Figure 6A). The separations between the oxidation and the corresponding reduction peaks suggest that the peak in a potential window of 0.1-0.3 V has relatively slower kinetics than the peak occurring in a potential window of  $\sim 0.53 - 0.55$ V.<sup>71,72</sup> AuCoCOF has a CV similar to that reported in the literature.<sup>73</sup> A reversible redox process I/I' for AuCoCOF is observed at 0.81/0.6 V corresponding to Au<sup>0/</sup>Au<sup>3+</sup>,<sup>74</sup> whereas the other peak at 0.87 V belongs to the irreversible water oxidation (Figure 6B). The peak separations between the oxidation and the corresponding reduction are very large for AuCoCOF (0.21 V) compared to CoCOF (0.02 and 0.06 V), implying slower dye reduction by AuCoCOF compared to CoCOF. However, the current density of AuCoCOF (0.8 mA) is an order of magnitude higher than that of CoCOF (0.08 mA), for the same catalyst loading, which reflects the observed higher catalytic activity of AuCoCOF compared to CoCOF.

Encouraged by the enhanced catalytic activity of the composite and the presence of cobalt-based and N-rich redox-active sites in AuCoCOF, we investigated if the dye reduction rate can further be boosted by applying a potential. For this, we resorted to spectroelectrochemical studies (refer to the Supporting Information for details). The CV curve (Figure S33) comparable to the earlier reported ones was obtained, and the simultaneous UV-vis spectrum with the characteristic peaks revealing the reduction of the dye was recorded, and it agreed well with the UV-vis spectrum measured without an applied potential. However, no kinetic enhancement in the dye reduction was observed even under a wide potential sweep of -1 to 3 V (Figure S34), suggesting that the applied potential does not decrease the activation energy required to reduce methyl orange. Given that the sizes of Au and Co NPs in AuCoCOF are evidently larger compared to Co NPs in CoCOF, the higher catalytic activity of AuCoCOF most likely has its origin in redox activity rather than in the size of the nanoparticles. In other words, though depositing Au and Co as nanoparticles brings advantages, the critical parameter responsible for improved reduction of methyl orange in AuCoCOF is the synergistic electronic effects between Au and Co nanoparticles.



Figure 7. Solid-state UV–vis absorption spectra of the as-made COF, CoCOF, and AuCoCOF (A). Tauc plot to obtain the band gap of the asmade COF (B), CoCOF (C), and AuCoCOF (D).

Band Gap Trends in COF, CoCOF, and AuCoCOF via Solid-State UV–Vis Absorption Studies. Realizing that this might have its origin in electronic properties, we decided to investigate the band gap of AuCoCOF for further insights. UV–vis absorption studies on NP-COF hybrids were carried out on a Shimadzu UV3600 UV/vis/NIR spectrophotometer in solid-state measurement mode over the range of 200–800 nm.

Photon-driven electron oscillations around the nanoparticle surface create a time-dependent charge separation with respect to the ionic lattice, resulting in a dipole oscillation along the direction of the electric field of light. The oscillation amplitude attains a maximum at a specific frequency, called the surface plasmon resonance (SPR). For cobalt and gold nanoparticles, SPR wavelengths are around 440 and 520 nm, respectively, depending on the size and shape of the nanoparticles.<sup>75,76</sup> The absorption spectra (Figure 7) show the presence of Co and Au within the COF framework and the observed SPR values of cobalt and gold nanoparticles are 430 and 535 nm, respectively.

The direct energy band gap  $(E_g)$  of the synthesized samples was determined by Tauc's equation.<sup>77,78</sup>

$$(\alpha hv)^{1/n} = A \times (hv - E_{\rm g}) \tag{2}$$

where  $\alpha$  is the absorption coefficient, hv is the photon energy,  $E_g$  is the band gap of the synthesized material, and *n* represents the optical transition parameter 1/2, 2, 3/2, or 3. If n = 1/2, the transition is the direct allowed transition; for n = 3/2, the transition is the direct forbidden transition; for n = 2, the transition is the indirect forbidden transition; and for n = 3. the transition is the indirect forbidden transition.<sup>77,78</sup> As the optical absorption was strong, suggesting a direct allowed transition, we chose n = 1/2. From the plots of  $(\alpha hv)$ 2 versus (hv), the direct band gap was found to be 2.8, 2.2, and 1.9 eV for the as-made COF, CoCOF, and AuCoCOF, respectively.

Hence, the higher activity of AuCoCOF can be attributed to its lowest band gap compared to other catalysts in this study.

## CONCLUSIONS

We demonstrated a simple synthesis process of AuCo nanoparticle-loaded COFs and characterized their structures using microscopy, N<sub>2</sub> adsorption, and spectroscopy. The COF and their composites displayed high thermal stability (~573 K), and the hybrids AuCOF and AuCoCOF displayed order of magnitude superior catalytic properties compared to the pristine COF, for the reduction of methyl orange. HRTEM and 3D tomography reveal a homogeneous distribution of gold and cobalt particles in the COF matrix. The rate constants for methyl orange reduction using AuCOF and AuCoCOF are 1.62 and 3.60 min<sup>-1</sup>, respectively, and their robustness and versatility in applications are distinctly observed for the catalytic reduction of methyl orange and methylene blue. The superior activity of AuCoCOF is attributed to the synergy between the Au and Co nanoparticles on the COF, which resulted in the lowering of the band gap of AuCoCOF ( $E_o$ : 1.9 eV) by 0.9 eV compared to the as-made, pristine COF, which ultimately facilitated the reduction of methyl orange.

Our studies highlight simple and straightforward syntheses of NP-COF hybrids (otherwise synthesized via complex and energy-intensive procedures involving prolonged heating at high temperatures) and provide characterization and insights into their catalytic properties. We believe that the methods described in this paper will guide researchers in developing better materials for various applications including catalytic degradation of dyes and organic pollutants.

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.1c04212.

Materials and methods describing the synthesis and characterization of the COF and nanoparticle–COF composites; schematic of the optical setup for in situ spectroscopy; and spectral data from the catalysis study (PDF)

# AUTHOR INFORMATION

## **Corresponding Authors**

Ramanathan Vaidhyanathan – Department of Chemistry, Indian Institute of Science Education and Research, Pune 411008, India; Centre for Energy Science, Indian Institute of Science Education and Research, Pune 411008, India; orcid.org/0000-0003-4490-4397; Email: vaidhya@ acads.iiserpune.ac.in

Eric Borguet – Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States; orcid.org/0000-0003-0593-952X; Email: eborguet@ temple.edu

### Authors

- Venkata Swaroopa Datta Devulapalli Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States; orcid.org/0000-0003-1860-9888
- Rinku Kushwaha Department of Chemistry, Indian Institute of Science Education and Research, Pune 411008, India; Centre for Energy Science, Indian Institute of Science Education and Research, Pune 411008, India; orcid.org/ 0000-0002-1169-4250
- Edwin Ovalle Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States
- Himan Dev Singh Department of Chemistry, Indian Institute of Science Education and Research, Pune 411008, India; Centre for Energy Science, Indian Institute of Science Education and Research, Pune 411008, India
- Pragalbh Shekhar Department of Chemistry, Indian Institute of Science Education and Research, Pune 411008, India; Centre for Energy Science, Indian Institute of Science Education and Research, Pune 411008, India; orcid.org/ 0000-0002-3766-122X
- **Debanjan Chakraborty** Department of Chemistry, Indian Institute of Science Education and Research, Pune 411008, India; Centre for Energy Science, Indian Institute of Science Education and Research, Pune 411008, India
- Chathakudath Prabhakaran Vinod Catalysis Division, CSIR-NCL Pune, Pune 411008, India; © orcid.org/0000-0001-9857-4907

Complete contact information is available at: https://pubs.acs.org/10.1021/acsanm.1c04212

## **Author Contributions**

<sup> $\perp$ </sup>V.S.D.D. and R.K. contributed equally. V.S.D.D. and R.K.: designed and performed experiments, manuscript writing and proof reading, and intellectual contributions. E.O.: designed and performed catalysis experiments. H.D.S., P.S., and D.C.: synthesis of IISERP-COF1 and performed N<sub>2</sub> adsorption experiments and structural and electrochemical characterization of COFs. C.P.V.: performed XPS experiments. R.V. and E.B.: designed experiments, manuscript writing and proof reading, and intellectual contributions. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This project received support from the Defense Threat Reduction Agency (DTRA) (Grant No. HDTRA1-16-1-0044) and Indo-U.S. Science and Technology Forum (IUSSTF). R.K. thanks IISER Pune for Graduate Fellowship. This material is based upon work supported by the "Air Force Office of Scientific Research under Award Number FA2386-21-1-4022." The authors thank DST-for material for energy storage (DST/TMD/MES/2k17/103) program and the "DST-Nanomission under the Thematic Unit Program" (EMR/2016/003553). Research reported in this publication was partially supported by the National Institute of General Medical Sciences (NIGMS) of the National Institutes of Health (Award No. T34GM087239). The authors thank Prof. Pramod Pillai (IISER Pune) for the solid-state UV measurement system.

## REFERENCES

(1) Hofmann, D. M.; Fairbrother, D. H.; Hamers, R. J.; Murphy, C. J. Two-Phase Synthesis of Gold-Copper Bimetallic Nanoparticles of Tunable Composition: Toward Optimized Catalytic CO<sub>2</sub> Reduction. *ACS Appl. Nano Mater.* **2019**, *2*, 3989–3998.

(2) Cheon, J.; Lee, J. H. Synergistically Integrated Nanoparticles as Multimodal Probes for Nanobiotechnology. *Acc. Chem. Res.* 2008, *41*, 1630–1640.

(3) Beaune, G.; Menager, C.; Cabuil, V. Location of magnetic and fluorescent nanoparticles encapsulated inside giant liposomes. *J. Phys. Chem. B* 2008, *112*, 7424–7429.

(4) Li, Z.; Ji, S. F.; Liu, Y. W.; Cao, X.; Tian, S. B.; Chen, Y. J.; Niu, Z. G.; Li, Y. D. Well-Defined Materials for Heterogeneous Catalysis: From Nanoparticles to Isolated Single-Atom Sites. *Chem. Rev.* **2020**, *120*, 623–682.

(5) Sil, D.; Lane, C.; Glor, E.; Gilroy, K. D.; Sylla, S.; Barbiellini, B.; Markiewicz, R.; Hajfathalian, M.; Neretina, S.; Bansil, A.; Fakhraai, Z.; Borguet, E. Synthesis and Properties of Au Hydride. *ChemistrySelect* **2019**, *4*, 4287–4292.

(6) Sil, D.; Gilroy, K. D.; Niaux, A.; Boulesbaa, A.; Neretina, S.; Borguet, E. Seeing Is Believing: Hot Electron Based Gold Nanoplasmonic Optical Hydrogen Sensor. *ACS Nano* **2014**, *8*, 7755–7762.

(7) Guo, H. Y.; Ruan, F. X.; Lu, L. H.; Hu, J. W.; Pan, J. A.; Yang, Z. L.; Ren, B. Correlating the Shape, Surface Plasmon Resonance, and Surface-Enhanced Raman Scattering of Gold Nanorods. *J. Phys. Chem.* C 2009, *113*, 10459–10464.

(8) Liu, J. B.; Yang, X. H.; Wang, K. M.; He, Y.; Zhang, P. F.; Ji, H. N.; Jian, L. X.; Liu, W. Single Nanoparticle Imaging and Characterization of Different Phospholipid-Encapsulated Quantum Dot Micelles. *Langmuir* **2012**, *28*, 10602–10609.

(9) Willets, K. A.; Wilson, A. J.; Sundaresan, V.; Joshi, P. B. Super-Resolution Imaging and Plasmonics. *Chem. Rev.* 2017, *117*, 7538– 7582.

(10) Aijaz, A.; Xu, Q. Catalysis with Metal Nanoparticles Immobilized within the Pores of Metal-Organic Frameworks. J. Phys. Chem. Lett. 2014, 5, 1400–1411.

(11) Gole, B.; Sanyal, U.; Banerjee, R.; Mukherjee, P. S. High Loading of Pd Nanoparticles by Interior Functionalization of MOFs for Heterogeneous Catalysis. *Inorg. Chem.* **2016**, *55*, 2345–2354.

(12) Li, D. G.; Wang, C.; Tripkovic, D.; Sun, S. H.; Markovic, N. M.; Stamenkovic, V. R. Surfactant Removal for Colloidal Nanoparticles from Solution Synthesis: The Effect on Catalytic Performance. *ACS Catal.* **2012**, *2*, 1358–1362.

(13) Thenuwara, A. C.; Cerkez, E. B.; Shumlas, S. L.; Attanayake, N. H.; McKendry, I. G.; Frazer, L.; Borguet, E.; Kang, Q.; Remsing, R. C.; Klein, M. L.; Zdilla, M. J.; Strongin, D. R. Nickel Confined in the Interlayer Region of Birnessite: an Active Electrocatalyst for Water Oxidation. *Angew. Chem., Int. Ed.* **2016**, *55*, 10381–10385.

(14) Attanayake, N. H.; Thenuwara, A. C.; Patra, A.; Aulin, Y. V.; Tran, T. M.; Chakraborty, H.; Borguet, E.; Klein, M. L.; Perdew, J. P.;

www.acsanm.org

Strongin, D. R. Effect of Intercalated Metals on the Electrocatalytic Activity of 1T-MoS<sub>2</sub> for the Hydrogen Evolution Reaction. ACS Energy Lett. **2018**, 3, 7–13.

(15) Villa, A.; Dimitratos, N.; Chan-Thaw, C. E.; Hammond, C.; Veith, G. M.; Wang, D.; Manzoli, M.; Prati, L.; Hutchings, G. J. Characterisation of gold catalysts. *Chem. Soc. Rev.* **2016**, *45*, 4953–4994.

(16) Lázár, I.; Szabo, H. J. Prevention of the Aggregation of Nanoparticles during the Synthesis of Nanogold-Containing Silica Aerogels. *Gels* **2018**, *4*, No. 55.

(17) Pachfule, P.; Panda, M. K.; Kandambeth, S.; Shivaprasad, S. M.; Diaz, D. D.; Banerjee, R. Multifunctional and robust covalent organic framework-nanoparticle hybrids. *J. Mater. Chem. A* **2014**, *2*, 7944–7952.

(18) Müller, M.; Hermes, S.; Kaehler, K.; van den Berg, M. W. E.; Muhler, M.; Fischer, R. A. Loading of MOF-5 with Cu and ZnO nanoparticles by gas-phase infiltration with organometallic precursors: properties of Cu/ZnO@MOF-5 as catalyst for methanol synthesis. *Chem. Mater.* **2008**, *20*, 4576–4587.

(19) White, J. C.; Dutta, P. K. Assembly of Nanoparticles in Zeolite Y for the Photocatalytic Generation of Hydrogen from Water. *J. Phys. Chem. C* 2011, *115*, 2938–2947.

(20) Samanta, S.; Khilari, S.; Bhunia, K.; Pradhan, D.; Satpati, B.; Srivastava, R. Double-Metal-Ion-Exchanged Mesoporous Zeolite as an Efficient Electrocatalyst for Alkaline Water Oxidation: Synergy between Ni-Cu and Their Contents in Catalytic Activity Enhancement. J. Phys. Chem. C 2018, 122, 10725–10736.

(21) Chen, Z. J.; Feng, L.; Liu, L. M.; Bhatt, P. M.; Adil, K.; Emwas, A. H.; Assen, A. H.; Belmabkhout, Y.; Han, Y.; Eddaoudi, M. Enhanced Separation of Butane Isomers via Defect Control in a Fumarate/Zirconium-Based Metal Organic Framework. *Langmuir* **2018**, *34*, 14546–14551.

(22) Hu, Y. L.; Liao, J.; Wang, D. M.; Li, G. K. Fabrication of Gold Nanoparticle-Embedded Metal-Organic Framework for Highly Sensitive Surface-Enhanced Raman Scattering Detection. *Anal. Chem.* **2014**, *86*, 3955–3963.

(23) Duan, D. B.; Liu, H.; Xu, M. X.; Chen, M. Q.; Han, Y. X.; Shi, Y. X.; Liu, Z. B. Size-Controlled Synthesis of Drug-Loaded Zeolitic Imidazolate Framework in Aqueous Solution and Size Effect on Their Cancer Theranostics in Vivo. *ACS Appl. Mater. Interfaces* **2018**, *10*, 42165–42174.

(24) Zhang, Y.; Wang, F. M.; Liu, C. Q.; Wang, Z. Z.; Kang, L. H.; Huang, Y. Y.; Dong, K.; Ren, J. S.; Qu, X. G. Nanozyme Decorated Metal-Organic Frameworks for Enhanced Photodynamic Therapy. *ACS Nano* **2018**, *12*, 651–661.

(25) Zhang, M.; Pu, Z. J.; Chen, X. L.; Gong, X. L.; Zhu, A. X.; Yuan, L. M. Chiral recognition of a 3D chiral nanoporous metal-organic framework. *Chem. Commun.* **2013**, *49*, 5201–5203.

(26) Song, F. J.; Wang, C.; Lin, W. B. A chiral metal-organic framework for sequential asymmetric catalysis. *Chem. Commun.* 2011, 47, 8256–8258.

(27) Xie, S. M.; Zhang, Z. J.; Wang, Z. Y.; Yuan, L. M. Chiral Metal-Organic Frameworks for High-Resolution Gas Chromatographic Separations. *J. Am. Chem. Soc.* **2011**, *133*, 11892–11895.

(28) Guan, X. Y.; Chen, F. Q.; Fang, Q. R.; Qiu, S. L. Design and applications of three dimensional covalent organic frameworks. *Chem. Soc. Rev.* **2020**, *49*, 1357–1384.

(29) Zhu, L. J.; Zhang, Y. B. Crystallization of Covalent Organic Frameworks for Gas Storage Applications. *Molecules* **201**7, *22*, No. 1149.

(30) Guo, L. P.; Jin, S. B. Stable Covalent Organic Frameworks for Photochemical Applications. *ChemPhotoChem* **2019**, *3*, 973–983.

(31) Haldar, S.; Kushwaha, R.; Maity, R.; Vaidhyanathan, R. Pyridine-Rich Covalent Organic Frameworks as High-Performance Solid-State Supercapacitors. *ACS Mater. Lett.* **2019**, *1*, 490–497.

(32) Kushwaha, R.; Haldar, S.; Shekhar, P.; Krishnan, A.; Saha, J.; Hui, P.; Vinod, C. P.; Subramaniam, C.; Vaidhyanathan, R. Exceptional Capacitance Enhancement of a Non-Conducting COF through Potential-Driven Chemical Modulation by Redox Electrolyte. *Adv. Energy Mater.* **2021**, *11*, No. 2003626.

(33) Zhang, H.; Dai, R.; Zhu, S.; Zhou, L.; Xu, Q.; Min, Y. Bimetallic nitride modified separator constructs internal electric field for high-performance lithium-sulfur battery. *Chem. Eng. J.* **2022**, *429*, No. 132454.

(34) Mullangi, D.; Dhavale, V.; Shalini, S.; Nandi, S.; Collins, S.; Woo, T.; Kurungot, S.; Vaidhyanathan, R. Low-Overpotential Electrocatalytic Water Splitting with Noble-Metal-Free Nanoparticles Supported in a sp<sup>3</sup> N-Rich Flexible COF. *Adv. Energy Mater.* **2016**, *6*, No. 1600110.

(35) Wang, Z.; Reddy, C. B.; Zhou, X.; Ibrahim, J. J.; Yang, Y. Phosphine-Built-in Porous Organic Cage for Stabilization and Boosting the Catalytic Performance of Palladium Nanoparticles in Cross-Coupling of Aryl Halides. *ACS Appl. Mater. Interfaces* **2020**, *12*, 53141–53149.

(36) Mullangi, D.; Nandi, S.; Shalini, S.; Sreedhala, S.; Vinod, C. P.; Vaidhyanathan, R. Pd loaded amphiphilic COF as catalyst for multifold Heck reactions, C-C couplings and CO oxidation. *Sci. Rep.* **2015**, *5*, No. 10876.

(37) Nandi, S.; Singh, S. K.; Mullangi, D.; Illathvalappil, R.; George, L.; Vinod, C. P.; Kurungot, S.; Vaidhyanathan, R. Low Band Gap Benzimidazole COF Supported Ni<sub>3</sub>N as Highly Active OER Catalyst. *Adv. Energy Mater.* **2016**, *6*, No. 1601189.

(38) Dursun, S.; Yavuz, E.; Cetinkaya, Z. In situ reduction of chloroauric acid (HAuCl<sub>4</sub>) for generation of catalytic Au nanoparticle embedded triazine based covalent organic polymer networks. *RSC* Adv. **2019**, *9*, 38538–38546.

(39) Tao, R.; Shen, X. R.; Hu, Y. M.; Kang, K.; Zheng, Y. Q.; Luo, S. C.; Yang, S. Y.; Li, W. L.; Lu, S. L.; Jin, Y. H.; Qiu, L.; Zhang, W. Phosphine-Based Covalent Organic Framework for the Controlled Synthesis of Broad-Scope Ultrafine Nanoparticles. *Small* **2020**, *16*, No. 1906005.

(40) Gasnier, A.; Amica, G.; Juan, J.; Troiani, H.; Gennari, F. C. N-Doped Graphene-Rich Aerogels Decorated with Nickel and Cobalt Nanoparticles: Effect on Hydrogen Storage Properties of Nanoconfined LiBH<sub>4</sub>. *J. Phys. Chem. C* **2020**, *124*, 115–125.

(41) Zhang, C. H.; Guo, X. X.; Yuan, Q. C.; Zhang, R. L.; Chang, Q.; Li, K.; Xiao, B.; Liu, S. Y.; Ma, C. P.; Liu, X.; Xu, Y. Q.; Wen, X. D.; Yang, Y.; Li, Y. W. Ethyne-Reducing Metal-Organic Frameworks to Control Fabrications of Core/shell Nanoparticles as Catalysts. *ACS Catal.* **2018**, *8*, 7120–7130.

(42) Xu, Y.; Shan, W. X.; Liang, X.; Gao, X. H.; Li, W. Z.; Li, H. M.; Qiu, X. Q. Cobalt Nanoparticles Encapsulated in Nitrogen-Doped Carbon Shells: Efficient and Stable Catalyst for Nitrobenzene Reduction. *Ind. Eng. Chem. Res.* **2020**, *59*, 4367–4376.

(43) Mondal, A.; Adhikary, B.; Mukherjee, D. Room-temperature synthesis of air stable cobalt nanoparticles and their use as catalyst for methyl orange dye degradation. *Colloids Surf.*, A **2015**, 482, 248–257.

(44) Kushwaha, R.; Kaleeswaran, D.; Haldar, S.; Chakraborty, D.; Mullangi, D.; Borah, A.; Vinod, C. P.; Murugavel, R.; Vaidhyanathan, R. Nanoporous Covalent Organic Framework Embedded with Fe/ Fe<sub>3</sub>O<sub>4</sub> Nanoparticles as Air-Stable Low-Density Nanomagnets. *ACS Appl. Nano Mater.* **2020**, *3*, 9088–9096.

(45) Liang, X.; Zhao, L. Room-temperature synthesis of air-stable cobalt nanoparticles and their highly efficient adsorption ability for Congo red. RSC Adv. **2012**, *2*, 5485–5487.

(46) Hudson, R.; Feng, Y. T.; Varma, R. S.; Moores, A. Bare magnetic nanoparticles: sustainable synthesis and applications in catalytic organic transformations. *Green Chem.* **2014**, *16*, 4493–4505. (47) Chung, K. T. The Significance of Azo-Reduction in the Mutagenesis and Carcinogenesis of Azo Dyes. *Mutat. Res.* **1983**, *114*.

Mutagenesis and Carcinogenesis of Azo Dyes. *Mutat. Res.* **1983**, *114*, 269–281.

(48) He, S. J.; Yin, B.; Niu, H. Y.; Cai, Y. Q. Targeted synthesis of visible-light-driven covalent organic framework photocatalyst via molecular design and precise construction. *Appl. Catal., B* **2018**, 239, 147–153.

www.acsanm.org

(49) Georgiou, D.; Melidis, P.; Aivasidis, A.; Gimouhopoulos, K. Degradation of azo-reactive dyes by ultraviolet radiation in the presence of hydrogen peroxide. *Dyes Pigm.* **2002**, *52*, 69–78.

(50) Rosu, M. C.; Coros, M.; Pogacean, F.; Magerusan, L.; Socaci, C.; Turza, A.; Pruneanu, S. Azo dyes degradation using  $TiO_2$ -Pt/graphene oxide and  $TiO_2$ -Pt/reduced graphene oxide photocatalysts under UV and natural sunlight irradiation. *Solid State Sci.* **2017**, *70*, 13–20.

(51) Liu, W. H.; Hu, Q. Z.; Mo, F.; Hu, J. J.; Feng, Y.; Tang, H. W.; Ye, H. N.; Miao, S. D. Photo-catalytic degradation of methyl orange under visible light by MoS<sub>2</sub> nanosheets produced by H<sub>2</sub>SiO<sub>3</sub> exfoliation. J. Mol. Catal. A **2014**, 395, 322–328.

(52) Zhang, X.; Wang, L. J.; Han, Z.; Meng, X.; Wang, H. N.; Zhou, Z. Y.; Su, Z. M. Degradation of azo dyes under visible light with stable MOF based on tetrastyrene imidazole ligand. *Dalton Trans.* **2020**, *49*, 4352–4357.

(53) Dutta, A.; Dutta, R. K. Fluorescence behavior of cis-methyl orange stabilized in cationic premicelles. *Spectrochim. Acta, Part A* **2014**, *126*, 270–279.

(54) Mullangi, D.; Chakraborty, D.; Pradeep, A.; Koshti, V.; Vinod, C. P.; Panja, S.; Nair, S.; Vaidhyanathan, R. Highly Stable COF-Supported  $Co/Co(OH)_2$  Nanoparticles Heterogeneous Catalyst for Reduction of Nitrile/Nitro Compounds under Mild Conditions. *Small* **2018**, *14*, No. 1801233.

(55) Sing, K. S. W. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (Recommendations 1984). *Pure Appl. Chem.* **1985**, *57*, 603–619.

(56) Thommes, M.; Kaneko, K.; Neimark, A. V.; Olivier, J. P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K. S. W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069.

(57) Barrett, E. P.; Joyner, L. G.; Halenda, P. P. The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J. Am. Chem. Soc.* **1951**, *73*, 373–380.

(58) Thomson, W. LX. On the equilibrium of vapour at a curved surface of liquid. *Lond., Edinb. Dublin Philos. Mag. J. Sci.* 1871, 42, 448–452.

(59) Zhang, Y.; Lam, F. L.-Y.; Yan, Z.-F.; Hu, X. Review of Kelvin's Equation and Its Modification in Characterization of Mesoporous Materials. *Chin. J. Chem. Phys.* **2006**, *19*, 102–108.

(60) Pramanik, G.; Humpolickova, J.; Valenta, J.; Kundu, P.; Bals, S.; Bour, P.; Dracinsky, M.; Cigler, P. Gold nanoclusters with bright nearinfrared photoluminescence. *Nanoscale* **2018**, *10*, 3792–3798.

(61) Davey, W. P. Precision Measurements of the Lattice Constants of Twelve Common Metals. *Phys. Rev.* **1925**, *25*, 753–761.

(62) Nabika, H.; Mizuhata, M.; Kajinami, A.; Deki, S.; Akamatsu, K. Preparation and characterization of Au/Co nano-alloys. *J. Electroanal. Chem.* **2003**, *559*, 99–102.

(63) Lu, D.-l.; Domen, K.; Tanaka, K.-i. Electrodeposited Au–Fe, Au–Ni, and Au–Co Alloy Nanoparticles from Aqueous Electrolytes. *Langmuir* **2002**, *18*, 3226–3232.

(64) Qumar, U.; Ikram, M.; Imran, M.; Haider, A.; Ul-Hamid, A.; Haider, J.; Riaz, K. N.; Ali, S. Synergistic effect of Bi-doped exfoliated MoS<sub>2</sub> nanosheets on their bactericidal and dye degradation potential. *Dalton Trans.* **2020**, *49*, 5362–5377.

(65) Lan, L. D.; Liu, F.; Dan, Y.; Jiang, L. Facile fabrication of triphenylamine-based conjugated porous polymers and their application in organic degradation under visible light. *New J. Chem.* **2020**, *44*, 2986–2995.

(66) Yi, X. H.; Wang, F. X.; Du, X. D.; Fu, H. F.; Wang, C. C. Highly efficient photocatalytic Cr(VI) reduction and organic pollutants degradation of two new bifunctional 2D Cd/Co-based MOFs. *Polyhedron* **2018**, *152*, 216–224.

(67) Lv, H. Z.; Zhao, X. L.; Niu, H. Y.; He, S. J.; Tang, Z.; Wu, F. C.; Giesy, J. P. Ball milling synthesis of covalent organic framework as a

highly active photocatalyst for degradation of organic contaminants. *J. Hazard. Mater.* **2019**, *369*, 494–502.

(68) Lin, Y. F.; Wan, H.; Chen, F. S.; Liu, X. H.; Ma, R. Z.; Sasaki, T. Two-dimensional porous cuprous oxide nanoplatelets derived from metal-organic frameworks (MOFs) for efficient photocatalytic dye degradation under visible light. *Dalton Trans.* **2018**, *47*, 7694–7700.

(69) Pachfule, P.; Kandambeth, S.; Diaz, D. D.; Banerjee, R. Highly stable covalent organic framework-Au nanoparticles hybrids for enhanced activity for nitrophenol reduction. *Chem. Commun.* **2014**, *50*, 3169–3172.

(70) Bao, F.; Li, J.-F.; Ren, B.; Gu, R.-A.; Tian, Z.-Q.; et al. Synthesis and Characterization of Au@Co and Au@Ni Core–Shell Nanoparticles and Their Applications in Surface-Enhanced Raman Spectroscopy. J. Phys. Chem. C 2008, 112, 345–350.

(71) Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. A Practical Beginner's Guide to Cyclic Voltammetry. *J. Chem. Educ.* **2018**, *95*, 197–206.

(72) Choudhary, Y. S.; Jothi, L.; Nageswaran, G. Electrochemical Characterization. In *Spectroscopic Methods for Nanomaterials Characterization*; Thomas, S.; Thomas, R.; Zachariah, A. K.; Mishra, R. K., Eds.; Elsevier, 2017; Chapter 2, pp 19–54.

(73) Gotti, G.; Fajerwerg, K.; Evrard, D.; Gros, P. Electrodeposited gold nanoparticles on glassy carbon: Correlation between nanoparticles characteristics and oxygen reduction kinetics in neutral media. *Electrochim. Acta* **2014**, *128*, 412–419.

(74) Zhao, G.; Liu, G. Electrochemical Deposition of Gold Nanoparticles on Reduced Graphene Oxide by Fast Scan Cyclic Voltammetry for the Sensitive Determination of As(III). *Nanomaterials* **2019**, *9*, No. 41.

(75) Huang, X. H.; El-Sayed, M. A. Gold nanoparticles: Optical properties and implementations in cancer diagnosis and photothermal therapy. *J. Adv. Res.* **2010**, *1*, 13–28.

(76) Gzara, L.; Rehan, Z. A.; Khan, S. B.; Alamry, K. A.; Albeirutty, M. H.; El-Shahawi, M. S.; Rashid, M. I.; Figoli, A.; Drioli, E.; Asiri, A. M. Preparation and characterization of PES-cobalt nanocomposite membranes with enhanced anti-fouling properties and performances. *J. Taiwan Inst. Chem. Eng.* **2016**, *65*, 405–419.

(77) Makuła, P.; Pacia, M.; Macyk, W. How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV-Vis Spectra. *J. Phys. Chem. Lett.* **2018**, *9*, 6814–6817.

(78) Jubu, P. R.; Yam, F. K.; Igba, V. M.; Beh, K. P. Tauc-plot scale and extrapolation effect on bandgap estimation from UV–vis-NIR data - A case study of beta- $Ga_2O_3$ . J. Solid State Chem. 2020, 290, No. 121576.