

Research Article

Synthesis of CuO/Co₃O₄ Coaxial Heterostructures for Efficient and Recycling Photodegradation

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Received 16 September 2015; Revised 2 November 2015; Accepted 4 November 2015

Academic Editor: Wanjun Wang

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The highly efficient CuO/Co₃O₄ composite photocatalyst with different morphologies has been synthesized directly on Cu wire mesh by controlling the composition of cobalt-containing solid precursors via a simple hydrothermal method. The structure morphology and composition of the composite photocatalyst have been characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and UV-visible diffuse reflectance spectra. The photocatalytic result shows that the CuO/Co₃O₄ coaxial heterostructure is easy to recycle and exhibit enhanced photodegradation activity for methylene blue compared to single CuO nanorod arrays under full spectrum solar light irradiation. The enhanced photocatalytic efficiency of the composite could be ascribed to the synergistic effect of CuO and Co₃O₄. This study provides a general and effective method in the fabrication of 1D composition NRs with sound heterojunctions that show enhancement of photocatalytic performance and facility of recycling.

1. Introduction

Organic dyes, which are widely used in various industrial processes, form an integral part of industrial wastewater. Photocatalytic degradation of organic pollutants by semiconductor photocatalysts is promising for environmental purification and energy conversion [1–5], because it has been successfully employed to treat a wide range of toxic and nondegradable organic pollutants into readily biodegradable compounds in the wastewater without involving complex technologies [6–10].

Nevertheless, most of the widely used photocatalysts have two main limitations: one is the low solar energy conversion efficiency due to their wide band gap and the high recombination ratio of photoinduced electron-hole pairs, and the other is the difficulties of the catalysts' recycling. Therefore, seeking highly active photocatalysts which are easy to recycle is still an intensifying endeavor worldwide. One-dimensional (1D) nanostructures including nanorods (NRs), nanowires (NWs), nanotubes (NTs), and nanofibers (NFs) have drawn particular attention because of their high specific surface area and facility of electronic transmission [11, 12].

Therefore, many oxides with 1D nanostructures have been widely used as catalysts in photocatalytic reactions. However, photocatalysis, in general, is blamed for the low quantum yields caused by the electron/hole recombination. For further improvement of photocatalytic activity, the p-n, n-n, and p-p junctions formed in combination with both p-type and n-type semiconductors can effectively reduce the recombination rate of photogenerated electro/hole pairs, which subsequently enhances the photocatalytic activity [13, 14]. 1D nanowire (NW) heterostructures grown directly on conductive substrate are of great interest because of their large surface areas, efficient electron transfer, fast ion transport, easy electrolyte access to electrode, and good strain accommodation [15–18].

CuO, as a p-type semiconductor with a narrow band gap (1.2 eV in bulk), is one of the most prominent catalysts and is extensively used in environmental catalysis. Spinel cobalt tetroxide (Co₃O₄) is a compound of CoO and Co₂O₃ with rich oxygen content and thus also exhibits p-type semiconducting properties. In this study, we presynthesized CuO NRs array grown directly on Cu wire mesh via thermal oxidation and the synthesis of Co₃O₄ nanostructures with

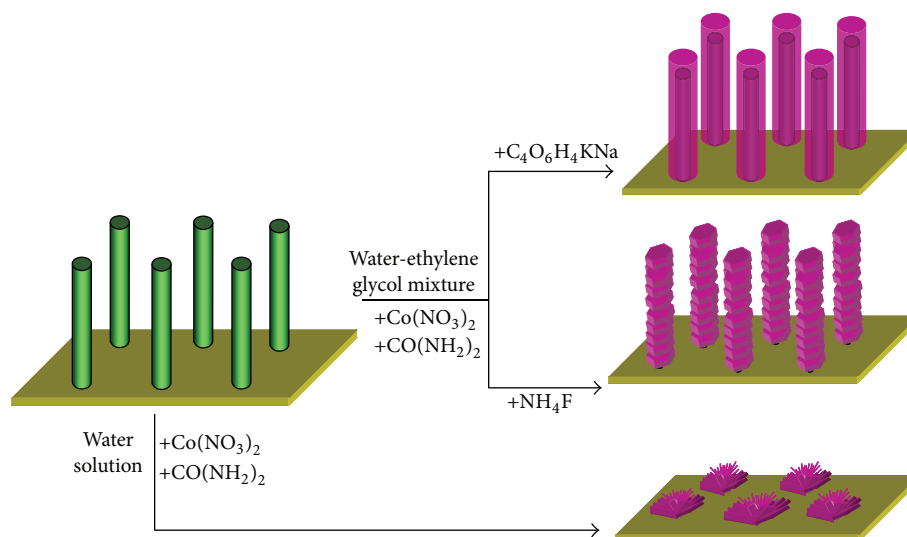


FIGURE 1: Schematic illustration of different morphologies of CuO/Co₃O₄ composites.

different morphologies by simple and effective hydrothermal method at relatively low temperature on CuO NRs arrays. These hybrid nanostructures were aligned on Cu substrates, which can directly serve as a physical support of these structures. Thus, the photocatalysts can be easily recycled after photocatalytic reactions. Compared with the single CuO NRs and Co₃O₄ nanoflowers, the composite exhibits a potential synergistic effect with remarkably enhanced photocatalytic performances in terms of MB degradation.

2. Experimental

2.1. Sample Preparation

2.1.1. Growth of CuO NRs. All chemicals (purity of 99.9%) used in this research were of analytical purity and used without further purification. CuO NR arrays were synthesized on copper mesh using a simple and low cost thermal oxidation method as reported before [19–21]. First, small pieces (9 cm²) of Cu mesh were cut and cleaned by acetone, ethanol, and water, 5 minutes in each, consecutively and finally rinsed with DI water and dried with air blowing. Then, the Cu mesh was immediately transferred into an open furnace and annealed under air at 500°C for 2 hours. After cooling down to room temperature, a dense array of copper oxide NRs was obtained on copper mesh.

2.1.2. Synthesis of Co₃O₄/CuO Composite. CuO/Co₃O₄ composite was produced by a hydrothermal growth method. CuO/Co₃O₄ coaxial heterostructures: 0.07 M cobaltous nitrate (Co(NO₃)₂·6H₂O) was dissolved in 30 mL mixture solution of ethylene glycol and water (15 mL:15 mL). 0.04 M Seignette salt (C₄O₆H₄KNa) and 0.36 M urea (CO(NH₂)₂) were introduced in the solution above subsequently. CuO/Co₃O₄ nanosheets: 0.07 M cobaltous nitrate (Co(NO₃)₂·6H₂O) was dissolved in 30 mL mixture solution of ethylene glycol and water (15 mL:15 mL). 0.14 M

ammonium fluoride (NH₄F) and 0.36 M urea (CO(NH₂)₂) were introduced in the solution above subsequently. Co₃O₄ nanoflowers: 0.07 M cobaltous nitrate (Co(NO₃)₂·6H₂O) and 0.36 M urea (CO(NH₂)₂) were dissolved in 30 mL deionized water. The solutions were then transferred to Teflon-lined stainless steel autoclave and the copper mesh with CuO NRs was immersed in this solution. The autoclave was maintained at 90°C for 5 hours. After natural cooling, the copper meshes with CuO NRs were removed from the autoclave and washed multiple times with distilled water and then dried in air. Subsequently, the as-synthesized Co₃O₄/CuO composites were calcined at 350°C for 2 hours. There were three kinds of CuO/Co₃O₄ composites that were synthesized in the hydrothermal growth process as shown in Figure 1.

2.2. Sample Characterization. The surface morphology and structure of samples were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi S-4800), X-ray diffraction (XRD, RIGAKU/DMAX), and transmission electron microscopy (TEM, Philips Tecnai G2 F20). Surface chemical analysis of CuO/Co₃O₄ coaxial heterostructures was performed by X-ray photoelectron spectroscopy (XPS) using a PHL1600ESCA instrument equipped with a monochromatic Mg Ka X-ray source ($E = 1253.6$ eV) operating at 250 W. The Raman spectra were collected by using DXR Microscope (Thermo Electron Corporation). Room temperature photoluminescence (PL) spectra were recorded using Jobin Yvon Fluorolog-3-21 spectrofluorometer equipped with Xe lamp (excitation wavelength = 325 nm). Nitrogen adsorption isotherms of the CuO NRs and Co₃O₄/CuO composites were measured at 77 K using an autosorb iQ instrument (Quantachrome, USA). The total surface was calculated from the Brunauer-Emmett-Teller (BET) method and the pore size distribution data was calculated using the Barrett-Joyner-Halenda (BJH) method based on the adsorption and desorption data.

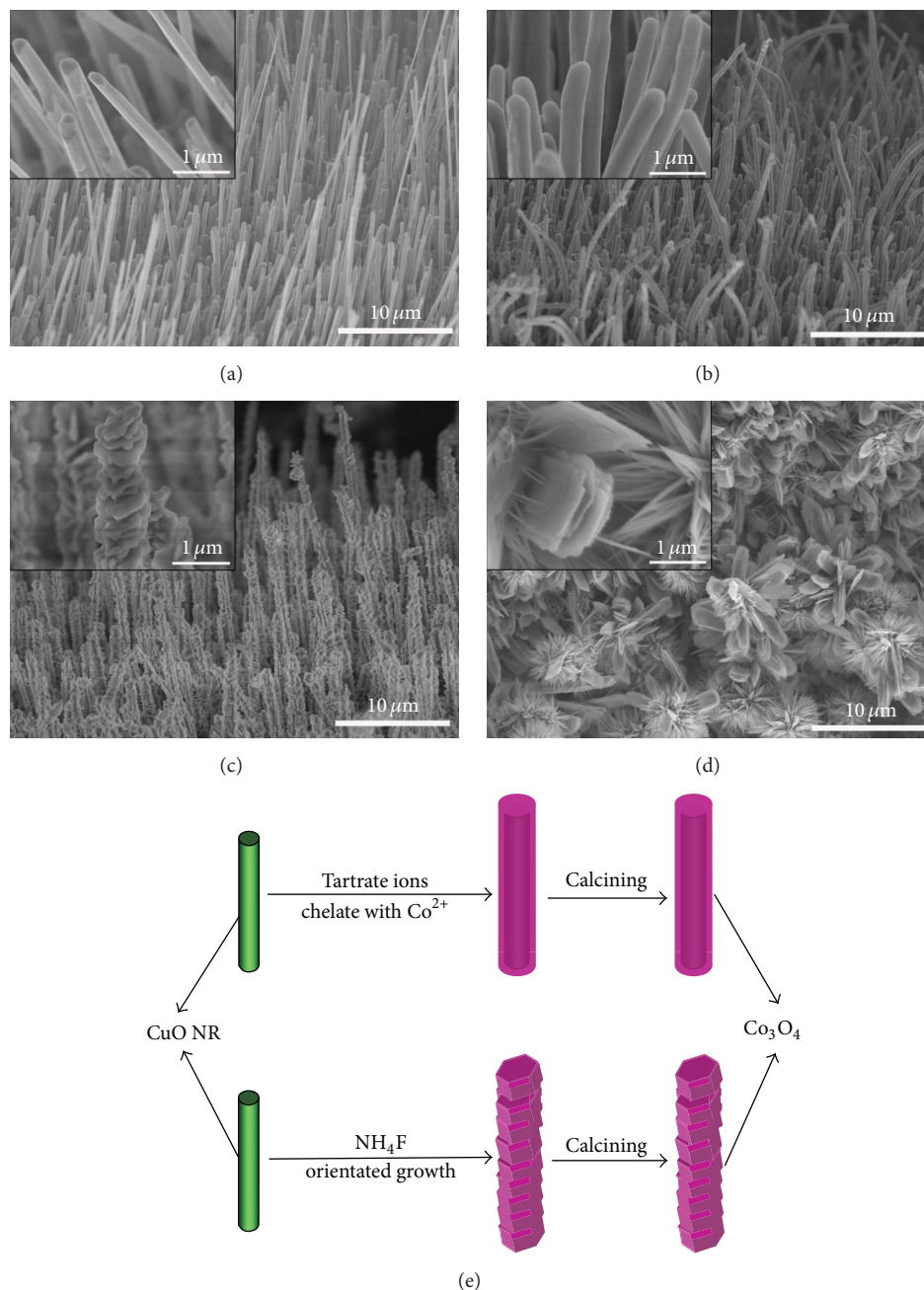


FIGURE 2: SEM images of (a) CuO NR arrays and different morphology of CuO/Co₃O₄ composite, (b) CuO/Co₃O₄ coaxial heterostructures, (c) CuO/Co₃O₄ nanosheets, and (d) Co₃O₄ nanoflowers. The insets show the high-magnification images of the corresponding samples. (e) Schematic diagram of the growth mechanism of the CuO/Co₃O₄ composite photocatalyst.

2.3. Photocatalytic Activity. Degradation of methylene blue was used to evaluate the photocatalytic activity of Co₃O₄/CuO composites. The methylene blue without photocatalysts was designed as the blank control experiment. A little piece (9 cm²) of copper mesh with CuO NRs and Co₃O₄/CuO composites was put in a 50 mL of aqueous solution with methylene blue concentration of 10 mg/L. In order to establish an adsorption/desorption equilibrium, the solution was stirred in the dark for 30 min. A 500 W Xenon lamp was served as the light source. The residual

concentration of methylene blue was evaluated by ultraviolet-visible (UV-Vis) spectrometry.

3. Results and Discussion

3.1. Morphology and Structure. The morphology of Co₃O₄/CuO composites was studied by SEM as shown in Figure 2. The Co₃O₄/CuO composites were developed on the basis of CuO NRs arrays, which are composed of vertically arranged CuO nanorods with the diameter of 100 nm and

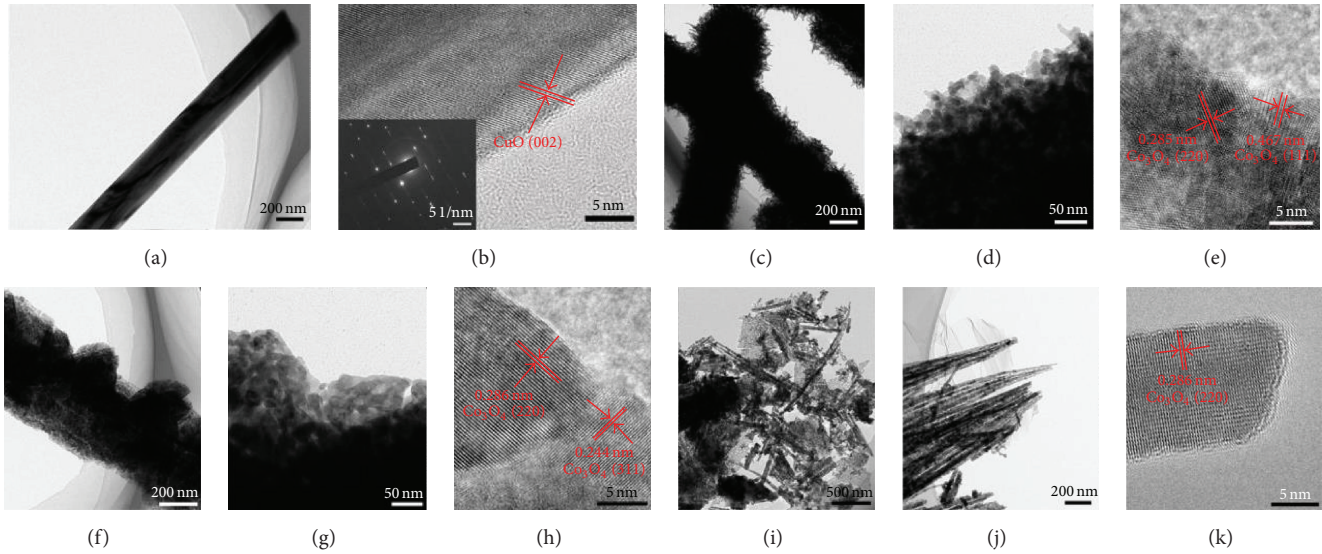


FIGURE 3: TEM/HRTEM images of CuO NR (a) and (b), (c–e) for CuO/Co₃O₄ coaxial heterostructures, (f–h) for CuO/Co₃O₄ nanosheets, and (i–k) for Co₃O₄ nanoflowers.

the length of 4–10 μm (Figure 2(a)). Figure 2(b) shows the SEM image of CuO/Co₃O₄ coaxial heterostructures after a typical hydrothermal treatment and annealing. It is observed that the CuO NRs were fully covered by Co₃O₄. We can conclude from the inset high-magnification image that the surfaces of the nanowires are smooth and the diameter of CuO/Co₃O₄ coaxial heterostructures is about 350 nm which is apparent larger than CuO NRs. The morphology of CuO/Co₃O₄ nanosheet is observed in Figure 2(c). Many pieces of nanosheets neatly covered CuO NRs and the diameter increases to about 400 nm. Figure 2(d) shows the microstructure of Co₃O₄ nanoflowers which are mainly composed of Co₃O₄ nanosheets and nanoneedles but the CuO NRs cannot be found.

The formation mechanism of Co₃O₄ nanostructures could be proposed as follows (Figure 2(e)). According to our previous work [22], there will be two kinds of cobalt-containing solid precursors: cobalt oxide acetate (C₈H₁₂Co₃O₉) and cobalt acetate hydrate (C₄H₆CoO₄·4H₂O). The Co₃O₄ grains were obtained by calcining the precursors which will react with oxygen to produce Co₃O₄, water, and carbon dioxide. Urea in these reactions served mainly as a source for the generation of both ammonia cations and hydroxyl anions. The tartrate ions which are generated by adding Seignette salt will chelate with divalent cobalt cations and enwrap the CuO NRs, thus forming CuO/Co₃O₄ coaxial heterostructures [22]. The wall-like, organized, hierarchical structures will be obtained with the presence of NH₄F which is used to provide ammonia cations [23]. The absence of ethylene glycol will make the CuO NRs broken, and the Co₃O₄ nanoflower will be grown separately on the Cu substrate; see Figure 2(d). Further experiments are needed to illustrate the specific growth mechanism.

TEM image of a single CuO NR is shown in Figure 3(a), exhibiting a diameter of 200 nm. The single-crystalline nature of CuO NR is exhibited by the high-resolution TEM (HRTEM) image (Figure 3(b)). The calculated lattice spacing is about 0.25 nm corresponding to (002) plane of monoclinic CuO, which is consistent with that reported elsewhere for the CuO NRs synthesized with the same method [24]. The CuO/Co₃O₄ coaxial heterostructures were dispersed in ethanol and analyzed by TEM, as shown in Figures 3(c)–3(e). The CuO/Co₃O₄ coaxial heterostructures are covered by numerous interconnected Co₃O₄ nanoparticles with an average diameter of 10 nm. In the crystallography, both (220) planes with a lattice spacing of 0.285 nm and (111) planes with a lattice spacing of 0.467 nm were observed.

The TEM image shown in Figures 3(f) and 3(g) indicates that the CuO/Co₃O₄ nanosheets are composed of numerous Co₃O₄ nanoparticles. The diameter of each Co₃O₄ nanoparticle is about 20 nm. The HRTEM was employed to further characterize the Co₃O₄ nanoparticle. As can be seen from Figure 3(h), the nanoparticles are linked together and the lattice fringes with a lattice spacing of about 0.286 and 0.244 nm correspond to (220) and (311) planes.

The panoramic morphology of the Co₃O₄ nanoflowers is shown in Figure 3(i). The Co₃O₄ nanoflowers disintegrated into layers and needles during the ultrasonic in alcohol. It can be clearly observed from Figure 3(j) that the Co₃O₄ nanoneedle consisted of many Co₃O₄ nanoparticles with a typical diameter of about 20 nm. Figure 3(k) shows an HRTEM image recorded near the edge of the Co₃O₄ nanoneedle. The fringe spacing of about 0.286 nm corresponds to the (220) plane.

The XRD pattern (Figure 4) reveals the crystal structure and phase purity of the CuO NR and CuO/Co₃O₄ coaxial heterostructures. The XRD pattern of CuO NRs (red line in

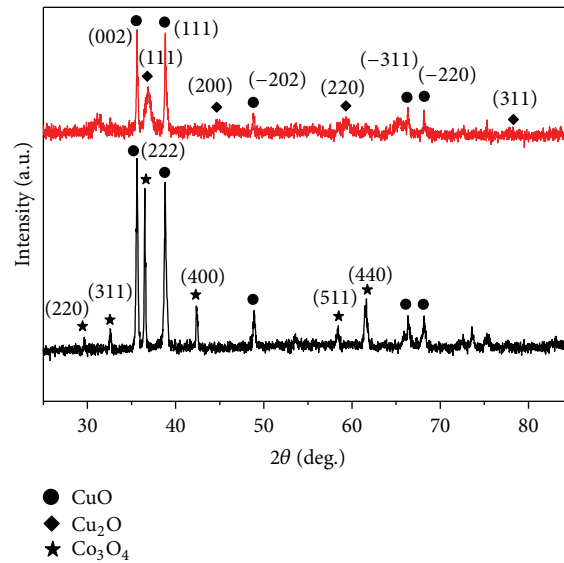


FIGURE 4: XRD patterns of as-prepared CuO NRs and CuO/Co₃O₄ coaxial heterostructures.

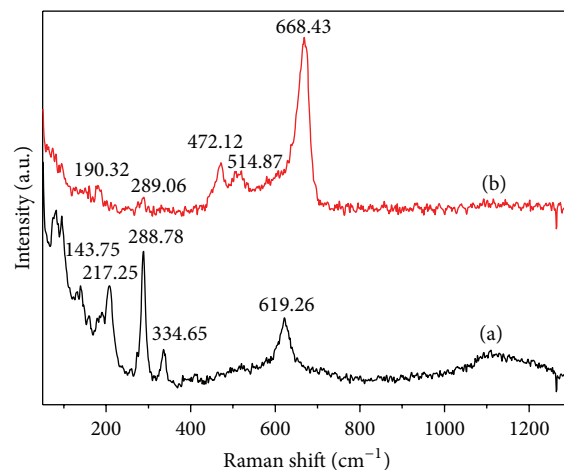


FIGURE 5: Raman spectra of CuO NRs (a) and CuO/Co₃O₄ coaxial heterostructures (b).

Figure 4) can be indexed to the monoclinic CuO (JCPDS number 43-1004) and the hexagonal phase of Cu₂O (JCPDS number 05-0667). All Co₃O₄ diffraction peaks are clearly seen in the black line and match very well with those of face-centered cubic Co₃O₄ phase of spinel cobalt oxide with a lattice constant of $a = 8.084 \text{ \AA}$ (JCPDS number 09-0418).

In addition, the formation of Co₃O₄ crystal was also confirmed by Raman spectra, as depicted in Figure 5. The wavenumbers were observed at around 289, 334, and 619 cm⁻¹, all of which belong to Ag and Bg modes of CuO [25–27]. Two weak characteristic peaks at about 143 and 217 cm⁻¹ for the Cu₂O structures are observed in the Raman spectrum [28, 29]. The band at approximately 191 cm⁻¹ was ascribed to the F_{2g} mode of Co₃O₄ [30, 31]. The bands with medium intensity located at approximately 472 and 514 cm⁻¹ were corresponding to the E_g and F_{2g} symmetry modes, respectively. The band positioned at 668 cm⁻¹ is close to the

11g peaks of Co₃O₄ [32, 33]. In fact, the Raman spectra of the CuO/Co₃O₄ coaxial heterostructures show a combination of the characteristic bands of CuO and Co₃O₄.

Figure 6 illustrates the further XPS measurements for the CuO NRs and CuO/Co₃O₄ coaxial heterostructures. The survey spectrum of CuO NRs shows only peaks corresponding to Cu and O, while the spectrum corresponding to the CuO/Co₃O₄ coaxial heterostructures shows the peaks corresponding to Cu, O, and Co. The Cu 2p spectrum of the CuO NRs was shown in the Figure 6(a). XPS analysis illustrates that copper oxides are present in two oxidation states, Cu²⁺ in cupric oxide (CuO) and Cu¹⁺ in cuprous oxide (Cu₂O). The band at a binding energy of 934.3, 942.4 eV, and 961.7 eV corresponds to Cu 2p_{1/2} and Cu 2p_{3/2} in CuO. The bands at 952.2, 932.3, and 963.2 eV correspond to Cu 2p_{1/2} and Cu 2p_{3/2} in Cu₂O [34, 35]. Figure 6(b) shows the spectrum of O of the CuO NRs. The present O 1s spectrum at 529.9 eV belongs to the CuO, and the O 1s peak at 531.7 eV

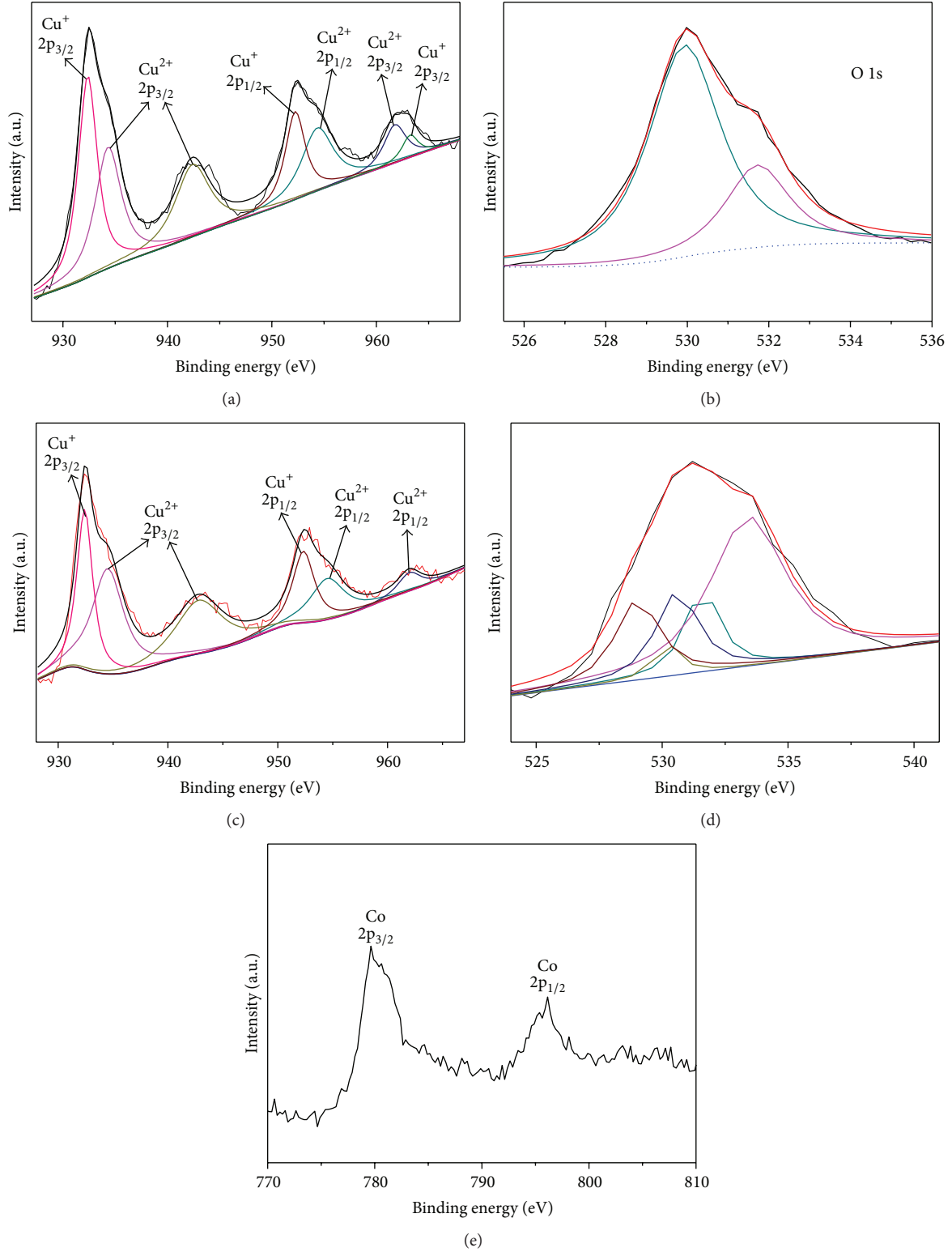


FIGURE 6: XPS spectra of (a) Cu 2p, (b) O 1s for CuO NRs, (c) Cu 2p, and (d) O 1s for CuO/Co₃O₄ coaxial heterostructures. (e) XPS spectra of Co 2p for CuO/Co₃O₄ coaxial heterostructures.

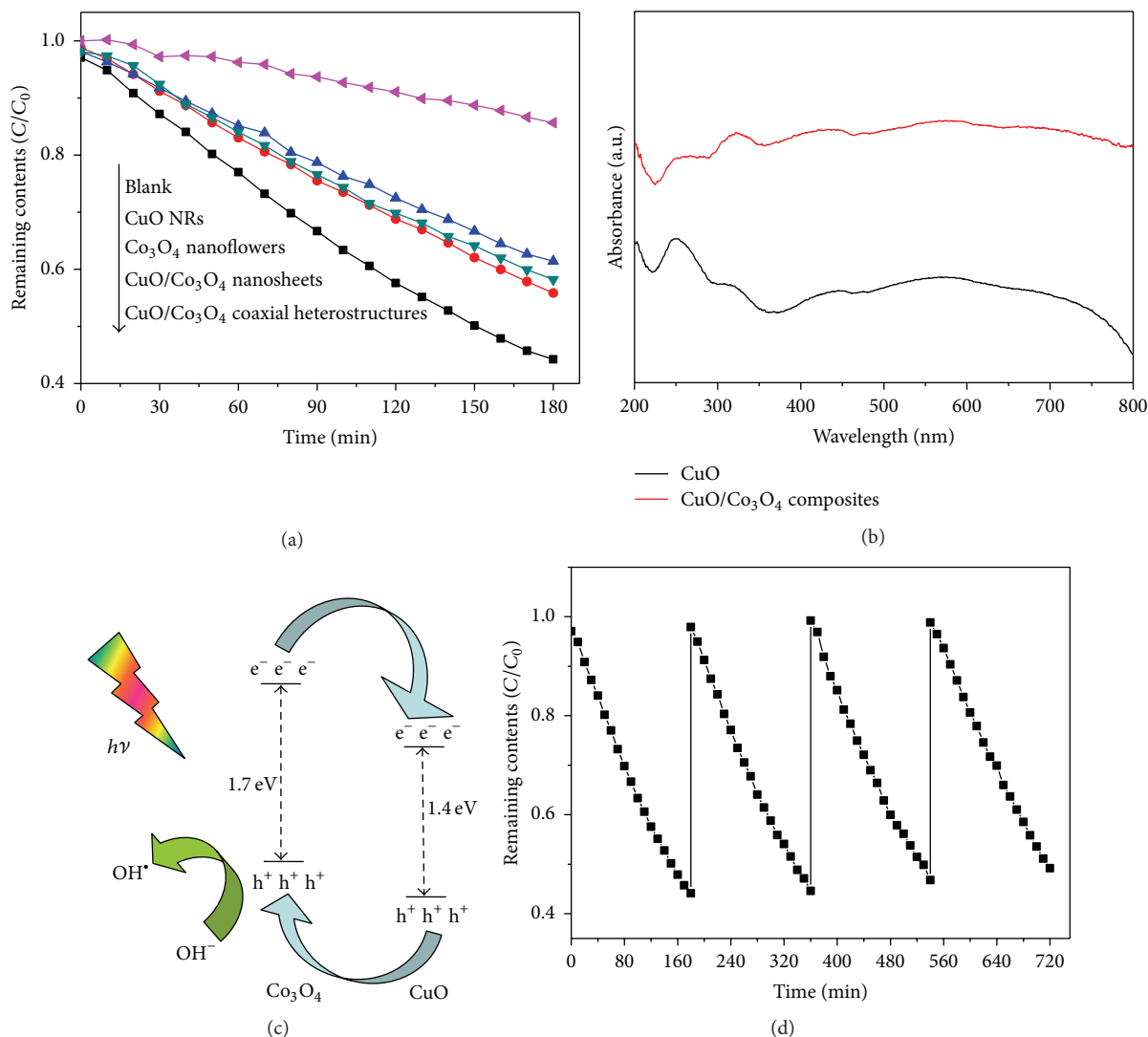


FIGURE 7: (a) Comparison of photocatalytic activities of bare CuO NRs and CuO/Co₃O₄ composites for the photocatalytic decolorization of MB in water. (b) UV-Vis absorption spectra of CuO NRs and CuO/Co₃O₄ coaxial heterostructures. (c) Proposed charge separation for CuO/Co₃O₄ coaxial heterostructures under light irradiation. (d) Cycling degradation curves for CuO/Co₃O₄ coaxial heterostructures.

is due to the absorption of the O atom in the Cu₂O [36]. The Cu 2p spectrum of the CuO/Co₃O₄ coaxial heterostructures (Figure 6(c)) is similar to that of the CuO NRs. O 1s spectra of CuO/Co₃O₄ coaxial heterostructures were deconvoluted into five peaks (Figure 6(d)). The peaks at 529.2 eV and 530.6 eV are attributed to lattice oxygen in CuO and Cu₂O. The peak located at 530.2 eV is attributed to the lattice oxygen in Co₃O₄ [22, 37]. The peaks which were found at 531.6 and 533.4 eV imply the existence of Co-OH and H₂O molecules [38, 39].

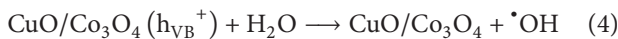
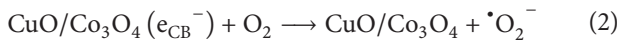
The Co 2p_{3/2} and Co 2p_{1/2} main peaks are located at 780.8 and 797.0 eV (shown in Figure 6(e)), which is approximately the same as the standard spectrum of Co₃O₄ [22, 40].

3.2. Photocatalysis. The photocatalytic degradation of MB dye on CuO/Co₃O₄ composites was carried out under full spectrum solar light irradiation. The blank test was carried

out to determine the contribution of photolysis of MB. Under the full spectrum solar light irradiation in a period of 180 minutes, self-degradation of MB is about 15% of the original organic MB dye under irradiation. Both CuO NRs and Co₃O₄ nanoflowers show apparent photocatalytic activity for the MB degradation, while limited improvements were observed by combining the two semiconductors in the sample of CuO/Co₃O₄ nanosheets. It is clear to see that large amount of Co₃O₄ grains is accumulated on CuO NRs, and the grain boundaries of Co₃O₄ particles would impede electronic transfers in CuO/Co₃O₄ nanosheets. Therefore, the photocatalytic performance of CuO/Co₃O₄ nanosheets was not improved dramatically. However, CuO/Co₃O₄ coaxial heterostructures exhibit highest photocatalytic activity among the four samples. After irradiation for 180 minutes, the CuO/Co₃O₄ coaxial heterostructures are able to degrade

about 56% of the original organic MB dye, while the degradation rate of CuO NRs is only about 40% (Figure 7(a)).

The enhanced photocatalytic performance of CuO/Co₃O₄ composite can mainly be explained by the electron-hole (e-h) charge separation which results in the synergism and coupling effect between the two semiconductors. The conduction band (CB) and valence band (VB) potentials of Co₃O₄ and CuO can be calculated based on the previous literatures [41, 42]. Semiconductors could use the irradiation light which corresponds to the band gap to make valence band electron excited to the conduction band while creating a hole in the valence band. Compared with CuO NRs, the CuO/Co₃O₄ coaxial heterostructures show stronger capability of light absorption (Figure 7(b)). There was a wide peak at around 250–400 nm which indicates that the CuO/Co₃O₄ coaxial heterostructures increase the coefficient of light utilization. The band structure of the heterostructures permits the transfer of electrons from CB of Co₃O₄ to CB of CuO and transfer of holes from VB of CuO to VB of Co₃O₄, as shown in Figure 7(c). Therefore, the recombination of electron-hole pairs will be hindered and the photocatalytic property would be improved. The holes transferred to cobalt oxides are trapped by H₂O and OH⁻ to further produce [•]OH and OH⁻ species. On the basis of this discussion, the proposed mechanisms in expression form are as follows:



The recycle experiments were conducted to evaluate the photostability of CuO/Co₃O₄ coaxial heterostructures. Compared with powder, copper substrate can make the catalyst easy to recycle. After each cycle, we washed the CuO/Co₃O₄ coaxial heterostructures with DI water and dried them in air and refreshed MB dye was added in the reactor. The degradation efficiencies at 180 minutes of CuO/Co₃O₄ coaxial heterostructures photocatalyst were in sequence of 44.15%, 44.59%, 46.79%, and 49.2% (Figure 7(d)). Results showed that the changing trend of degradation efficiency of the sample was almost the same as the fresh CuO/Co₃O₄ coaxial heterostructures. The recycle experiments indicate that the CuO/Co₃O₄ coaxial heterostructures are sufficiently stable and do not exhibit any significant loss after four terms of recycling; thus, it has potentially practical applications in treating contaminated water.

In order to examine the efficiency of charge carrier trapping, immigration, and transfer, as well as understanding the fate of e⁻/h⁺ pairs in semiconductor particles, the CuO

NRs and Co₃O₄/CuO composites were subjected to photoluminescence (PL) measurements. The PL spectra of the samples are shown in Figure 8(a). The PL spectrum of the CuO NRs shows a broad emission band centered at 440 nm, which indicated CuO emission [43–45]. By contrast, the PL spectrum of the Co₃O₄/CuO composites samples shows much lower intensity, which indicates that the recombination of electron-hole pairs is restrained. Based on the above results, we can conclude that the Co₃O₄/CuO composites could act as an active center for hindering the rapid recombination of photoinduced electron-hole pairs, thus enhancing the photocatalytic performance. Figures 8(b)–8(d) show the N₂ adsorption-desorption isotherm of the CuO NRs and Co₃O₄/CuO composites. The Brunauer-Emmett-Teller (BET) specific surface area calculated from N₂ isotherms at 77 K of the CuO NRs, CuO/Co₃O₄ coaxial heterostructures, and CuO/Co₃O₄ nanosheets is 6.386 m² g⁻¹, 3.526 m² g⁻¹, and 3.979 m² g⁻¹, respectively. In addition, the pore size distribution diagram (the inset) based on Barrett-Joyner-Halenda (BJH) method clearly indicates that pore is in the mesoporous region. The pore size distributions of the CuO NRs and CuO/Co₃O₄ coaxial heterostructures are around 4 nm. However, the pore size of the CuO/Co₃O₄ nanosheets increased to 9 nm. Notice that although the specific surface area of Co₃O₄/CuO composites is decreased compared to CuO NRs, the photocatalytic performance increases significantly. This indicates that the synergism and coupling effects between CuO and Co₃O₄ play more dominant role than specific surface area of the catalysts in improving photocatalytic properties. It is noteworthy that CuO/Co₃O₄ coaxial heterostructures and CuO/Co₃O₄ nanosheets possess almost same specific surface area but different pore size distributions. The smaller pore size of CuO/Co₃O₄ coaxial heterostructures may result in the higher photocatalytic activity than that of CuO/Co₃O₄ nanosheets.

4. Conclusions

In summary, novel CuO/Co₃O₄ coaxial heterostructures were prepared by hydrothermal methods. The morphology of composite strongly affects the efficiency of photodegradation. Compared with CuO NRs, CuO/Co₃O₄ nanosheets, and Co₃O₄ nanoflowers, the synthesized CuO/Co₃O₄ coaxial heterostructures catalysts showed high photocatalytic efficiency for the degradation of MB under full spectrum solar light irradiation. The overlapping of band structure plays an important role in charge transfer and separation for high photocatalytic activity. Because of its stability and being easy to recycle, the CuO/Co₃O₄ coaxial heterostructures are promising for practical application for water purification.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

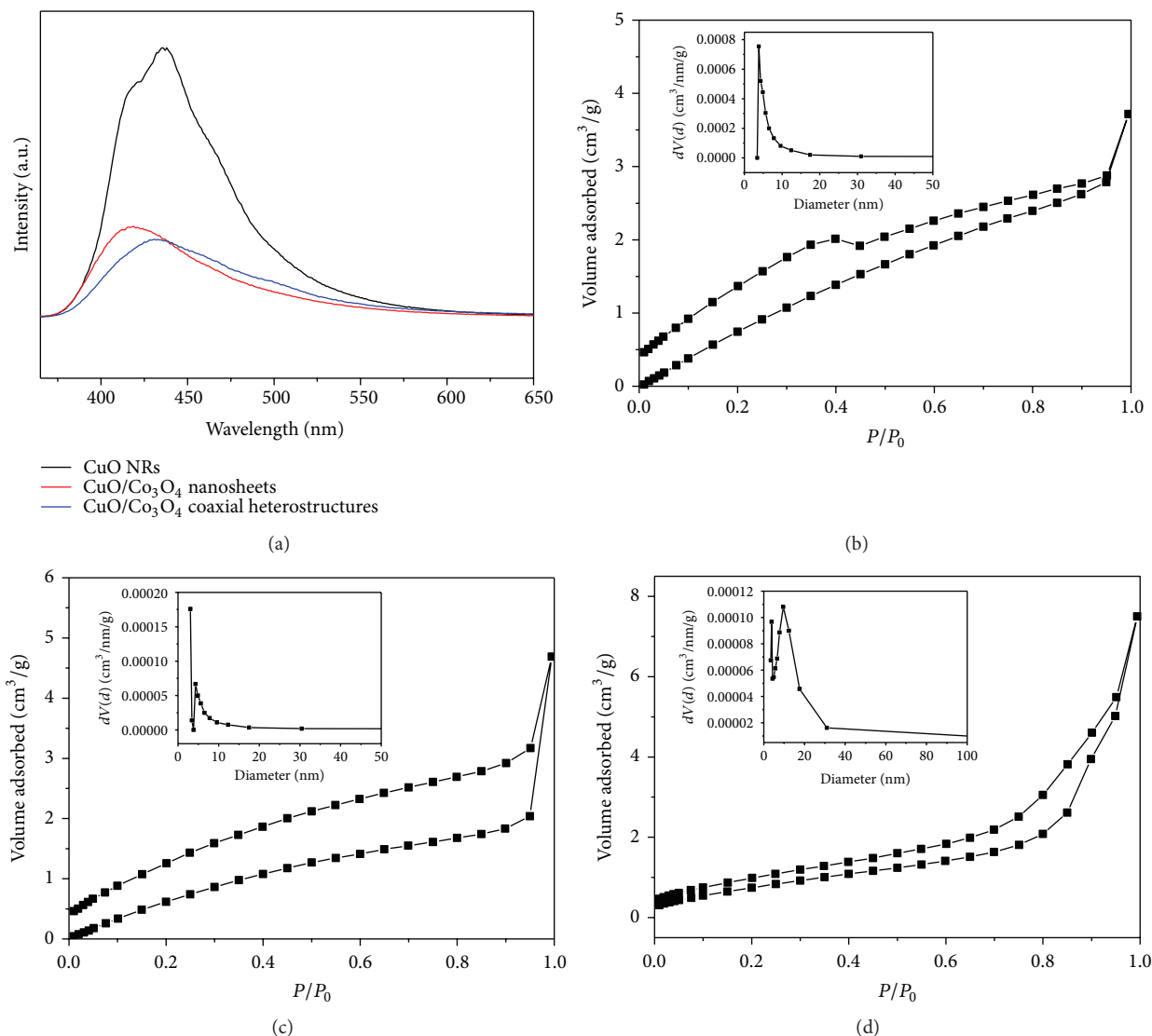


FIGURE 8: (a) The photoluminescence (PL) spectra of the CuO NRs, CuO/Co₃O₄ coaxial heterostructures, and CuO/Co₃O₄ nanosheets. Nitrogen adsorption-desorption isotherm for mesoporosity and BJH pore size distribution plot (inset): (b) CuO NRs; (c) CuO/Co₃O₄ coaxial heterostructures; (d) CuO/Co₃O₄ nanosheets.

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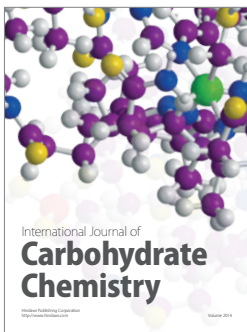
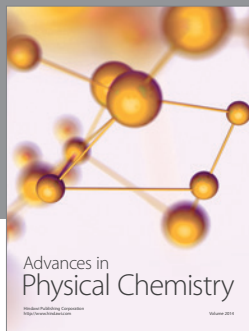
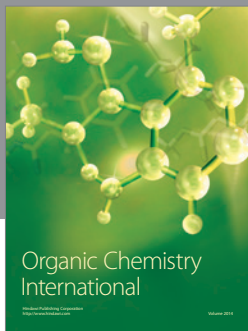
Financial supports by National Natural Science Foundation of China (51402211) and Natural Science Foundation of Tianjin (15JQJNC03600) are gratefully acknowledged.

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