Enhanced photoelectrochemical and photocatalytic behaviors of MFe$_2$O$_4$ (M = Ni, Co, Zn and Sr) modified TiO$_2$ nanorod arrays

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Modified TiO$_2$ nanomaterials are considered to be promising in energy conversion and ferrites modification may be one of the most efficient modifications. In this research, various ferrites, incorporated with various cations (MFe$_2$O$_4$, M = Ni, Co, Zn, and Sr), are utilized to modify the well aligned TiO$_2$ nanorod arrays (NRAs), which is synthesized by hydrothermal method. It is found that all MFe$_2$O$_4$/TiO$_2$ NRAs show obvious red shift into the visible light region compared with the TiO$_2$ NRAs. In particular, NiFe$_2$O$_4$ modification is demonstrated to be the best way to enhance the photoelectrochemical and photocatalytic activity of TiO$_2$ NRAs. Furthermore, the separation and transfer of charge carriers after MFe$_2$O$_4$ modification are clarified by electrochemical impedance spectroscopy measurements. Finally, the underlying mechanism accounting for the enhanced photocatalytic activity of MFe$_2$O$_4$/TiO$_2$ NRAs is proposed. Through comparison among different transition metals modified TiO$_2$ with the same synthesis process and under the same evaluating condition, this work may provide new insight in designing modified TiO$_2$ nanomaterials as visible light active photocatalysts.
magnetic property of transition metal ferrites. It is scarce on study of the visible responsiveness of MFeO$_4$ to increase utilization of solar energy as well as to enhance the photoelectrochemical and photocatalytic performance of TiO$_2$. 

ZnFeO$_4$, with a relatively small band-gap (ca. 1.9 eV), is the most frequently studied to modify TiO$_2$ in enhancing the photoelectrochemical capacity, but the ZnFeO$_4$/TiO$_2$ nanocomposite is more effective as a photocatalyst in the phenol degradation than pure TiO$_2$. However, the mechanism of the enhanced photocatalysis of the ZnFeO$_4$/TiO$_2$ composite is still needed to be further understood. Furthermore, the following researches proposed similar theory to explain the role of ZnFeO$_4$ in enhancing photocatalytic performance of TiO$_2$, that is, the adoption of ZnFeO$_4$ makes the ZnFeO$_4$/TiO$_2$ composite could use visible light, and the good match of band edges between ZnFeO$_4$ and TiO$_2$ is in favor of charge carriers separating effectively. Reports about other MFeO$_4$ modified TiO$_2$, such as NiFeO$_4$/TiO$_2$, Mn$_5$Zn$_3$FeO$_4$/TiO$_2$, MgFeO$_4$/TiO$_2$, and CuFeO$_2$/TiO$_2$ all show higher photocatalytic performance. It seems that MFeO$_4$ is such a promising material to improve the photocatalytic performance of TiO$_2$. However, comparison among the photoelectrochemical and photocatalytic performances of transition metal ferrites modified TiO$_2$ reported in the literatures is extremely difficult, because the experimental conditions were very different, such as catalysts synthesis process, light irradiation wavelength, reactor geometric configuration, catalyst loading and so on. Moreover, the origin and the crystalline structure of TiO$_2$, which strongly affect its electronic and photoactivity, are also different. Therefore, the same condition should be taken into consideration when assessing the real effect of transition metal ferrites on the photoactivity of TiO$_2$, such as using the same bare TiO$_2$ as the starting material, taking the same procedure to modify TiO$_2$ by transition metal ferrites, and finally evaluating their performances with unified standards. NiFeO$_4$, CoFeO$_4$, ZnFeO$_4$ and SrFeO$_4$ are four common transition metal ferrites which have been frequently studied. Among them, the two are not common in modifying TiO$_2$ to enhance its photoactivity, so we select the four as research objects, making a comparison between the common one (ZnFeO$_4$/TiO$_2$) and the uncommon ones (CoFeO$_4$, ZnFeO$_4$, and SrFeO$_4$ modified TiO$_2$).

In addition to incorporate other materials to modify TiO$_2$, structural design is another important method to enhance the photoactivity of TiO$_2$. One-dimensional (1D) nanostructure such as nanowire, nanotube, nanorod have attracted lots of attention due to the unique physical and chemical properties. 1D TiO$_2$ nanomaterials possess all the typical features of TiO$_2$ nanoparticles. Electron diffusion length (up to ~100 μm) can be prolonged by using vertically aligned 1D nanostructures and excited electrons can easily pass along 1D nanostructure to the transparent conducting oxide electrode, which facilitate charge transfer and promote charge separating efficiency. However, the relatively low specific surface area on a smooth surface of 1D nanostructures may decrease the absorption ability and a single crystal phase of 1D nanostructures may pose certain constraints on the photoelectrochemical performance. Fortunately, these disadvantages can be surmounted by introducing the second phase, i.e., doping metals/nonmetals or forming heterojunctions. Among 1D nanostructures, 1D nanorod arrays with large area can be easily obtained by hydrothermal method, which is facile, economic and controllable. Therefore, coupling the traits of one-dimensional TiO$_2$ nanorods (TiO$_2$ NRAs) and visible light responsive MFeO$_4$ nanoparticles seems to be a promising way to enhance the solar energy conversion efficiency of TiO$_2$.

To the best of our knowledge, there is few systematic research on the photoelectrochemical and photocatalytic capacity of various MFeO$_4$ modified one-dimensional TiO$_2$ NRAs so far. In this study, large area uniform TiO$_2$ NRAs were synthesized hydrothermally and ferrites containing various cations (MFeO$_4$, M = Ni, Co, Zn, and Sr) were utilized to modify the as-prepared TiO$_2$ NRAs. The morphology, crystalline structures and optical properties as well as photoelectrochemical performances of TiO$_2$, MFeO$_4$/TiO$_2$ NRAs were investigated. Moreover, the photocatalytic activities of the MFeO$_4$/TiO$_2$ NRAs were evaluated in the degradation of Cr(VI) aqueous solution under visible light irradiation. Finally, the underlying photocatalytic mechanism was discussed.

Results and Discussion

Figure 1(a) displays the XRD patterns collected from the TiO$_2$ NRAs and MFeO$_4$/TiO$_2$ NRAs. It can be seen that the TiO$_2$ NRAs and MFeO$_4$/TiO$_2$ NRAs all feature the characteristic peaks at 2θ = 25.8°, 37.9°, 48.0°, and 53.9°, indicative of rutile TiO$_2$ (PDF NO. 21–1276). Other peaks can be attributed to the diffraction of FTO substrate. There is no typical diffraction peaks of MFeO$_4$ after modification, which may be owing to the low content of MFeO$_4$. The content of MFeO$_4$ will be discussed in the following SEM characterization.

In order to further examine the phase composition of the samples and confirm the existence of MFeO$_4$, Raman spectroscopy was employed. As is shown clearly in Fig. 1(b), there are three Raman peaks at 241.4, 445.6 and 609.5 cm$^{-1}$ for all samples, which are assigned to the Raman active modes of rutile TiO$_2$. The peak at 117 cm$^{-1}$ is due to plasma emission of the Ar$^+$ laser.

In order to further confirm the existence of MFeO$_4$, XPS measurement was carried out. The XPS survey spectra are shown in Fig. 2(a). The peaks located at the binding energies of ca. 458–464 eV, 529–531 eV, 711–725 eV and 284–288 eV in all samples are ascribed to the Ti 2p, O 1s, Fe 2p, and C 1s, respectively. On the other hand, these MFeO$_4$/TiO$_2$ NRAs materials also show their characteristic peaks located between 850 and 875 eV (Ni 2p) for NiFeO$_4$/TiO$_2$ NRAs, 781 and 796 eV (Co 2p) for CoFeO$_4$/TiO$_2$ NRAs, 1021 and 1044 eV (Zn 2p) for ZnFeO$_4$/TiO$_2$ NRAs, and 134 eV (Sr 2p) for SrFeO$_4$/TiO$_2$ NRAs.

As is shown in Fig. 2(b), the Ni 2p peaks of NiFeO$_4$/TiO$_2$ NRAs consist of two characteristics of Ni 2p3/2 (855.72 eV) and Ni 2p1/2 (874.12 eV), indicative of the presence of Ni$^{2+}$. Similar to the Ni 2p peaks in NiFeO$_4$/TiO$_2$ NRAs, the Co 2p XPS spectra recorded from the CoFeO$_4$/TiO$_2$ NRAs sample, containing Co 2p3/2 (781.03 eV, Co$^{2+}$ in Tet-site) and Co 2p1/2 (796.67 eV, Co$^{3+}$ in Tet-site), indicate that Co$^{2+}$ exists in the CoFeO$_4$/TiO$_2$ NRAs according to the literature reports. For the ZnFeO$_4$/TiO$_2$ NRAs, the recorded Zn 2p XPS
spectra indicate that Zn$^{2+}$ exists in the ZnFe$_2$O$_4$/TiO$_2$ NRAs, which is also consistent with literature reports$^{34,35}$. Furthermore, the manganese valences were determined by the position of the multiplet splitting of Sr 2p peaks, the positions of Sr 2p3/2 and Sr 2p1/2 were all assigned to Sr$^{2+}$. As for high-resolution XPS spectra of Fe 2p in Fig. 2(d), one can see that the peaks at ca. 711.6 eV and ca. 724.9 eV can be attributed to Fe 2p3/2 and Fe 2p1/2 for Fe$^{3+}$, respectively, which reveals the oxidation state of Fe$^{3+}$ in the MFe$_2$O$_4$/TiO$_2$ heterostructure$^{33,36}$.

The high resolution XPS spectra of Ti 2p, O 1s, and C 1s are shown in Fig. 3. The Ti 2p spectra, as presented in Fig. 3(a), all show the main peak located at ca. 458.5 eV and ca. 464.2 eV, which can be attributed to Ti 2p3/2 and Ti 2p1/2 in TiO$_2$, respectively$^{37}$. It is clear that the O 1s spectra of these MFe$_2$O$_4$/TiO$_2$ NRAs samples can be deconvoluted into two components centered at ca. 529.8 eV and ca. 531.4 eV using two Gaussian curve fittings (Fig. 3(b)). The components at the lower and higher binding energy side can be assigned to the crystal lattice oxygen of TiO$_2$ and MFe$_2$O$_4$ and chemisorbed oxygen in a defective lattice site (i.e.-OH), respectively$^{32,38-41}$. It is suggested that the hydroxyl group can capture the photogenerated holes and form highly reactive hydroxyl free radicals, which plays an important role in enhancing photocatalytic activity$^{18}$. The high resolution XPS spectrum of C 1s is shown in Fig. 3(c). The primary peak located at ca. 284.6 eV is assigned to C–C/C–H bonds from adventitious carbon$^{42}$, while the peaks at ca. 286.2 eV and ca. 288.4 eV can be attributed to the formation of carbonate species, resulting mainly from CO$_2$ adsorption$^{38,43-45}$. Especially, the peak at 288.4 eV can be ascribed to the Ti–O–C structure in carbon doped TiO$_2$ by substituting some of the lattice titanium atoms$^{46-48}$. Interestingly, carbon doping is beneficial to light absorption capability as well as absorption of organic molecules to some extent$^{34,35}$.

The SEM images of the bare TiO$_2$ NRAs and MFe$_2$O$_4$/TiO$_2$ NRAs are shown in Fig. 4. It is noteworthy that, after MFe$_2$O$_4$ modification as shown in Fig. 4(c–f) from the top view images, the samples have no obvious changes in morphology compared with the bare TiO$_2$ NRAs in Fig. 4(a), which indicates that the deposited MFe$_2$O$_4$ nanocrystals are of extremely fine size. The vertically or slantingly aligned TiO$_2$ nanorods arrays, with diameter of 60–120 nm and length of 2.2 μm, are grown homogeneously on FTO substrate with rectangular cross section. In order to measure the content of MFe$_2$O$_4$ in MFe$_2$O$_4$/TiO$_2$ NRAs heterojunction, energy dispersive x-ray spectrum (EDS) analysis was carried out. The results, shown in Fig. 4(g–i), are obtained from collecting the EDS data in red square region of the MFe$_2$O$_4$/TiO$_2$ NRAs in Fig. 4(c–f), respectively. It is confirmed that Ni, Co, Zn and Sr are present in NiFe$_2$O$_4$, CoFe$_2$O$_4$, ZnFe$_2$O$_4$ and SrFe$_2$O$_4$ modified TiO$_2$ NRAs, respectively. Indeed, only a trace amount of Ni, Co, Zn and Sr can be observed in these samples.

Furthermore, structural characterizations of the MFe$_2$O$_4$ modified TiO$_2$ nanorods were investigated by TEM. Figure 5(a) shows the TEM image of the bare TiO$_2$ nanorod. Essentially, the diameter of the bare TiO$_2$ nanorod under TEM observation is consistent with the SEM result. It can be seen clearly that the bare TiO$_2$ nanorod is very
smooth. After MFe$_2$O$_4$ modification shown in Fig. 5(c), the nanorod surface becomes rough, and the ultrafine NiFe$_2$O$_4$ particles, with diameter of ca. 3–5 nm as shown in Fig. 5(d), are uniformly deposited on the nanorod. In addition, the high resolution HRTEM image gives lattice fringes of about 0.481 nm and 0.251 nm, corresponding to the d (111) and d (311) space of NiFe$_2$O$_4$, respectively. Analysis of TEM was also applied to CoFe$_2$O$_4$, ZnFe$_2$O$_4$ and SrFe$_2$O$_4$ modified TiO$_2$ NRAs (shown in Supplementary Fig. S1), and all show the same morphology, i.e., the smooth surface of TiO$_2$ nanorod become rough after MFe$_2$O$_4$ modification. The corresponding lattice fringes of CoFe$_2$O$_4$, ZnFe$_2$O$_4$ and SrFe$_2$O$_4$ are shown in Figure S1(b,d,f), respectively.

The optical absorption spectra of TiO$_2$ NRAs and MFe$_2$O$_4$/TiO$_2$ NRAs are shown in Fig. 6. All samples exhibit typical UV absorption ($\lambda < 380$ nm). It is noteworthy that, compared with bare TiO$_2$ NRAs, all MFe$_2$O$_4$/TiO$_2$ samples exhibit strong light absorption in a wide region from 380 nm to 900 nm, which can be attributed to the intrinsic band gap absorption of MFe$_2$O$_4$. However, unlike other pure TiO$_2$, tiny absorption of the as-prepared TiO$_2$ sample in the visible light range can be observed. There are two reasons accounting for this abnormal phenomenon, one is the scattering of light caused by the nanorod arrays, and the other is the impurity doping during the hydrothermal and sintering process$^{49-51}$. The absorption capacity of CoFe$_2$O$_4$/TiO$_2$ NRAs is the biggest, followed by ZnFe$_2$O$_4$, SrFe$_2$O$_4$ and NiFe$_2$O$_4$ modified TiO$_2$ NRAs sequentially. The corresponding band gaps are calculated from the plots of $E_g = 1240/\lambda$ by extrapolating the linear portion of absorbance to the wavelength

![Figure 2. (a) XPS survey spectra of MFe$_2$O$_4$/TiO$_2$ NRAs and high-resolution XPS spectra of (b) Ni 2p, (c) Co 2p, (d) Zn 2p, (e) Sr 2p and (f) Fe 2p.](image-url)
axis where absorbance is zero. As is shown in Fig. 6, the steep absorption edge of the bare TiO₂ NRAs locates at about 410 nm, corresponding to band gap \(E_g\) of about 3.02 eV. MFe₂O₄ modified TiO₂ NRAs samples all exhibit red-shift with smaller band gaps compared with bare TiO₂ NRAs, and the \(E_g\) is 1.84 eV, 1.63 eV, 1.81 eV and 1.53 eV for NiFe₂O₄/TiO₂ NRAs, ZnFe₂O₄/TiO₂ NRAs, SrFe₂O₄/TiO₂ NRAs, and CoFe₂O₄/TiO₂ NRAs, respectively.

To evaluate the effect of MFe₂O₄ modification on the photoelectrochemical properties of TiO₂ NRAs, the photocurrent intensity versus potential \(I-V\) and photocurrent density versus time \(I-T\) measurements of MFe₂O₄/TiO₂ NRAs were performed. The \(I-V\) characteristics of MFe₂O₄/TiO₂ NRAs are shown in Fig. 7(a). The photocurrent density in dark can be neglected for all samples. Under visible light irradiation, the photocurrent density of bare TiO₂ NRAs varies little with increase in bias potential, while the photocurrent density of MFe₂O₄/TiO₂ NRAs increases significantly at more positive bias potentials, except for CoFe₂O₄/TiO₂ NRAs with only a slight increase. For example, at bias potential of 0.4 V vs. Ag/AgCl, the photocurrent density of NiFe₂O₄, ZnFe₂O₄ and SrFe₂O₄ modified TiO₂ NRAs is 6.13, 3.31 and 2.81 μA/cm², respectively, while the photocurrent density of CoFe₂O₄/TiO₂ NRAs is only 0.95 μA/cm², which is far lower than that of other MFe₂O₄ modified samples, and only a little higher than that of the bare TiO₂ NRAs (0.46 μA/cm² at 0.4 V vs. Ag/AgCl). It is reported that the more negative open circuit potential \(Voc\) means better charge carrier separation and electron accumulation in semiconductor-semiconductor heterojunctions. After MFe₂O₄ modification, Voc for NiFe₂O₄/TiO₂ NRAs, ZnFe₂O₄/TiO₂ NRAs and SrFe₂O₄/TiO₂ NRAs is −0.323, −0.156 and −0.133 V, respectively, which becomes more negative than that of the bare TiO₂ NRAs (−0.121 V), except for CoFe₂O₄ modified one (−0.117 V). From the varying trend of Voc, one can see that MFe₂O₄/TiO₂ NRAs (M = Ni, Zn and Sr) heterjunction facilitates the separation and transfer of the charge carriers, while CoFe₂O₄/TiO₂ NRAs is not favourable for charge carriers separation. Figure 7(b) plots the \(I-T\) characteristics of the MFe₂O₄/TiO₂ NRAs. It is observed that all the samples exhibit a quick response to the on/off of the incident light, and the current density of MFe₂O₄ modified TiO₂ NRAs shows an enhancement compared with that of bare TiO₂ NRAs. NiFe₂O₄/TiO₂ NRAs displays the biggest photocurrent density of ca. 4.13 μA/cm², followed by ZnFe₂O₄, SrFe₂O₄ and CoFe₂O₄ modified ones, with 1.73, 1.68 and 1.01 μA/cm², respectively. The enhancement induced by CoFe₂O₄ modification is relatively low, only 0.4 μA/cm² higher than that of bare TiO₂ NRAs (0.61 μA/cm²). The changing trend of \(I-T\) result is consistent with the \(I-V\) characteristics of the MFe₂O₄/TiO₂ NRAs.

To investigate the photocatalytic capacity of the MFe₂O₄/TiO₂ NRAs, experiments were carried out for Cr(VI) photoreduction under visible light irradiation. The concentration changes are detected by the absorption peak (365 nm) of Cr(VI) in the UV-vis spectrum. The photodegradation results are shown in Fig. 7(c). After irradiation for 180 minutes, little Cr(VI) was reduced without catalyst (the reduction rate is only 3.8%). Under the same condition, only 45.1% of Cr(VI) was reduced when bare TiO₂ NRAs was used as a photocatalyst. However, the photoreduction capacity of NiFe₂O₄, ZnFe₂O₄ and SrFe₂O₄ modified TiO₂ NRAs are enhanced greatly (94.18%, 94.086% and 92.39%, respectively), reaching the same level. This may be attributed to the function of citric acid serving as a sacrificial electron donator to quickly consume the photogenerated holes, thus greatly promote charge separation and further improve photocatalytic reactions. Unfortunately, CoFe₂O₄ modification makes the photocatalytic degradation rate of Cr(VI) even lower. The following reason may account for this abnormal
phenomenon. Eventhough CoFe2O4 modified TiO2 NRAs can be excited more easily under visible light irradiation, and then generates more charge carriers, the recombination rate of CoFe2O4/TiO2 NRAs seems to be higher than that of the bare TiO2 NRAs which can be deduced from the Voc changes, thus leading to the lower photocatalytic capacity of CoFe2O4/TiO2 NRAs.

In order to clarify the enhancement in the phototectochemical and photocatalytic capacity of TiO2 NRAs after MFe2O4 modification, it is important to figure out the separating and transferring efficiency of the charge carriers, so electrochemical impedance spectroscopy (EIS) measurements were conducted. As shown in Fig. 7(d), except for CoFe2O4/TiO2 NRAs, other MFe2O4 modified TiO2 NRAs samples all have a smaller arc radius compared with that of the bare TiO2 NRAs. It is generally assumed that the smaller arc radius on the EIS Nyquist plot suggests a more effective separation of the photogenerated electron-hole pairs and a faster interfacial charge transfer. From the EIS spectra, it can be seen clearly that NiFe2O4, ZnFe2O4 and SrFe2O4 modified TiO2 NRAs have a smaller arc radius than the bare TiO2 NRAs. It means that the charge carriers separate and transfer more effectively in NiFe2O4/TiO2 NRAs, ZnFe2O4/TiO2 NRAs and SrFe2O4/TiO2 NRAs, thus leading to the significant enhancement of the phototectochemical and photocatalytic capacity of the modified TiO2 NRAs. While the arc radius of CoFe2O4/TiO2 NRAs is even bigger than that of the bare TiO2 NRAs, suggesting lower separating rate of charge carriers in CoFe2O4/TiO2 NRAs and thus resulting in the limited enhancement of the phototectochemical capacity and even decrease in photocatalytic performance. This EIS result of CoFe2O4/TiO2 NRAs is in accordance with the Voc value of CoFe2O4/TiO2 NRAs in the I-V curves as well as the deduction from the band matching between CoFe2O4 and TiO2 in previous literature, that is, the CoFe2O4/TiO2 heterojunction is not conducive to effective separation of carriers.

Photocatalytic schematic of Cr(VI) by MFe2O4/TiO2 NRAs is shown in Fig. 8. Under visible light illumination, MFe2O4 is effectively excited to generate electrons and holes. Because the conduction band of MFe2O4 is more positive than that of TiO2, the excited electrons can quickly transfer from MFe2O4 to the conduction band of TiO2, whereas the generated holes accumulate in the valence band of MFe2O4. Consequently, the excited electron/hole

Figure 4. SEM images of (a) the bare TiO2 NRAs, (b) the cross section image of the bare TiO2 NRAs, (c) NiFe2O4/TiO2 NRAs, (d) CoFe2O4/TiO2 NRAs, (e) ZnFe2O4/TiO2 NRAs and (f) SrFe2O4/TiO2 NRAs. The insets of (c–f) are the corresponding cross section images. (h,i,g,k) are the EDS results of the red square region in (c–f), respectively.
pairs could be separated effectively, which contributes to the improvement of photoelectrochemical properties of MFe$_2$O$_4$/TiO$_2$ NRAs, except for CoFe$_2$O$_4$/TiO$_2$ NRAs. Due to the efficient separation of the photogenerated electrons and holes by MFe$_2$O$_4$ modification, the lifetime of the charge carriers are prolonged, leading to an efficient oxidation-reduction reaction, so the photodegradation activity can be enhanced. When the photoreduction is carried out in the presence of citric acid, it can quickly consume the accumulated holes in the valence band, and thus the electrons in the conduction band have enough time to function with the Cr(VI) in the aqueous solution.

**Figure 5.** (a,b) TEM images of TiO$_2$ NRAs, (c,d) TEM images of NiFe$_2$O$_4$/TiO$_2$ NRAs.

**Figure 6.** Absorption spectra of MFe$_2$O$_4$/TiO$_2$ NRAs. The dash lines are the extension of the linear portion of absorbance.
Conclusions

The effect of different ferrits (MFe$_2$O$_4$, M = Ni, Co, Zn and Sr) modification on improving the photoelectrochemical and photocatalytic properties of TiO$_2$ have been probed. By changing the incorporated cations in the MFe$_2$O$_4$, we have found that NiFe$_2$O$_4$ modification can greatly enhance the photoelectrochemical and photocatalytic performance of TiO$_2$ NRAs, while CoFe$_2$O$_4$ has relative limited effect. Compared with the bare TiO$_2$ NRAs, the photocurrent density of NiFe$_2$O$_4$/TiO$_2$ NRAs is twelve-fold higher in the I-V curve at 0.4 V vs. Ag/AgCl. Under visible light irradiation, the Cr(VI) photoreduction rate of NiFe$_2$O$_4$/TiO$_2$ NRAs achieves one-fold higher than that of the bare TiO$_2$ NRAs. The EIS measurement provides a clearer understanding of the role that MFe$_2$O$_4$ have in photogenerated charge carriers effectively separating and transferring. Except for CoFe$_2$O$_4$/TiO$_2$ NRAs, other MFe$_2$O$_4$ modified TiO$_2$ NRAs have more effective separation and transfer of the charge carriers, thus leading to the difference in the photoelectrochemical and photocatalytic performance of MFe$_2$O$_4$ modified TiO$_2$ NRAs. The obtained results point that the visible active MFe$_2$O$_4$ modification may be a promising way to improve TiO$_2$ for applications in photocatalytic activity as well as in photoelectrochemical conversion with solar light.

Figure 7. (a) Photocurrent density versus potential of the MFe$_2$O$_4$/TiO$_2$ NRAs, (b) Photocurrent density versus time measurements of MFe$_2$O$_4$/TiO$_2$ NRAs under 0 V versus Ag/AgCl bias, (c) Photocatalytic reduction of Cr(VI) by MFe$_2$O$_4$/TiO$_2$ NRAs under visible light, (d) Nyquist plots of the EIS spectra of MFe$_2$O$_4$/TiO$_2$ NRAs.

Figure 8. Photocatalytic schematic of Cr(VI) by MFe$_2$O$_4$/TiO$_2$ NRAs.
Methods

Materials synthesis. All reagents used were analytical grade chemicals and used without further treatment.

Synthesis of MFe2O4 modified TiO2 nanorod arrays. Aligned TiO2 NRAs were vertically grown on transparent fluorine-doped tin oxide (FTO) substrates by the hydrothermal method. Deionized water (DI, 10 mL) was mixed with hydrochloric acid (36.8 wt%, 10 mL) and stirred for 10 min before tetraethyl titanate (98%, 0.4 mL) was added. When the solution was stirred until clear clarification, it was transferred to a Teflon-lined stainless steel autoclave. Clean FTO substrates were immersed with the conducting side face down. The autoclave was put in an oven at a temperature of 150 °C and was taken out from the oven after 5 h. After the autoclave was cooled to room temperature, the FTO substrate was rinsed with DI water and dried naturally at room temperature. The final area of the nanorod arrays was approximately 4.5 cm2.

For the preparation of ZnFe2O4/TiO2 NRAs, briefly, zinc nitrate and iron nitrate were dissolved in DI water at room temperature to form a mixture, the as-prepared TiO2 NRAs were soaked in the Fe(NO3)3 and Zn(NO3)2 mixed solution (with concentrations of 0.25 M and 0.125 M, respectively) for 1 h, followed by dipping in DI water for 5s. Afterwards the nanorod arrays were dried in air for 24 h and then annealed at 500 °C in air for 2 h with heating and cooling rates of 5 °C·min⁻¹. The MFe2O4/TiO2 NRs (M = Ni, Co and Sr) were prepared using the same method by replacing the zinc nitrate with other nitrate.

Characterization. The surface morphology was obtained with a scanning electron microscopy (SEM, VEDAIIXMUINCN) equipped with an energy dispersive X-ray spectroscopy (EDS) system. The film microstructure was further characterized by transmission electron microscopy (TEM). X-ray diffraction (XRD, PANalytical) with Cu-Kα (λ = 0.15401 nm) was operated at 40 kV and 40 mA in a 20 range of 20–80° at a scanning speed of 5° min⁻¹ to characterize the crystal structure. Raman spectra were recorded at room temperature using a via Reflex Raman spectrometer under Ar⁺ (532 nm) laser excitation. The optical properties were probed by a UV–vis spectrophotometer (UV1800, Shimadzu) with a FTO substrate as a blank. X-ray photoelectron spectroscopy (XPS) was obtained using a ESCALAB 250Xi (The binding energy of the XPS spectra was calibrated with the C 1s peak at 284.8 eV.)

Photoelectrochemical and photocatalytic measurement. Photoelectrochemical measurements were performed in a 250 mL quartz cell using a three-electrode configuration, including the prepared samples as working electrode, a Pt foil as counter electrode, a saturated Ag/AgCl as reference electrode, and 0.5 M Na2SO4 aqueous solution as an electrolyte. The working electrode was illuminated within an area of about 1 cm² at zero bias voltage versus the Ag/AgCl electrode under solar-simulated (AM 1.5 G filtered, 100 mW·cm⁻², CEL-HXF300) light sources with a UV cutoff filter (providing visible light with λ ≥ 420 nm). The electrochemical impedance spectroscopy (EIS) measurements were recorded by employing an AC voltage of 5 mV amplitude with the initial potential at 0.4 V (vs. Ag/AgCl) over the frequency range from 100 kHz to 100 mHz without light illumination.

The Cr(VI) photoreduction was performed in a quartz cell. In the photoreduction experiments, 15 mL of aqueous solution containing 20 mg·L⁻¹ of K2Cr2O7 and 85 mg·L⁻¹ of citric acid was used. The citric acid served as a sacrificial electron donor. Prior to irradiation, the photocatalyst (area about 6 cm²) was immersed into the Cr(VI) solution in the dark for 30 minutes to establish an adsorption/desorption equilibrium. The relative concentration of Cr(VI) in the solution was derived by comparing its UV–vis absorption intensity with that of the initial Cr(VI) solution at 365 nm. The light source was a 300 W xenon lamp with visible light illumination of 26.5 mW·cm⁻².

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Author Contributions
X.G. and Z.X. designed the study, proposed the mechanism, and wrote the manuscript. X.G., Z.X. and Z.Z. performed the experiments, analyzed the data, and prepared figures. X.L. and X.W. gave many suggestions during this work process. All authors reviewed the manuscript.

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