Hexagonal-like Nb$_2$O$_5$ Nanoplates-Based Photodetectors and Photocatalyst with High Performances

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Ultraviolet (UV) photodetectors are important tools in the fields of optical imaging, environmental monitoring, and air and water sterilization, as well as flame sensing and early rocket plume detection. Herein, hexagonal-like Nb$_2$O$_5$ nanoplates are synthesized using a facile solvothermal method. UV photodetectors based on single Nb$_2$O$_5$ nanoplates are constructed and the optoelectronic properties have been probed. The photodetectors show remarkable sensitivity with a high external quantum efficiency (EQE) of 9617%, and adequate wavelength selectivity with respect to UV-A light. In addition, the photodetectors exhibit robust stability and strong dependence of photocurrent on light intensity. Also, a low-cost drop-casting method is used to fabricate photodetectors based on Nb$_2$O$_5$ nanoplate film, which exhibit singular thermal stability. Moreover, the hexagonal-like Nb$_2$O$_5$ nanoplates show significantly better photocatalytic performances in decomposing Methylene-blue and Rhdamine B dyes than commercial Nb$_2$O$_5$.

Two dimensional (2D) nanostructures have attracted increasing attention due to the unique nanoscale phenomena and their potentials in many areas ranging from energy storage to environmental protection. Compared with one dimensional (1D) and zero dimensional (0D) nanostructures, 2D nanostructures show great advantages in some special applications. It has been theoretically and experimentally demonstrated that some 2D nanostructures of noble metals or upconversion materials have higher optical activities, and the related properties can even be precisely tuned by controlling the 2D morphologies. Further to that, ZnO nanowires with a high population of polar Zn (0001) faces show higher photocatalytic activity in H$_2$O$_2$ generation, compared with ZnO nanorods. Nanoplates of SnS$_2$, LiCoPO$_4$, and carbon-coated LiFePO$_4$ exhibit superior capacities for Lithium ion batteries. Also, 2D nanostructures with highly faceted planes are favorable for self-assembling into desired 2D or 3D patterns, and further for the production of complex nanoscale architectures useful for practical applications, such as solar cells and plasmonic metamaterials. In addition, it has been reported that the nanomaterials from single-component systems or nanoplate mixtures with sulphur-doped pnictogen chalcogenide exhibit higher figure of merit in thermoelectricity than their bulk counterparts.

Niobium pentaoxide (Nb$_2$O$_5$), one of the most influential inorganic semiconductors, is known for its dielectric strength and effectiveness in catalysis. Up to now, various interesting morphologies of Nb$_2$O$_5$ nanostructures, such as nanowires, nanobelts, nanorods, nanotubes, opal nanostructure, mesoporous, hollow nanospheres, nanosheets, and nanoparticles, have been synthesized. These nanostructures offer Nb$_2$O$_5$ several unique features for a variety of device applications, involving field emitters, lithium ion batteries, photodetectors, photocatalysts, biosensors, gas sensors, etc. Owing to its bandgap, which rests in a relatively wide range from about 2.8 to 3.8 eV depending on the preparation methods, Nb$_2$O$_5$ is a potential candidate for UV-A light (wavelengths ranging from 400 nm to 320 nm) detection. However, until now, studies of the UV-A light photodetectors based on Nb$_2$O$_5$ nanostructures have been rather limited, compared with those based on the nanostructures of ZnO, ZnS, and SnO$_2$. In fact, although the photodetectors based on single Nb$_2$O$_5$ nanobelts and hollow nanospheres were reported, the time response performances were not satisfactorily resolved. Furthermore, the synthesis of both nanostructures needs a complicated template-assisted process. The photodetectors based on single Nb$_2$O$_5$ nanowires were also reported. Nevertheless, the studied response wavelengths of the nanowire were 808 nm (~1.5 eV) and 532 nm (~2.3 eV), which were deduced to result from the defect level states of nanowire. This means the corresponding photon energy is much lower than the bandgap, and therefore, these Nb$_2$O$_5$ nanowires cannot be used as UV-A photodetectors. In this work, by using a facile one pot
solvothermal method, we synthesize hexagonal-like Nb$_2$O$_5$ nanoplates without using any templates or surfactants, and, based on the as-prepared samples, fabricate UV-A photodetectors. The temperature-dependent current-voltage characteristics of the photodetector made from Nb$_2$O$_5$ nanoplate film using a low-cost drop-casting method are analyzed. It is demonstrated that the resulted photodetectors based on Nb$_2$O$_5$ nanoplates exhibit remarkable selectivity, thermal stability, and sensitivity with a high EQE. Furthermore, the as-obtained products also show significantly better photocatalytic performances than commercial Nb$_2$O$_5$.

**Results**

**Characterization of Nb$_2$O$_5$ samples.** From the low and high resolution field emission scanning electron microscopy (SEM) images of Fig. 1a–c, it is noticed that the as-prepared samples mainly display hexagonal-like nanoplate morphologies, with typical diameters ranging from 0.5 to 2 µm and thickness around 100 nm. Statistical analysis shows the nanoplates take a significant percentage (> 80%) of the yield, which is interspersed with a few nanorods about 1.5 µm long and a few nanoparticles. Powdered X-ray diffraction (XRD) pattern of the as-obtained samples is shown in Fig. 1d. All diffraction peaks are indexed to the hexagonal Nb$_2$O$_5$ (PDF#07-0061) phase and monoclinic Nb$_2$O$_5$ (PDF#19-0862) phase and no impurities are observed. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) have been performed to further confirm the morphology and structure. Fig. 2a shows the TEM image of the nanoplates, which substantiates the hexagonal-like morphology. The SAED pattern taken of individual Nb$_2$O$_5$ nanoplates can be indexed to the [001] zone axis, exhibiting a hexagonally arranged diffraction spot, as shown in Fig. 2h. This is consistent with the XRD result that the hexagonal phase is formed in the as-prepared sample. Also, to confirm the chemical composition and elemental distribution, X-ray dispersive spectroscopy (EDS) has been conducted on the hexagonal-like nanoplates, as shown in Fig. 2c–e. The results indicate that the samples only consist of Nb and O elements with a stoichiometric Nb$_2$O$_{4.8}$ composition, where the Cu signal originates from the TEM copper grid. The mapping images in Fig. 2c and 2d show that they are homogeneously distributed within the nanoplates. Besides, high resolution transmission electron microscopy (HRTEM) image and SAED pattern are shown in Fig. S1, consistent with the XRD result that the nanorods exhibit a monoclinic Nb$_2$O$_5$ phase. The EDS elemental mapping images of both hexagonal-like nanoplates and nanorods also confirm the uniform distribution of Nb and O in the nanorods. Further to that, additional analysis using X-ray photoelectron spectroscopy (XPS) has been performed and shown in Fig. 3. XPS survey scan implies that only Nb and O elements are present in the sample, apart from some residual carbon signal which is believed to arise from adventitious contamination (Fig. 3a). However, the Nb peak can be deconvoluted into two peaks with binding energies of 207.2 eV and 205.8 eV, and are assigned to Nb$^{5+}$ and Nb$^{4+}$, respectively. This agrees well with the reported literature values (207.0 to 207.6 eV for Nb 3d5/2 in Nb$_3$O$_5$ and 205.2 to 206.1 eV for Nb 3d5/2 in NbO$_2$ according to the NIST database$^{32,43}$. Furthermore, these results also suggest that there are small amounts of suboxide species such as NbO$_2$ in the Nb$_2$O$_5$, in accordance with the EDS stoichiometric Nb$_2$O$_{4.8}$ composition.

**Discussion**

The single hexagonal-like nanoplate photodetector was fabricated according to the experimental section. The schematic illustration of the single nanoplate-based photodetector and a typical SEM image are shown in Fig. 4a and 4b, respectively. It is noticed that the gap between the two electrodes is about 1.3 µm. The optoelectronic properties of the nanoplate-based photodetector are measured using a two-probe method under ambient conditions. Fig. 4c displays the typical current-voltage (I-V) curves of the device either illuminated with light of different wavelengths or in dark conditions. The device has shown a very low dark current of less than 1 pA under the bias
voltage of 1.0 V. When the wavelength of the light source is 450 nm, there is almost no change in photocurrent, which fairly overlaps with the curve of the dark current. However, when the device is illuminated by the light with shorter wavelengths, for example of 350 nm and 320 nm, the photocurrent increases drastically and reaches up to 36.5 pA and 59.9 pA, respectively. This indicates that the present Nb2O5 nanoplate-based photodetector is significantly more sensitive to UV-A light than to visible light. The nonlinear behaviors of I-V curves may be caused by the blocking at the metal/semiconductor contacts. In fact, the almost rectifying I-V characteristic of the present device can be ascribed to the metal-semiconductor-metal structure involving two Schottky barriers connected back to back and a resistor in between, where the current in the nano-Schottky barrier structure becomes dominant and has greater tendency to become tunneling rather than thermionic. The dramatic increase in photocurrent under 350 nm and 320 nm light illuminations is ascribed to the enhanced numbers of excited electron-hole pairs when the photons’ energy is larger than the bandgap of Nb2O5. This high wavelength selectivity is also confirmed by the spectral photoresponses of the device under a bias of 1.0 V against wavelengths ranged from 630 nm to 250 nm, where stronger absorption occurs under the wavelengths below 400 nm, as shown in Fig. 4d. The bandgap is deduced from the UV-vis absorption spectrum, as shown in Fig. 4e and 4f. As for direct bandgap semiconductors, it is known that the relationship between absorption coefficient ($\alpha$ near the absorption edge and the optical bandgap obeys the following equation:

$$\alpha h^2 \approx A(hv - E_g)$$

where $A$ is the absorption constant that relates to the effective masses associated with the valence and conduction bands, and $hv$ is the photon energy. Hence, the optical bandgap for the absorption edge can be obtained by extrapolating the linear portion of the plot of $(\alpha h^2)$ against $hv$ down to the point where $a = 0$. Fig. 4f shows the plot of $(\alpha h^2)$ against $hv$ calculated from Fig. 4e. It is noticed that the optical absorption in the edge region fits well with the relation of $(\alpha h^2) \propto (hv - E_g)$, which indicates that the Nb2O5 sample have a direct bandgap of 3.15 eV (393 nm). This relatively low value of bandgap is consistent with the results of Nb2O5 samples synthesized using sol-gel methods at low temperatures, while it is reported that Nb2O5 samples made by evaporation, sputtering, anodization and CVD have higher values of bandgap.

Responsivty ($R_s$) and EQE are two critical parameters to determine the sensitivity of a photodetector, and they are defined as the number of carriers circulating through a photodetector per absorbed photon and per unit time, respectively. A larger $R_s$ or EQE means a higher sensitivity, and they can be expressed as $R_s = D/PS$ and $EQE = R_s hc/e\lambda$, respectively, where $D$ is the difference between the photocurrent and the dark current, $P$ is the light power, $S$ is the irradiated area on the nanoplate, $h$ is Planck’s constant, $c$ is the velocity of light, $e$ is the electronic charge, and $\lambda$ is the excitation wavelength. The calculated $R_s$ and EQE of the present nanoplate device are as high as 24.7 A/W and 96.17% under an applied voltage of 1 V, respectively, when the illumination wavelength is 320 nm (134 $\mu$W/cm²).

Apart from sensitivity and selectivity, stability is also a very important factor for photodetectors. Fig. 5a and 5b show the time-dependent responses of the photodetector, which are obtained either using or without using the mechanical chopping method upon the illumination of 320 nm light, under a bias of 1.0 V. When the condition is changed from dark to light, the current increases to a stable

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**Figure 2** | Nb2O5 sample synthesized through a solvothermal method. (a) TEM image of hexagonal-like nanoplates. (b) SAED pattern of a single nanoplate Nb2O5. The corresponding EDS mapping images for Nb and O of the hexagonal-like nanoplates marked in the rectangle area in (a) are shown in (c) and (d), respectively. (e) EDS spectrum.

**Figure 3** | Nb2O5 sample synthesized through a solvothermal method. (a) XPS survey scan of Nb2O5 samples. (b) and (c) high resolution XPS spectra for O and Nb.
value around 55 pA, and, after the light is turned off, decreases dramatically to the original value of less than 1 pA, as shown in Fig. 5a. The rise time and decay time (defined as the time required for the peak photocurrent to increase from 10% to 90% or drop from 90% to 10%) of the present photodetector are 28 s and 12 s, respectively. Furthermore, upon constant illumination, the photocurrent fluctuates very little and no obvious degradation is observed for the average photocurrent of 55 pA over 1400 s. These critical parameters from the measurements are comparable to those of some other existing semiconductor photodetectors listed in Table S1 in the Supplementary Information. Compared with individual Nb_2O_5 nanobelt UV-A photodetector, the present single nanoplate photodetector exhibit a stable time response and higher responsivity.

The efficiency of photocurrent generation depends on the balance among charge carriers generation, recombination, and transport. It is generally accepted that chemisorption/desorption of oxygen molecules plays a very important role in regulating the photoconductive process in semiconductors. Due to the large surface-to-volume ratio of the Nb_2O_5 nanoplates resulting from its hexagonal-like geometry with the width of 0.5 to 2 μm and the thickness around 100 nm, chemisorption/desorption on the surface of Nb_2O_5 nanoplates may also play a fairly important role in the photoconductive behaviors, as previously reported of Nb_2O_5 nanobelts.

Therefore, we investigate the I-V characteristics of Nb_2O_5 nanoplate photodetector upon the 320 nm illumination in air and vacuum, as shown in Fig. 5d. The photocurrent measured under the pressure of 100 Pa is 454 pA, which is about 7.5 times higher than that in air (59.9 pA). This phenomenon is ascribed to the reason same to that for the previously reported Nb_2O_5 nanobelts. Because Nb_2O_5 is an n-type semiconductor, oxygen molecules are absorbed onto the surface and then capture the free electron of the nanoplate through the reaction \[O_2(g) + e^- \rightarrow O_2^-(ad)\] at ambient conditions, giving rise to a low-conductivity depletion layer and the band bending near the surface. Upon UV illumination, electron-hole pairs are generated and the holes will migrate to the surface, leading to the desorption of oxygen...
molecules from the nanoplate surface, expressed as \( [h^+ + O_2 \rightarrow O_2(g)] \). Thus, the photo-induced electrons will lead to an apparent enhancement of photocurrent in air. In vacuum, more adsorbed oxygen molecules are desorbed from the surface, hence bringing up a higher photocurrent than that in air. This is consistent with previous reports of an enhancement of both photocurrent and photoluminescence in vacuum 50–52.

In a bid to explore both the probability of low-cost manufacturing and the thermal stability of photodetectors, Nb_2O_5 nanoplate film has been prepared by using the drop-casting method on SiO_2/Si substrates. Tungsten carbide (WC) electrodes (50 nm) were utilized for higher temperature measurement, and patterned, using a hard mask with 20 μm gaps, as shown in Fig. 6a. All measurements performed were similar to those for the single-nanoplate photodetector. I-V and current-time characteristics are shown in Fig. 6b and 6c. The linear behaviors of I-V curves suggest good Ohmic contacts between the nanoparticles and the electrodes. The responses of current under different wavelengths show the same trend to that of the single Nb_2O_5 nanoplate photodetector, where the photocurrent changes obviously upon the 350 nm and 320 nm illuminations. The current steadily changes as the light is turned on and off, as shown in Fig. 7a. However, the current-time responses in vacuum in Fig. 7b display a gradual increase of both photocurrent and dark current, which is attributed to the reduction in oxygen reabsorption rate in oxygen-deficient environments 53. The changes in photocurrent under the bias of 1.0 V upon 320 nm illumination in air or vacuum at different temperatures are summarized in Table S2 in Supporting Information. It can be seen that the photocurrent of the Nb_2O_5 nanoplate film photodetector is about only one third of that of the single Nb_2O_5 nanoplate photodetector. The possible reason for this large difference in photocurrent is that shorter gap distances may result in shorter time for the carriers to transit through the gap, and thus higher photocurrent 53. Besides, when the temperature increases from 298 K to 358 K, both the photocurrent and the dark current, as well as the responsivity, are only slightly increased, indicating good thermal stability of the Nb_2O_5 nanoplate film photodetector and great potential for the photodetector to work efficiently at higher temperatures.

Apart from being used as a photodetector, the Nb_2O_5 nanoplates are also testified of its semiconductor property to decompose Methylene-blue and Rhodamine B. The concentrations of these two dyes are determined based on Beer’s law, and the absorbance of 664 nm and 554 nm is investigated, respectively 54. From Fig. 8, it is noticed that the as-prepared Nb_2O_5 nanoplates show a faster decomposition rate than commercial Nb_2O_5 (Aladdin, 99.99%, particles, several μm in diameter, Fig. S2) of these two dyes. The appearance of a new peak around 495 nm in Fig. 8d, after 40 minutes’ irradiation, is assigned to rhodamine (the full N-deethylated products of Rhodamine B) 55,56. The absorbance changes are also summarized in Table S3. It is clear that nearly 91% and 99% of the initial dyes still remain in the solution after 60 minutes of irradiation without any photocatalyst. The Nb_2O_5 nanoplates show a higher adsorp-
Figure 6 | Device image and optoelectronic characteristics of nanoplate film photodetector. (a) Photograph and SEM images of the nanoplate film photodetector produced using the drop-casting method. (b) and (c) I-V characteristics of the device illuminated with light under four different wavelengths and in dark conditions under the bias of 1.0 V, in air and vacuum, respectively.

Figure 7 | Photoresponse and temperature dependence of nanoplate film photodetector. (a) and (b) Current-time responses of the nanoplate film photodetector illuminated upon the 320 nm light measured using the mechanical chopping method under the bias of 1.0 V in air and vacuum, respectively. (c) and (d) I-V characteristics of the device, under the temperatures of 328 K and 358 K, respectively, in vacuum.
tion and decomposition ratio of dye molecules than commercial Nb$_2$O$_5$ (The absorbance changes from 92% at 0 minute to 54% at 60 minute for Methylene-blue, and from 98% at 0 minute to 14% at 60 minute for Rhodamine B, respectively, after 60 minutes of irradiation). This higher adsorption of dye molecules is attributed to the strong Lewis acidic Nb$^{5+}$ on the surface and the big surface-to-volume ratio of Nb$_2$O$_5$ nanoplates (See Table S3 and Fig. S3, the surface areas are 31.7 cm$^2$/g and 5.3 cm$^2$/g for Nb$_2$O$_5$ nanoplates and commercial Nb$_2$O$_5$, respectively). It has been reported that Nb$_2$O$_5$ exhibits a different decomposition mechanism from the conventional radical-produced process. With regard to the strong adsorption of dye molecules, it seems that the dye molecules are immobilized at the solid acid sites, where the photoinduced electrons and holes on the surface can attack dye species without producing any radicals\cite{32}. Therefore, the higher adsorbed amounts of dye molecules as well as the bigger surface-to-volume ratio of Nb$_2$O$_5$ nanoplates lead to the higher degree decomposition of dyes than commercial Nb$_2$O$_5$.

Figure 8 | Photocatalytic performances of Nb$_2$O$_5$. (a) and (b) Absorbance changes of Methylene-blue in the presence of commercial Nb$_2$O$_5$ and as-prepared Nb$_2$O$_5$ nanoplates. (c) and (d) Absorbance changes of Rhodamine B in the presence of commercial Nb$_2$O$_5$ and as-prepared Nb$_2$O$_5$ nanoplates. (e) and (f) Comparison of Methylene-blue and Rhodamine B decomposition efficiencies between the solutions with as-prepared Nb$_2$O$_5$ nanoplates, the solutions with commercial Nb$_2$O$_5$ and the solutions without catalyst, respectively.
It has been reported that Nb$_2$O$_5$ is an efficient photocatalyst for the decomposition of indigo carmine, and almost 100% of dye decomposition occurs at 20, 45 and 90 minutes for TiO$_2$, ZnO and Nb$_2$O$_5$, respectively. However, despite the fact that the as-prepared Nb$_2$O$_5$ nanoplates are reasonably efficient for the decomposition of dyes, the efficiency is not yet comparable to that of p25 (Fig. S4). The higher decomposition efficiency of p25 is due to its even larger surface-to-volume ratio (around 50 cm$^2$/g$^{3/2}$, and rapid electron transfer between the mixed-phase of rutile and anatase. The relationship between $\ln(c_0/c)$ and irradiation time (See Fig. S4b and S4d, c$_0$ and c are the concentrations of dyes in the solutions before and after irradiation) is not linear, suggesting that the decomposition of Methylene-blue and Rhodamine B does not follow pseudo-first-order kinetics of the Langmuir-Hinshelwood model. The convex function characterization of the as-prepared Nb$_2$O$_5$ nanoplates (Fig. S4b and S4d) may be ascribed to the self-accelerated effect due to the acidic intermediates produced during the compositing process. Further to that, it has also been reported that the decomposition of indigo carmine dye by Nb$_2$O$_5$ can be improved at lower pH values. Because the decomposition of Methylene-blue molecules and Rhodamine B will produce carboxylic acid, NO$_3^-$, SO$_4^{2-}$, etc.,$^{3/4}$ these intermediates may result in the slightly lower pH value of the solution. The above results indicate that the as-prepared Nb$_2$O$_5$ nanoplates have significantly better photocatalytic performances than commercial Nb$_2$O$_5$.

In summary, photodetectors based on Nb$_2$O$_5$ nanoplates have been fabricated and investigated. The Nb$_2$O$_5$ nanoplates are synthesized using a facile solvothermal method. On the one hand, the single Nb$_2$O$_5$ nanoplate photodetectors show remarkable sensitivity and wavelength selectivity with respect to UV-A light. They also exhibit robust stability and the generated photocurrent is substantially dependent on light intensity. On the other hand, good thermal stability is further observed of the Nb$_2$O$_5$ nanoplate films photodetector produced using the drop-casting method. In addition, the photocatalytic performance of the hexagonal-like Nb$_2$O$_5$ nanoplates in decomposing Methylene-blue and Rhodamine B dyes is significantly better than that of commercially purchased Nb$_2$O$_5$. These results considerably justify the potential of Nb$_2$O$_5$ nanoplates for high-performance UV-A photodetectors and photocatalyst.

**Methods**

The synthesis of Nb$_2$O$_5$ materials. In a typical synthesis of Nb$_2$O$_5$ nanoplates, a facile pre-hydrolysis reaction was conducted by adding NbCl$_5$ (0.27 g, 99.9%, Aladdin) and absolute ethanol (30 ml, >95%, sinopharm) into deionized water (30 ml), which was subsequently kept for two hours at 25°C. After being stirred for another two hours, the aqueous suspension was immediately transferred into a Teflon lined autoclave (100 ml), and kept in oven at 250°C for 2 days. The white precipitate was collected using centrifugation, washed repeatedly with deionized water and ethanol several times, and dried at 60°C for five hours.

Device fabrication and characterization. For the fabrication of single hexagonal-like nanoplate photodetector, a droplet of Nb$_2$O$_5$ suspensions (2 mg of Nb$_2$O$_5$ powder dispersed in certain amounts of ethanol) was delved gently on a thermally oxidized Si substrate covered with a 300 nm thick SiO$_2$ layer. After being stirred for another two hours, the aqueous suspension was immediately transferred into a Teflon lined autoclave (100 ml), and kept in oven at 250°C for 2 days. The white precipitate was collected using centrifugation, washed repeatedly with deionized water and ethanol several times, and dried at 60°C for five hours.

Materials characterization. The phase of as-obtained Nb$_2$O$_5$ nanoplates was identified by a Rigaku D/max-RB X-ray diffractometer using Cu K$_\alpha$ radiation ($\lambda=0.15406\ nm$) in the 20 range from 20° to 70°. The morphology characterization of the products was carried out by using field-emission scanning microscopy (FESEM, JEOL JSM-6701F) and transmission electron microscopy (TEM, JEOL JEM-2100F) equipped with an X-ray energy dispersive spectrometer (EDS). The UV-visible absorption spectra were obtained using a Hitachi U-4100 spectrophotometer with the scanning wavelength from 700 nm to 200 nm. The XPS measurements were performed by a monochromatic Al K$_\alpha$ X-ray source ($hv=1486.6\ eV$) with vacuum pressure of $1.0 \times 10^{-6}\ Torr$. Specific surface areas (BET analysis) was made using a Quantachrome instrument, and the software used was the Tristar 3000 v6.04.

Photocatalytic activity measurements. The photocatalytic activity of the as-prepared nanocrystals was evaluated by degrading Methylene-blue (dye content, >90%, Aladdin, (HPLC)), which is a dye resistant to biodegradation. The photocatalytic reactions were performed in a 50-ml Pyrex beaker at room temperature. For each run, 10 mg of powdered photocatalyst was added to 50 ml of distilled water solution (2.5 mg/ml) to deionized water, followed by a magnetic stir in the dark for 40 min to attain adsorption-desorption equilibrium. The beaker was then placed under a Hg arc lamp (Philips PL-S UV 100 W) positioned 20 cm above the base of the reaction vessel and illuminated during the entire photocatalytic reaction process. The slurry was continuously stirred to ensure full suspension of the nanocrystals throughout the solution. A solution of the reaction was collected at given time intervals and centrifuged at 16500 rpm for 3 minutes prior to spectrometric analysis. UV-Vis absorption measurements were performed to analyze the degradation of Methylene-blue. The procedure of decomposition of Rhodamine B is the same as Methylene-blue, except the concentration of Rhodamine B and catalyst was changed to 15 mg/L and 30 mg, respectively.

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Author contributions
L.H. and F.X.S. supervised the project, conceived the experiments, analyzed the results and wrote the paper. G.N. helped for the linguistic polish. L.M.Y. helped with collected and analysis the data. All authors participated in analysis and discussion the results and commented on the manuscript.

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