



Article QD/SnO₂ Photoactivated Chemoresistive Sensor for Selective Detection of Primary Alcohols at Room Temperature

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Abstract: Sensors based on nanocomposites of quantum dots (QDs) and wide-gap metal oxides are of exceptional interest for photoactivated detection of toxic and pollutant gases without thermal heating. However, the class of detecting gases has been limited almost exclusively to oxidizing gases like NO₂. Here, we designed a photoactivated sensor for the selective detection of primary alcohols at room temperature using CdSe quantum dots coupled to a wide-gap SnO₂ semiconductor matrix. Our concept of the sensor operations is based on the photochemical reaction of primary alcohols via photoactivated QD-SnO₂ charge transfer and does not involve chemisorbed oxygen, which is traditional for the operation of metal oxide sensors. We demonstrated an efficient sensor response to C₁–C₄ primary alcohols of ppm concentration under photoexcitation with a yellow LED in the absence of a signal from other volatile organic compounds (VOCs). We believe that proposed sensor concept opens up new ways to design photoactivated sensors without heating for the detection of VOCs.

Keywords: room temperature gas sensor; quantum dots; primary alcohols; photoactivation; photoactalysis; selectivity

1. Introduction

Semiconductor nanoparticles or quantum dots (QDs) obtained in colloidal systems have become one of the promising scientific and technological achievements of recent years due to unique photophysical properties [1,2]. An important advantage of QDs is the ability to control the band gap in a wide range by simply changing the QD. In addition, the composition and surface modification of QDs can be controlled in colloidal synthesis, and QDs exhibit high thermal and photostability. These benefits open up wide possibilities for technological applications such as LEDs, lasers, and photovoltaic and optoelectronic devices for telecommunications, metrology, imaging, and medical diagnostics [3–5].

Sensor applications of QDs are driven by their variable band gaps, narrow luminescence bands, stability, large surface areas, and tunable surface chemistry. First of all, luminescent sensors for biomedical applications are known to utilize the luminescent properties of QDs [6,7]. Recently, sensor applications of QDs in practically important, compact, and low-cost resistive-type gas sensors have been developing [8]. Reversible changes in the concentration of charge carriers in conducting PbS QDs arrays as a result of adsorption of molecules from the gas phase allowed a room-temperature sensor of NO₂ molecules to be made [9–12]. Another example is the use of nanocomposites of QDs and wide-gap metal oxides for the detection of oxidizing gases. Upon photoexcitation, electrons are effectively



Received: 7 December 2024 Revised: 10 January 2025 Accepted: 15 January 2025 Published: 16 January 2025

Citation: Skrypnik, M.Y.; Platonov, V.B.; Kurtina, D.A.; Sinyashin, O.G.; Rumyantseva, M.N.; Vasiliev, R.B. QD/SnO₂ Photoactivated Chemoresistive Sensor for Selective Detection of Primary Alcohols at Room Temperature. *Chemosensors* 2025, *13*, 20. https://doi.org/ 10.3390/chemosensors13010020

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/ licenses/by/4.0/). transferred from the QDs into the wide-gap metal oxide matrix [13,14], changing the electron concentration. This allows the coverage of chemisorbed oxidizing gas molecules to be modulated to create gas sensors at room temperature. For example, nanocomposites of wide-bandgap SnO₂, In₂O₃, and ZnO oxides sensitized with CdSe QDs demonstrate high responses to sub-ppm concentrations of NO₂ molecules under photoexcitation at room temperature [15]. In addition to CdSe QDs, CdSe/CdS and CdS/ZnSe core/shell nanoparticles have been used for sensitization, making it possible to control charge transfer and modulate the response behavior to NO₂ [16]. Photoactivated sensors for NO₂ molecules based on ZnO nanorods decorated with PbS QDs have also been demonstrated [17]. Other examples of photoactivated sensors are MoS₂ nanostructures decorated with CdTe QDs or WS₂ nanostructures decorated with core/shell QDs for room-temperature NO₂ sensing [18,19]. However, in all the given examples of photoactivated sensor systems based on QDs, the sensor signal is achieved exclusively for the NO₂-oxidizing gas. This significantly limits the capabilities and development of photoactivated QD-based resistive sensors, despite the significant advantage of operating without heating.

Here, we present the concept of a photoactivated QD-based sensor for the detection of volatile organic compounds (VOCs). We designed a resistive sensor based on CdSe quantum dots coupled to a wide-gap SnO₂ semiconductor matrix. We considered the use of photocatalysis with quantum dots, a recent direction of the development of QDs [20–27], which are a versatile platform for photocatalytic organic transformations. The proposed sensing operations involve photochemical reactions with VOCs via photoactivated QD-SnO₂ charge transfer and do not involve the chemisorbed oxygen required for the operation of traditional metal oxide sensors [28–31], resulting in a novel operating principle. As model VOCs, we selected C_1 - C_4 primary alcohols. We demonstrated an efficient and selective sensor response to alcohol molecules under photoexcitation with a yellow LED, in the absence of a signal from other VOCs, using aldehydes as a representative.

2. Materials and Methods

Cadmium acetate dihydrate (Cd(CH₃COO)₂·2H₂O, \geq 98%), selenium powder (Se, 99.99%), trioctylphosphine (TOP, 90%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), N-acetyl-L-cysteine (L-AcCys, \geq 99%), acetic acid (AcA, \geq 99%), thioglycolic acid (TGA, \geq 97%), and solvents were purchased from Sigma-Aldrich.

Nanocrystalline SnO₂ was synthesized by the precipitation method from tin (IV) chloride [13]. SnCl₄·5H₂O was dissolved in deionized water, and 25% aqueous ammonia was slowly added under stirring until the precipitation of α -stannic acid appeared. The resulting gel was centrifuged, washed with deionized water to remove contaminants of the chloride ions (AgNO₃ test), and dried at 80 °C for 24 h. Then, the product was calcined in air at 500 °C for 24 h.

CdSe quantum dots (QDs) were obtained with the colloidal method similarly to previous research [13]. Briefly, 0.5 mmol of cadmium acetate and 1.5 mmol of oleic acid (OA) were added to 5 mL of octadecene (ODE), and the mixture was degassed under argon flow for 1 h at a temperature of 140 °C. Then, the system was heated to the injection temperature (200 °C), and under intense stirring, 0.5 mL of 1 M Se solution in TOP was injected rapidly into the reaction mixture, initiating nucleation of QDs. The growth of QDs was controlled with absorption spectroscopy. Finally, CdSe QDs were precipitated from the solution, washed with acetone, and redispersed in hexane. The precipitation–redispersion procedure was repeated 2–3 times to remove unreacted precursors and the excess of stabilizer. Afterward, a long-chain native ligand OA was exchanged into a series of a short-chain organic acids (N-acetyl-L-cysteine; acetic acid; thioglycolic acid) similarly to Ref. [32]. Shortly, an excess of ligand was added to a solution of QDs coated with OA in

tetrahydrofurane (THF) and left at room temperature for 24 h. The resulting precipitate was centrifuged and washed with pure acetone several times to remove the traces of ligand. The resulting QDs were redispersed in 2 mL of methanol.

CdSe nanoplatelets (NPLs) with a thickness of 3 monolayers were also synthesized with the colloidal method, similarly to previous research [32]. A quantity of 160 μ L of oleic acid was added to 20 mL of octadecene in a flask during intensive stirring. Then, the solution was heated up to a temperature of 170 °C under argon flow for degasification. After that, the mixture was cooled to 60 °C, and 0.26 g of cadmium acetate was added. Next, the mixture was heated up to 200 $^{\circ}$ C for the injection of 200 μ L of 1 M solution of selenium in trioctylphosphine diluted up to 1 mL with ODE. The growth of CdSe nanoparticles proceeded for 45 min. After the synthesis was completed, 3 mL of oleic acid was added to the resulting solution as a stabilizer and the mixture was centrifuged. The mixture of acetone and hexane was washed in a 1:3 proportion and redispersed in 2 mL hexane. Ligand exchange similar to that in [33,34] was provided using 8 mL dioxane previously degassed under argon flow at 75 °C. Then, 1 mL NPL solution and 300 mg of N-acetyl-Lcysteine were added to the flask and left at 75 °C for 2 h for pre-exchange. Next, NPLs were centrifuged, new portions of dioxane and L-AcCys for full ligand exchange were added to the mixture, and the mixture was left at the same temperature for 4 h. The completion of the ligand exchange was proven using FTIR spectroscopy; then, NPLs were washed with pure acetone several times and redispersed in 2 mL of methanol.

Sensor prototypes were created by applying the photocatalyst onto a microelectronic chip with $2 \times 2 \times 0.1$ mm alumina microhotplates. Nanocrystalline SnO₂ was mixed with α -terpineol and applied as a thick film onto the chip. It was provided with Pt contacts on the front side and a Pt-meander on the back side, serving as a heating element and a temperature probe. The distance between the electrodes was 0.1 mm. Then, the thick films were dried at room temperature for 24 h and sintered at 500 °C for 10 h in air. The final SnO_2 film thickness was about 50–80 μ m. After that, the SnO_2 films on the chip were coated with CdSe QDs covered with L-AcCys dissolved in methanol, washed with pure methanol, and dried. The measurements were carried out in a flow cell under a nitrogen atmosphere at a flow rate of 100 mL/min, with periodic illumination of a yellow LED ($\lambda_{max} = 595$ nm) operating at a voltage of 3 V and a current of 40 mA. The characteristics of the LED and the emission spectrum of the LED are shown in Figure S1 in the Supporting Information. The resistance measurement was carried out on a laboratory-made setup at a bias voltage of 1 V. Attested gas mixtures of alcohols in nitrogen with concentrations of 1000 ppm were used as sources of analyte gases. Gas mixtures with preassigned concentrations in dry nitrogen as a carrier gas were created using electronic gas flow regulators (RRG12) (Eltochpribor, Zelenograd, Russia). A schematization of the experimental setup is shown in Figure S2. The sensor signal S, both in the dark and under irradiation, was calculated as the ratio of:

$$S = \frac{Rdark - Rled}{Rled} \tag{1}$$

where *Rdark* is the resistance of the sensor material in darkness; *Rled* is the resistance of the sensor material under LED irradiation.

Photocatalysis in the liquid phase was carried out under UV LED irradiation ($\lambda_{max} = 392 \text{ nm}$) in an argon atmosphere, with NPLs of CdSe coated with N-acetyl-L-cysteine as the photocatalyst. Briefly, the procedure consisted of irradiation with 100 µL of ethanol dissolved in 5 mL dioxane and the addition of 100 mg of photocatalyst under intensive stirring. The products were analyzed by FTIR spectroscopy.

Fourier transform infrared spectroscopy (FTIR) spectra were collected on a Perkin-Elmer Frontier FTIR spectrometer (Perkin Elmer, Waltham, MA, USA) in the wavenumber range of 400–4000 cm⁻¹. Transmission electron microscopy (TEM) was performed with a JEOL JEM2100 microscope (JEOL, Tokyo, Japan), which was operated at a voltage of 200 kV. Scanning electron microscopy (SEM) was carried out with an LEO Supra 50VP OMEGA microscope. Absorption spectra were collected on a Varian Carry50 (Agilent Technologies, Santa Clara, CA, USA) spectrophotometer in the 200–800 nm wavelength range with a scanning speed of 60 nm/min. For optical measurements, dilute colloidal solutions of nanoparticles in hexane for long-chain ligands or methanol for short-chain ligands were used. Circular dichroism (CD) spectra were recorded on a spectropolarimeter (Chirascan) (Applied Photophysics, Leatherhead, UK) in the 300–500 nm wavelength range, with a scanning speed of 10 nm/min and a 1 nm step (integration time 3 s). The measurements were carried out at room temperature.

3. Results and Discussion

3.1. Photoactivated QD/SnO₂ Sensor Design and Working Scheme

We constructed a photoactivatable sensor with photochemical reactions based on CdSe QDs coupled to an SnO₂ matrix (Figure 1). This nanocomposite exhibited efficient photoexcited charge transfer [13]. To improve the charge transfer efficiency, we used the short bifunctional ligand L-AcCys with an anchor sulfhydryl group for attachment to the CdSe QD and an anchor carboxylate group for attachment to the SnO₂ grain surface. We propose the use of selective photooxidation of alcohols to aldehydes with the participation of QDs, where QDs are responsible for selective photochemical reactions [35], and the SnO₂ matrix provides electron transport for an easily detectable resistive response. The use of QDs for selective conversion of alcohols to carbonyl compounds in an aqueous solution has been demonstrated previously [36–39]. We used the fact that alcohol molecules are effective hole scavengers during photochemical reactions, as was shown in [40] using methanol as an example. In another example of benzyl alcohol oxidation on CdS QDs, a photoexcited hole oxidized alcohol molecules and an electron was captured by Cd islands [41]. In our case, a photoexcited electron was transferred from the QD to SnO₂, and the photoexcited hole oxidized the alcohol molecule.



Figure 1. Schematic diagram of the processes during operation of a photoactivated resistive sensor using photochemical reactions based on CdSe QDs coupled to SnO₂ matrix. For clarity, only one CdSe QD–SnO₂ grain pair is shown. Electron transport was carried out along the SnO₂ grain layer. Thick arrows indicate charge transfer; thin arrows indicate chemical transformations.

The proposed working processes were as follows. Upon photoexcitation, an electronhole pair was generated in CdSe QD (2). Immediately after photoexcitation, the electron was transferred to the SnO_2 grain, and the hole remained in the CdSe QD (3).

$$CdSe/SnO_2 \rightarrow CdSe(h^+ + \bar{e})/SnO_2$$
 (2)

$$CdSe(h^{+} + \bar{e})/SnO_{2} \rightarrow CdSe(h^{+})/SnO_{2}(\bar{e})$$
(3)

$$CdSe(h^+)/SnO_2(\bar{e}) \rightarrow CdSe/SnO_2$$
 (4)

$$CdSe(h^+)/SnO_2(\bar{e}) + R-CH_2-OH \rightarrow CdSe/SnO_2(\bar{e}) + 2H^+ + R-CHO$$
(5)

$$CdSe/SnO_2(\bar{e}) + H^+ \rightarrow CdSe/SnO_2 + \frac{1}{2}H_2$$
(6)

In the absence of alcohol molecules, the electron and hole annihilated at the QD-SnO₂ heterojunction after the relaxation time, according to the process (4). In the presence of alcohol molecules on the QD surface after adsorption from gas phase, the relaxation processes changed. The photoexcited hole oxidized the R-CH₂-OH alcohol molecule into R-CHO aldehyde, and a proton appeared for charge compensation according to the process (5). We supposed that the proton then migrated to the SnO₂ grain surface and was reduced to molecular hydrogen (6) by the free electron previously added in step (2). Thus, the presence of alcohol molecules in the gas phase changed the charge balance in the system upon photoexcitation. Since the rates of processes (5)–(6) relative to the rate of process (4) depend on the presence of alcohol molecules in the gas phase, the concentration of free electrons in SnO₂ grain changed due to the presence of alcohol molecules. This was easily detected by a change in the resistance of the nanocomposite. At the same time, process (5) ensured the selectivity of the sensor to primary alcohol molecules, which were easily oxidized by the photogenerated hole.

Figure 2 shows a photograph of a microelectronic chip with an SnO_2 layer deposited on the heating element before (a) and after (b) the attachment of CdSe QDs. The red coloration of the SnO_2 layer after the attachment of CdSe QDs is clearly visible, which confirms the attachment of CdSe QDs to SnO_2 grains. Note that the sample after attaching of CdSe QDs was carefully washed with a solvent from unattached CdSe QDs. Figure 2 shows an SEM image of the SnO_2 –CdSe QDs nanocomposite. One can see the porous structure of the matrix, consisting of nanocrystalline aggregates of SnO_2 grains. TEM images of the agglomerated SnO_2 crystallites with CdSe QDs complemented with EDX analysis are shown in Figure 2d and Figure S3. The smaller CdSe nanoparticles with sizes of 3 nm (marked with arrows) were attached to the larger SnO_2 grains with sizes of 20–30 nm.



Figure 2. Photographs of microelectronic chip with nanocrystalline SnO_2 layer covered on a plate before (**a**) and after (**b**) attachment of CdSe QDs. (**c**) SEM image of porous nanocrystalline SnO_2 matrix. (**d**) TEM image of SnO_2 crystallites with attached CdSe QDs marked with arrows.

3.2. FTIR Analysis of Ligand Exchange

To cover CdSe QDs with the bifunctional ligand N-acetyl-L-cysteine, the native oleic acid (OA) ligand was exchanged. We performed the exchange for CdSe QDs as well as for the CdSe nanoplatelets (NPLs) used in liquid-phase photocatalysis experiments. The completeness of the ligand exchange for CdSe NPLs and QDs was analyzed using the FTIR method. Figure 3 demonstrates the FTIR spectra of the pure L-AcCys and samples of CdSe NPLs and QDs coated with native OA and exchanged L-AcCys ligands. The FTIR spectra of the initial OA-capped CdSe QDs and NPLs displayed intense (C–H) vibrations at 2856 and 2923 cm⁻¹ and less intense (=C–H) vibration at 3006 cm⁻¹. Native OA ligands had negatively charged carboxylate (COO⁻) groups with vibration bands at 1533 cm⁻¹ for both samples. The completeness of the ligand substitution for QDs and NPLs proved the disappearance of a series of intense (C–H) and (COO⁻) vibrations from oleic acid, and showed the absence of residual OA molecules attached to the surface of exchanged QDs. A summary of essential vibration assignments from the FTIR spectra is given in Table 1.



Figure 3. (a) FTIR spectra of free N-acetyl-L-cysteine ligand (violet line) and CdSe quantum dots with initial ligand of oleic acid (black line) and N-acetyl-L-cysteine (green line); (b) FTIR spectra of free L-AcCys ligand (violet line), CdSe NPLs with OA ligand (cyan line) and L-AcCys (dark blue line).

Assignments	N-Acetyl-L-Cysteine	QD_L-AcCys	NP_L-AcCys
$v_{as}(NH_2)$	3375	3376	3420
$v_{as}(CH_3)$	2902	2928	2936
$\nu_{\rm s}({\rm CH}_3)$	2809	2839	2848
$v_{as}(SH)$	2549	-	-
$v_{as}(C=O)$	1720	1720	-
ν _{as} (amide I)	1581	1640	1632
v_{as} (amide II)	1536	1541	1561
$v_{s}(C-H_{CH2})$	1413	1422	1429
$\nu_{\rm s}({\rm COO^-})$	1372	1378	1389

Table 1. Summary of essential vibration assignments from the FTIR spectra of N-acetyl-L-cysteine (clean), QD CdSe coated with N-acetyl-L-cysteine, and CdSe nanoparticles coated with N-acetyl-L-cysteine.

In the spectrum of pure L-AcCys (Figure 3, violet line) and the samples QDs_L-AcCys (Figure 3a) and NPL_L-AcCys (Figure 3b), the broadened band of about 3420 cm⁻¹ refers to -OH stretching vibrations, which can occur due to water absorbed by the tablet from the air during measurements. For the QDs_L-AcCys sample, 3375 cm⁻¹ band is attributed to valence vibrations of the NH₂ group, corresponding with the band of the same vibration of

pure L-AcCys. In comparison with pure L-AcCys, intense vibrations of (S-H) at 2549 cm⁻¹ disappear in the spectra of the sample QDs_L-AcCys, which points to the coordination of the ligand through the sulfhydryl group. The position of the (C=O) stretching vibration band of the carboxylic group ν (–COOH) at 1720 cm⁻¹ for QDs_L-AcCys coincides with a similar vibration band of the L-AcCys reference (Figure 3). At lower frequencies, L-AcCys has quite strong bands at 1581 and 1536 cm⁻¹, attributed to Amide I and Amide II bands, which were observed for QDs_L-AcCys sample with a shift into high frequencies.

For the CdSe NPLs sample coated with L-AcCys (Figure 3b), one can notice the valence vibrations of the NH₂ group (3420 cm⁻¹), as well as the Amide I (1632 cm⁻¹) and Amide II (1561 cm⁻¹) bands of the peptide group, with a shift into higher frequencies compared to pure L-AcCys. The disappearance of valence vibrations of (S-H) at 2549 cm⁻¹ and the (C=O) stretching vibration at 1720 cm⁻¹ in the spectra of NP_L-AcCys confirms the ligand coordination of the CdSe NPLs by these functional groups of L-AcCys.

3.3. Analysis of Optical Properties

The optical properties of the initial samples of QDs and NPLs coated with OA and the samples after ligand exchange with L-AcCys were studied by UV-vis spectroscopy. The absorbance spectra of CdSe_QD_OA (Figure 4a) exhibited absorption in the visible spectral range, with a sharp, low-energy excitonic transition at $\lambda = 564$ nm. This exitonic transition involved electronic transition from the 1s hole energy level to the lowest 1s electron level (1sh-1se). After the ligand exchange, the spectra of CdSe_QD_L-AcCys shifted to a longer wavelength ($\lambda = 566$ nm). Absorbance spectra of the CdSe_NP_OA are shown on Figure 4b, demonstrating pronounced narrow exciton transitions involving the heavy hole HH at the wavelength of 463 nm, the light hole LH (436 nm), and the spin-orbital SO bands (394 nm). After L-AcCys ligand exchange, the absorbance spectra of CdSe_L-AcCys NPLs demonstrated spectral shifts of both HH and LH exciton bands to longer wavelengths (Figure 4b). Furthermore, broadening exciton bands were found for NPLs coated with N-acetyl-L-cysteine compared to the as-grown CdSe_NP_OA sample.



Figure 4. (a) Absorbance spectra of CdSe QDs coated with native ligand OA (black line) and their modification after ligand exchange with L-AcCys (blue line); (b) absorbance spectra of CdSe NPLs with native ligand OA (dark blue line) and their modification after ligand exchange with L-AcCys (cyan line). Horizontal lines indicate the spectral shifts after ligand exchange.

The attachment of chiral L-AcCys ligand to CdSe NPLs and QDs was studied by circular dichroism (CD) spectroscopy. Figure 5 shows the typical CD spectra of CdSe NPLs and QDs coated with L-AcCys. The CD bands of NPLs coated with L-AcCys samples (Figure 5a) correlated quite well with the positions of the LH, HH, and SO transitions in

the absorption spectra. This confirms the exciton character of the induced CD bands. The most intense band of the CD corresponded to the HH-exciton and had a negative sign. For the sample of QDs covered with the chiral L-AcCys ligand (Figure 5b), CD with a lower intensity compared to CdSe_NP_L-AcCys and a shift of the CD band were also noticed.



Figure 5. CD spectra of (**a**) NP CdSe (dark blue line) and (**b**) QD CdSe (green line) samples coated with L-AcCys. Absorbance spectra are shown with dashed lines for comparison. Pointed lines show correspondence between CD and absorbance bands.

3.4. Sensor and Photocatalytic Properties

We investigated the sensor responses of the obtained nanocomposites to model gases under periodic photoexcitation with a yellow LED and a wavelength of 595 nm. This wavelength corresponded to the absorption of the lower-energy exciton maximum of CdSe_QD_L-AcCys, as shown in Figure 6a, and at the same time was not absorbed by the SnO₂ matrix. The sensor properties of the CdSe_QD_L-AcCys/SnO₂ nanocomposite were studied when detecting vapors of aliphatic alcohols-methanol, ethanol, and butanol, as well as acetaldehyde—for comparison. Figure 6a shows the sensor response of the CdSe_QD_L-AcCys/SnO₂ sample upon detection of 100 ppm methanol in dry nitrogen under periodic illumination. The periodic illumination mode was selected as 2 min LED off and 2 min LED on. It can be seen that the obtained CdSe_QD_L-AcCys/SnO₂ composite exhibited a photoresponse to the yellow LED that confirmed the photoexcited charge separation and the addition of electrons into the SnO_2 matrix corresponding to process (2). Moreover, when methanol molecules appeared, the photoresponse of the nanocomposite was modulated, and the value of S calculated by (1) increased. Since the irradiation intensity was fixed, the injection level by (2) was maintained. Thus, the increase in S clearly corresponded to the change in the charge balance and the decrease in the recombination level by processes (5) and (6), corresponding to the contribution of photochemical processes involving methanol molecules. Some drift of the base sensor resistance was observed, which was caused by the imbalance of accumulation/depletion of the SnO₂ matrix by photoexcited electrons. This could be eliminated by optimizing the ratio of the on/off times of the illumination [13]. Figure 6b shows the sensor response of the CdSe_QD_L- $AcCys/SnO_2$ nanocomposite compared to the pure SnO_2 matrix to 100 ppm of the set of analyte gases in a dry nitrogen environment. The enlarged region of resistance modulation is shown in the inset to Figure 6b. A clear sensor response to a series of aliphatic alcohols C_1 - C_4 can be seen, and with an increase in the length of the aliphatic chain, the sensor signal decreased, which corresponded to a decrease in the reactivity of the alcohols. In turn, the pure SnO₂ matrix at room temperature did not exhibit either a photoresponse when irradiated with LED or a sensor response to any of the studied analyte gases. The absence of

a photoresponse was due to the fact that the radiation energy with a wavelength of 595 nm was insufficient for the transition of an electron from the valence band to the conduction band for the pure SnO₂ matrix. It should also be noted that, in the absence of illumination, no sensor response was observed for the nanocomposite (Figure S4). Also, there was no sensor response of the CdSe_QD_L-AcCys/SnO₂ nanocomposite to acetaldehyde, as shown at the Figure 6b. That means that the sensor CdSe_QD_L-AcCys/SnO₂ has selectivity for alcohols that can be oxidized to another forms, compared to acetaldehyde, which represents the already-oxidized form of organic molecules.



Figure 6. (a) Typical sensor response of CdSe_QD_L-AcCys/SnO₂ nanocomposite to 100 ppm CH₃OH under periodic yellow LED excitation. (b) Sensor response on different organic molecules (concentration: 100 ppm) of CdSe_QD_L-AcCys/SnO₂ nanocomposites and pure SnO₂ matrix (green line). The insert shows the dynamic mode of photoactivation of the sensor material. The arrow pointing upward indicates illumination with yellow LED on; the arrow pointing downward indicates illumination off.

Figure 7a shows the concentration dependence of the sensor response of the CdSe_QD_L-AcCys/SnO₂ nanocomposite to methanol in the range of 100–1000 ppm. For comparison, the behavior of the pure SnO₂ matrix is shown. A regular increase in the sensor response to an increase in the concentration of the analyte in the gas phase was observed. With an increase in the concentration of methanol by 4 times, the sensor signal increased by 1.2 times. At the same time, the pure SnO₂ matrix did not exhibit a sensor response up to 1000 ppm methanol.

Figure 7b shows an enlarged section of the response to 765 ppm of methanol under periodic illumination for CdSe_QD_L-AcCys/SnO₂ nanocomposite. The measurements were carried out for 3 h in a methanol atmosphere and 3 h in pure nitrogen with 40 illumination cycles. In the first illumination cycle, the sensor response was at the maximum up to S = 0.4, then decreased to S = 0.2 and remained almost constant up to 40 cycles.



Figure 7. (a) Concentration dependence of sensor signal to 255–1020 ppm of CH₃OH for CdSe_QD_L-AcCys/SnO₂ nanocomposite (black line) and pure SnO₂ (green line). (b) Enlarged view of sensor response to 765 ppm of methanol under periodic illumination for CdSe_QD_L-AcCys/SnO₂ nanocomposite. (c) Sensor response to detection of CH₃OH (concentration 1020 ppm) of a series of CdSe_QD/SnO₂ composite materials coated with different ligands (L-AcCys—green line, OA—dark blue line, AcA—cyan line). The horizontal arrows show the correspondence between lines and axes.

Next, we studied the effect of the organic ligand on the surface of CdSe QDs on the sensory sensitivity of the composite material. For this purpose, CdSe_QD/SnO₂ composites with OA and AcA ligands of decreasing length compared to L-AcCys were prepared. The results of our measurement of the sensor's response to 100 ppm methanol are shown in Figure 7c. As can be seen, CdSe_QD_AcAc/SnO₂ had a higher sensor response compared to CdSe_QD_OA/SnO₂, which clearly indicates an increase in the response with a decrease in the ligand length. This confirms the contribution of photoexcited electron transfer to the formation of the sensor response. The CdSe_QD_L-AcCys/SnO₂ composite with a bifunctional ligand and the QD coupled to the surface of SnO₂ grains had the maximum response. It can be concluded that L-AcCys, which was selected in the work, is the most optimal ligand for creating a photoactivatable sensor.

To analyze the photochemical reactions, we carried out a model reaction of ethanol photooxidation in an inert medium in the liquid phase of dioxane for CdSe_NP_L-AcCys. The reaction products were analyzed after photoexcitation with a blue LED corresponding to the absorption of the lowest-energy exciton maximum for NPLs. Figure 8a shows the absorption spectra of the photocatalytic products depending on the time of ethanol photooxidation. It was found that photooxidation occurred with the formation of acetaldehyde and acetic acid. The formation of acetaldehyde corresponded to process (5) and clearly confirmed the scheme proposed by us. Based on process (5), a selective response to molecules of primary aliphatic alcohols could be expected. We tested the selectivity to primary alcohols by comparing the response of the CdSe_QD_L-AcCys/SnO₂ nanocomposite to methanol and acetaldehyde, as shown in Figure 8b. As can be seen, a sensor response was observed only to the primary alcohol, while there was no response to acetaldehyde. The absence of a sensor response to acetaldehyde indicated the absence of photooxidation, unlike aliphatic alcohols, which also confirmed our proposed scheme ((5) and (6)). Thus, the presented results indicate the selectivity of our proposed sensor to primary alcohols among other VOCs.



Figure 8. (a) Absorbance spectra of products produced after photooxidation of ethanol with CdSe NPLs coated with L-AcCys ligand; (b) sensor responses of CdSe_QD_L-AcCys/SnO₂ nanocomposite to 100 ppm of ethanol (blue line) and 100 ppm of acetaldehyde (dark blue line).

4. Conclusions

We demonstrated a concept of a photoactivatable gas sensor for the selective detection of primary alcohol molecules at room temperature through photooxidation by photoexcited holes instead of reactions with chemisorbed oxygen. We designed a resistive-type sensor using CdSe QDs coupled to a wide-gap SnO₂ semiconductor matrix. We demonstrated the sensor response of the CdSe QDs-SnO₂ nanocomposite sensor to a series of aliphatic alcohols C1-C4 under photoexcitation by a yellow LED in the absence of heat at room temperature. With an increase in the aliphatic chain length of alcohol molecules, the sensor signal decreased, which corresponded to a decrease in the reactivity of the alcohols. The measurements confirmed a stable response for 3 h in 100 ppm of methanol and 3 h in pure nitrogen, with a photoexcitation modulation of 40 times. Analysis of the concentration dependence of the sensor response to 100-1000 ppm methanol showed an increase in the sensor response with the increase in the analyte concentration in the gas phase, and with an increase in the concentration of methanol in the gas phase by 4 times, the sensor signal increased by 1.2 times. An analysis of the sensor selectivity showed the absence of a response to 100 ppm acetaldehyde as a model VOC. We believe that the proposed concept of sensor operations based on the photochemical reaction of primary alcohols via photoactivated QD-SnO₂ charge transfer will open up new ways to design photoactivated sensors without heating for the detection of VOCs.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/chemosensors13010020/s1. Figure S1. The emission spectrum of the yellow LED. Figure S2. Schematization of the experimental setup. Figure S3. (a) HAADF-STEM image of the SnO₂ matrix with attached CdSe QDs; and (b) EDX spectrum from the selected area confirming a presence of Cd and Se. Figure S4. Typical sensor response of CdSe_QD_L-AcCys/SnO₂ nanocomposite to 100 ppm CH₃OH without irradiation of the LED. Author Contributions: Conceptualization, R.B.V.; methodology, R.B.V., M.N.R., and V.B.P.; formal analysis, M.Y.S., V.B.P., and R.B.V.; investigation, M.Y.S., D.A.K., and V.B.P.; resources, O.G.S.; data curation, M.Y.S., D.A.K., and V.B.P.; writing—original draft preparation, R.B.V., M.Y.S., and V.B.P.; writing—review and editing, R.B.V. and M.N.R.; project administration, O.G.S.; funding acquisition, O.G.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by a grant from the Ministry of Science and Higher Education of the Russian Federation, grant number 075-15-2024-646.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in the study are included in the article; further inquiries can be directed to the corresponding author.

Acknowledgments: FTIR experiments were carried out using equipment purchased with funds from the Lomonosov Moscow State University Program of the Development.

Conflicts of Interest: The authors declare no conflicts of interest.

References

- Efros, A.L.; Brus, L.E. Nanocrystal quantum dots: From discovery to modern development. ACS Nano 2021, 15, 6192–6210. [CrossRef]
- 2. Pelayo García de Arquer, F.; Talapin, D.V.; Klimov, V.I.; Arakawa, Y.; Bayer, M.; Sargent, E.H. Semiconductor quantum dots: Technological progress and future challenges. *Science* **2021**, *373*, eaaz8541. [CrossRef]
- Liu, M.; Yazdani, N.; Yarema, M.; Jansen, M.; Wood, V.; Sargent, E.H. Colloidal quantum dot electronics. *Nat. Electron.* 2021, 4, 548–558. [CrossRef]
- 4. Agarwal, K.; Rai, H.; Mondal, S. Quantum dots: An overview of synthesis, properties, and applications. *Mater. Res. Express* 2023, 10, 062001. [CrossRef]
- Kovalenko, M.V.; Manna, L.; Cabot, A.; Hens, Z.; Talapin, D.V.; Kagan, C.R.; Klimov, V.I.; Rogach, A.L.; Reiss, P.; Milliron, D.J.; et al. Prospects of nanoscience with nanocrystals. ACS Nano 2015, 9, 1012–1057. [CrossRef] [PubMed]
- Wagner, A.M.; Knipe, J.M.; Orive, G.; Peppas, N.A. Quantum dots in biomedical applications. *Acta Biomater.* 2019, 94, 44–63. [CrossRef] [PubMed]
- Heuer-Jungemann, A.; Feliu, N.; Bakaimi, I.; Hamaly, M.; Alkilany, A.; Chakraborty, I.; Masood, A.; Casula, M.F.; Kostopoulou, A.; Oh, E.; et al. The Role of Ligands in the Chemical Synthesis and Applications of Inorganic Nanoparticles. *Chem. Rev.* 2019, 119, 4819–4880. [CrossRef] [PubMed]
- Mirzaei, A.; Kordrostami, Z.; Shahbaz, M.; Kim, J.-Y.; Kim, H.W.; Kim, S.S. Resistive-Based Gas Sensors Using Quantum Dots: A Review. Sensors 2022, 22, 4369. [CrossRef] [PubMed]
- Li, M.; Voznyy, O.; Hu, L.; Fu, Q.; Zhou, D.; Xia, Z.; Sargent, E.H.; Tang, J. Physically flexible, rapid-response gas sensor based on colloidal quantum dot solids. *Adv. Mater.* 2014, 26, 2718–2724. [CrossRef] [PubMed]
- 10. Mitri, F.; De Iacovo, A.; De Luca, M.; Pecora, A.; Colace, L. Lead sulphide colloidal quantum dots for room temperature NO₂ gas sensors. *Sci. Rep.* **2020**, *10*, 12556. [CrossRef]
- 11. Hu, Z.; Zhou, L.; Li, L.; Liu, J.; Li, H.-Y.; Song, B.; Zhang, J.; Tang, J.; Liu, H. Stabilization of PbS colloidal-quantum-dot gas sensors using atomic-ligand engineering. *Sens. Actuators B Chem.* **2023**, *388*, 133850. [CrossRef]
- 12. Hu, Z.; Zhou, L.; Li, L.; Ying, B.; Zhao, Y.; Wang, P.; Li, H.; Zhang, Y.; Liu, H. Quantum Dots-Sensitized High Electron Mobility Transistor (HEMT) for Sensitive NO₂ Detection. *Chemosensors* **2023**, *11*, 252. [CrossRef]
- Vasiliev, R.; Babynina, A.; Maslova, O.; Rumyantseva, M.; Ryabova, L.; Dobrovolsky, A.; Drozdov, K.; Khokhlov, D.; Abakumov, A.; Gaskov, A. Photoconductivity of nanocrystalline SnO₂ sensitized with colloidal CdSe quantum dots. *J. Mater. Chem. C* 2013, 1, 1005–1010. [CrossRef]
- 14. Li, Q.; Wu, K.; Zhu, H.; Yang, Y.; He, S.; Lian, T. Charge Transfer from Quantum-Confined 0D, 1D, and 2D Nanocrystals. *Chem. Rev.* 2024, 124, 5695–5763. [CrossRef]
- Chizhov, A.; Rumyantseva, M.; Vasiliev, R.; Filatova, D.; Drozdov, K.; Krylov, I.; Marchevsky, A.; Karakulina, O.; Abakumov, A.; Gaskov, A. Visible light activation of room temperature NO₂ gas sensors based on ZnO, SnO₂ and In₂O₃ sensitized with CdSe quantum dots. *Thin Solid Film.* 2016, *618*, 253–262. [CrossRef]
- Chizhov, A.; Vasiliev, R.; Rumyantseva, M.; Krylov, I.; Drozdov, K.; Batuk, M.; Hadermann, J.; Abakumov, A.; Gaskov, A. Light-Activated Sub-ppm NO₂ Detection by Hybrid ZnO/QD Nanomaterials vs. Charge Localization in Core-Shell QD. *Front. Mater.* 2019, *6*, 231. [CrossRef]

- 17. Chen, R.; Wang, J.; Xia, Y.; Xiang, L. Near infrared light enhanced room-temperature NO₂ gas sensing by hierarchical ZnO nanorods functionalized with PbS quantum dots. *Sens. Actuators B Chem.* **2018**, 255, 2538–2545. [CrossRef]
- 18. Jaiswal, J.; Sanger, A.; Tiwari, P.; Chandra, R. MoS₂ hybrid heterostructure thin film decorated with CdSe quantum dots for room temperature NO₂ gas sensor. *Sens. Actuators B Chem.* **2020**, *305*, 127437. [CrossRef]
- Tang, S.-Y.; Yang, C.-C.; Su, T.-Y.; Yang, T.-Y.; Wu, S.-C.; Hsu, Y.-C.; Chen, Y.-Z.; Lin, T.-N.; Shen, J.-L.; Lin, H.-N.; et al. Design of core–shell quantum dots–3d WS2 nanowall hybrid nanostructures with high-performance bifunctional sensing applications. ACS Nano 2020, 14, 12668–12678. [CrossRef] [PubMed]
- Cao, Q.; Feng, J.; Chang, K.T.; Liang, W.; Lu, H. Emerging Opportunities of Colloidal Quantum Dots for Photocatalytic Organic Transformations. *Adv. Mater.* 2024, 2409096. [CrossRef]
- Yuan, Y.; Jin, N.; Saghy, P.; Dube, L.; Zhu, H.; Chen, O. Quantum Dot Photocatalysts for Organic Transformations. J. Phys. Chem. Lett. 2021, 12, 7180–7193. [CrossRef] [PubMed]
- 22. Wu, H.-L.; Qi, M.-Y.; Tang, Z.-R.; Xu, Y.-J. Semiconductor quantum dots: A versatile platform for photoredox organic transformation. J. Mater. Chem. A 2023, 11, 3262–3280. [CrossRef]
- 23. Li, J.-Y.; Li, Y.-H.; Qi, M.-Y.; Lin, Q.; Tang, Z.-R.; Xu, Y.-J. Selective Organic Transformations over Cadmium Sulfide-Based Photocatalysts. *ACS Catal.* 2020, *10*, 6262–6280. [CrossRef]
- 24. Chen, Y.; Yu, S.; Fan, X.-B.; Wu, L.-Z.; Zhou, Y. Mechanistic insights into the influence of surface ligands on quantum dots for photocatalysis. *J. Mater. Chem. A* 2023, *11*, 8497–8514. [CrossRef]
- 25. Chakraborty, I.N.; Roy, P.; Pillai, P.P. Visible Light-Mediated Quantum Dot Photocatalysis Enables Olefination Reactions at Room Temperature. *ACS Catal.* **2023**, *13*, 7331–7338. [CrossRef]
- Xi, Z.-W.; Yang, L.; Wang, D.-Y.; Feng, C.-W.; Feng, C.-W.; Qin, Y.; Shen, Y.-M.; Pu, C.; Peng, X. Visible Light Induced Reduction and Pinacol Coupling of Aldehydes and Ketones Catalyzed by Core/Shell Quantum Dots. J. Org. Chem. 2021, 86, 2474–2488. [CrossRef]
- Dabbous, A.; Bauer, P.; Marcucci, C.; Périé, S.; Gahlot, S.; Lombard, C.; Caillat, S.; Ravanat, J.-L.; Mouesca, J.-M.; Kodjikian, S.; et al. Hybrid CdSe/ZnS Quantum Dot–Gold Nanoparticle Composites Assembled by Click Chemistry: Toward Affordable and Efficient Redox Photocatalysts Working with Visible Light. ACS Appl. Mater. Interfaces 2023, 15, 56167–56180. [CrossRef]
- 28. Korotcenkov, G.; Brinzari, V.; Pronin, I.A.; Ham, M.H.; Cho, B.K. Metal Oxides for Application in Conductometric Gas Sensors: How to Choose? *Solid State Phenom.* **2017**, *266*, 187–195. [CrossRef]
- Vasiliev, R.B.; Ryabova, L.I.; Rumyantseva, M.N.; Gaskov, A.M. Inorganic structures as materials for gas sensors. *Russ. Chem. Rev.* 2004, 73, 939. [CrossRef]
- 30. Barsan, N.; Weimar, U. Conduction Model of Metal Oxide Gas Sensors. J. Electroceramics 2001, 7, 143–167. [CrossRef]
- 31. Dey, A. Semiconductor metal oxide gas sensors: A review. Mater. Sci. Eng. B 2018, 229, 206-217. [CrossRef]
- Kurtina, D.A.; Garshev, A.V.; Vasil'eva, I.S.; Shubin, V.V.; Gaskov, A.M.; Vasiliev, R.B. Atomically-Thin Population of Colloidal CdSe Nanoplatelets: Growth of Rolled-up Nanosheets and Strong Circular Dichroism Induced by Ligand Exchange. *Chem. Mater.* 2019, 31, 9652–9663. [CrossRef]
- 33. Kurtina, D.A.; Grafova, V.P.; Vasil'eva, I.S.; Maksimov, S.V.; Zaytsev, V.B.; Vasiliev, R.B. Induction of Chirality in Atomically Thin ZnSe and CdSe Nanoplatelets: Strengthening of Circular Dichroism via Different Coordination of Cysteine-Based Ligands on an Ultimate Thin Semiconductor Core. *Materials* 2023, 16, 1073. [CrossRef] [PubMed]
- 34. Skrypnik, M.Y.; Kurtina, D.A.; Karamysheva, S.P.; Stepanidenko, E.A.; Vasil'eva, I.S.; Chang, S.; Lebedev, A.I.; Vasiliev, R.B. Menthol-Induced Chirality in Semiconductor Nanostructures: Chiroptical Properties of Atomically Thin 2D CdSe Nanoplatelets Capped with Enantiomeric L-(-)/D-(+)-Menthyl Thioglycolates. *Nanomaterials* 2024, 14, 1921. [CrossRef] [PubMed]
- Ye, C.; Zhang, D.-S.; Chen, B.; Tung, C.-H.; Wu, L.-Z. Interfacial Charge Transfer Regulates Photoredox Catalysis. ACS Cent. Sci. 2024, 10, 529–542. [CrossRef]
- Zhao, L.-M.; Meng, Q.-Y.; Fan, X.-B.; Ye, C.; Li, X.-B.; Chen, B.; Ramamurthy, V.; Tung, C.-H.; Wu, L.-Z. Photocatalysis with Quantum Dots and Visible Light: Selective and Efficient Oxidation of Alcohols to Carbonyl Compounds through a Radical Relay Process in Water. *Angew. Chem. Int. Ed.* 2017, 56, 3020–3024. [CrossRef]
- 37. Yang, X.; Su, Y.; Wang, T.; Hu, Y.; Li, Y.; Xie, W. Water enhanced photo-oxidation of alcohols on colloidal quantum dots. *Green Chem.* 2024, *26*, 7206–7211. [CrossRef]
- 38. Lee, S.G.; Kang, M.J.; Park, M.; Kim, K.-J.; Lee, H.; Kim, H.S. Selective photocatalytic conversion of benzyl alcohol to benzaldehyde or deoxybenzoin over ion-exchanged CdS. *Appl. Catal. B Environ.* **2022**, *304*, 120967. [CrossRef]
- 39. An, S.; Kang, M.J.; Lee, H.; Kim, H.S. Tunable Selectivity of Photocatalytic Benzyl Alcohol Transformation over Ag-Ion-Exchanged CdS Nanowires. *ACS Sustain. Chem. Eng.* **2023**, *11*, 4364–4373. [CrossRef]

- 40. Mureithi, A.W.; Sun, Y.; Mani, T.; Howell, A.R.; Zhao, J. Impact of hole scavengers on photocatalytic reduction of nitrobenzene using cadmium sulfide quantum dots. *Cell Rep. Phys. Sci.* **2022**, *3*, 100889. [CrossRef]
- 41. McClelland, K.P.; Weiss, E.A. Selective Photocatalytic Oxidation of Benzyl Alcohol to Benzaldehyde or C–C Coupled Products by Visible-Light-Absorbing Quantum Dots. *ACS Appl. Energy Mater.* **2019**, *2*, 92–96. [CrossRef]

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