Ag-Vanadates/GO Nanocomposites by Aerosol-Assisted Spray Pyrolysis: Preparation and Structural and Electrochemical Characterization of a Versatile Material

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ABSTRACT: In this article, we describe the deposition by aerosol-assisted spray pyrolysis of different types of silver vanadate nanocomposites with and without graphene oxide (GO) on different substrates (carbon paper (CP) and fluorine-doped tin oxide (FTO)). When deposited on CP, different amounts of GO were added to the Ag and V precursor solution to study the effect of GO on the physicochemical properties of the resulting Ag-vanadate. It is shown that the addition of GO leads mainly to the formation of nanoparticles of the Ag,V,O₁₁ phase, whereas Ag₃V₄O₁₁ and Ag₂VO₄ are obtained without the addition of GO. The morphology and chemical properties of the composites were determined by scanning and transmission electron microscopies, X-ray diffraction, X-ray photoemission spectroscopy, and UV–visible and Raman spectroscopies. In addition, the photoelectrochemical (PEC) properties of such composites were studied by CV, linear sweep voltammetry, and electrochemical impedance spectroscopy. The ideal Ag₂V₂O₇ and GO ratio was optimized for obtaining higher photocurrent values and a good stability. The results showed that the presence of GO improves the electrical conductivity of the catalyst layer as well as the electron injection from the oxide to the electrode surface. The deposition of pure Ag₃V₄O₁₁ on FTO does not lead to samples with stable PEC performances. Samples grown on CP supports showed an efficient electrochemical detection of small amounts of ethylenediamine in water solution.

INTRODUCTION

Silver vanadates, especially in the form of α-Ag₃V₄O₁₁ and AgVO₄, are photocatalysts characterized by a sufficiently large band gap (ca. 2.0–2.2 eV\(^{1–6}\)), potentially stable at water oxidation potentials due to the high oxidation state of V and the monovalent preference of Ag. Other Ag-vanadates, like Ag₃V₄O₁₁, have been studied and used as a cathode material in Li-ion batteries\(^9\) and, more recently, as active materials in gas sensing devices. In particular, nanoribbons of Ag₃V₄O₁₁ were used in the detection of amines and alcohols in the gas phase with good sensitivity.\(^8\) Nevertheless, up to now, the studies of these materials as photocatalysts have focused on particles dispersed in water, and most of them have addressed dye degradation. The particles are usually synthesized by hydrothermal methods or simple precipitation. Nevertheless, these experimental conditions (samples in the powder form) make difficult the accurate measurement of important quantities such as flat-band potential, photocurrent onset potential, and the photocurrent as a function of potential. α-Ag₃V₄O₁₁ thin films, like other vanadates, can be difficult to prepare by standard growth techniques (CVD and sputtering, for example, because of the difficulties in obtaining a definite stoichiometry), but very recently a study by Chemelewski et al. described the successive ionic layer adsorption and reaction (SILAR) growth of α-Ag₃V₄O₁₁ thin films and their characterization for photoelectrochemical water splitting (PEC-WS).\(^11\) The results of this study demonstrate that the as-grown material is characterized by p-type conductivity and therefore cannot be used as a photoanode. However, an annealing treatment in air up to 300 °C introduces n-type conductivity. Unfortunately, the resulting n-type behavior is unstable under photocatalytic water oxidation conditions, so that the photocurrent continuously decreases with a corresponding anodic shift of the flat-band potential. The authors interpreted this behavior to be due to the removal of oxygen vacancies by photo-oxidation. This hypothetical self-oxidation is also in agreement with the
evidence that hole scavengers are not able to increase the measured photocurrent. The conclusion of this study was that, although the results are not promising for the outlook of Ag-Ag3VO4 as a PEC-WS material per se, its low band gap still makes it interesting for developing nanosystems characterized by a more efficient charge extraction by further nanostructuring. This statement and the lack in the literature of methods for preparing controlled nanostructured thin films led us to investigate the use of aerosol-assisted spray pyrolysis as an alternative, easy, and highly scalable technique to deposit Ag-vanadates (Ag3VO4) on conductive substrates, either conventional carbon materials or transparent conductive oxides (such as fluorine-doped tin oxide (FTO)), to improve the photocurrent stability and charge extraction. Although probably not suitable as PEC-WS materials yet, Ag-vanadates are attractive materials for the sensing of organics in a water solution taking advantage of their n-type conductivity that allows their use as photoanodes enhancing the detection sensitivity as already done in the case of TiO2 thin films coupled with Cu2O nanoparticles. Moreover, the aerosol-assisted spray pyrolysis allows depositing a large variety of nanocomposite materials containing graphene oxide (GO) or reduced GO by a simple “one-pot” procedure. The rationale behind the addition of this second component lies in the possibility to improve the electrical contact among the oxide particles with the substrate, thus enhancing the injection of electrons on the electrode surface and therefore the PEC performances. Also, the presence of GO helps to obtain nanocomposites with a high surface area, by increasing the number of nucleation sites, acting as a sort of “fishing net” configuration and eventually inducing the formation of different crystal phases. We used a precursor solution (VO4x− and Ag+) in which Ag+ ions are kept solvated by complexation with NH3. The consequent alkaline pH also allows the stabilization of GO sheets forming a stable suspension. We have deposited Ag3VO4 NPs by the aerosol-assisted method with different amounts of GO on a carbon paper (CP) and on an FTO glass. After the characterization of the materials by Raman spectroscopy, X-ray photoemission spectroscopy (XPS), wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) measurements, we have verified that when GO is added to the mixture the main phase is Ag3VO4.&GO composite materials on the CP support. Moreover, the presence Ag+ ions in these materials makes them interesting candidates for the electrochemical detection of ammines.

**RESULTS AND DISCUSSION**

**Material Characterization.** In Figure 1, we report the SEM images of the deposits on CP obtained from pure Ag3VO4, solution and Ag3VO4.&GO 0.75 mg/mL. In the former case, it is well evident (Figure 1a) that the carbon fibers of the CP are coated with particles of very different shapes and sizes, whereas in the latter (Figure 1b,c) the particles are apparently smaller and more uniformly distributed. As evident from Figure 1b,c, the GO sheets are coating some areas of the carbon fibers like a “blanket”. In Figure 1c, the typical wrinkles of GO sheets are also clearly visible. In Figure 1d, the morphology of the deposit obtained on the FTO glass is shown. The particles have a rather large size distribution (30–200 nm) with spherical particles growing on platelet-like larger crystals.

Figure 2 shows the results from XPS and WAXD measurements on the Ag3VO4.&GO 0.75 mg/mL sample. The V 2p signals together with the O 1s peak are reported in Figure 2a. The V 2p3/2 signal is found, as expected, at 517.6 eV (V2+), and no other component is present. The O 1s peak (Figure 2a), instead, can be fitted with at least two components: the main one at 530.6 eV, corresponding to V=O bonds, and the component at about 532.5 eV, which can be assigned to −OH and −COOH groups in GO and adsorbed water molecules. Because the O 1s peak of GO is also characterized by a main component at 530.5 eV, it is not possible (spectra not reported) to calculate the accurate stoichiometry (V/O ratio). In any case, if only the first O 1s component is considered, the resulting stoichiometry would be V3O3.5. However, the Ag MNN Auger peak (Figure 2b) shows, very clearly, the presence of both Ag+ and metallic Ag. The fitting of the Ag MNN peak allows us to estimate the Ag+/Ag ratio (1:1), and consequently, the Ag+/V ratio in the vanadate was found to be 0.5. The presence of metallic Ag is also verified by WAXD (Figure 2c): the X-ray diffraction data show the presence of metallic Ag, Ag3VO4, and Ag2V4O11. The presence of the peak at 2θ = 29.4° is clearly attributable to the presence of Ag3VO4 (see also Raman spectra discussion below), whose structure is reported in Figure 2d. This peak should correspond to reflection from the (203) planes, which is particularly evident in the case of Ag3VO4 prepared at alkaline pH, as in our case. The intense peaks at 2θ = 38.1 and 44.3° confirm the presence of metallic Ag. It is noteworthy that in the case of the deposit obtained without GO, the peaks at 2θ = 31 and 32.4°, which can be attributed to Ag3VO4, are more intense, indicating that the presence of GO leads to a higher Ag3VO4.&GO ratio. To obtain the weight ratio of the different phases, we applied the quantitative analysis of the diffraction patterns of powder mixtures, which allows obtaining, considering the different absorption coefficients of each phase, the corresponding fraction by weight. To achieve greater accuracy, we...
proceeded to the deconvolution of the peaks, by the application of the least-squares fit elaborated by Hindeleh and Johnson and to the determination of the intensity, calculated as the area subtended by each peak. The results of this analysis are given in Table 1.

Deposits obtained on FTO, after annealing at 250 °C for 1 h, show only the presence of the Ag$_2$V$_4$O$_{11}$ phase, suggesting that this substrate favors the formation of such phases.

The presence of Ag$_2$V$_4$O$_{11}$ as the main component is confirmed by TEM images. In fact, as reported in the literature, Ag$_2$V$_4$O$_{11}$ crystals are commonly found with a nanostripe or needle shape, as can be clearly seen in the images reported in Figure 3. In Figure 3b, the Ag$_2$V$_4$O$_{11}$ needles can be clearly seen together on a GO sheet with typical wrinkles. The same crystalline shape is also found in the sample without GO. The darker spots correspond to metallic Ag nanoparticles and Ag$_3$VO$_4$, whose presence is also confirmed in the UV−vis spectra obtained on FTO glass. In Figure 3c,d, we report the EDX maps together with the corresponding SEM images acquired on Ag$_x$VO$_y$ and Ag$_x$VO$_y$&GO 0.75 mg/mL after electrochemical work. In the case of the material deposited without GO, it is evident that large needles and stripes are grown on the CP surface together with smaller particles. However, when the growth is performed with GO, the dimension of the particles is more uniform, and "worm-like" structures appear probably due to the presence of the thin GO blanket. The Ag/V atomic ratio (which includes metallic Ag) determined by EDX is 3:5 in the case of Ag$_x$VO$_y$ and 1:1 for Ag$_x$VO$_y$&GO 0.75 mg/mL. The UV−vis spectra of Ag$_x$VO$_y$ and Ag$_x$VO$_y$&GO 0.75 mg/mL grown on FTO and presented in Figure 2.
in Figure 4, are similar, and the main component, at about 430−450 nm, is overlapping with localized surface plasmon resonances (LSPRs) of Ag NPs embedded in the crystalline nanostripes or needles of Ag$_2$V$_4$O$_{11}$. These resonances are typically found at about 400 nm in the case of NPs with a diameter of 30−40, whereas a shift toward a longer wavelength is characteristic of larger aggregates. The absorption maximum, at 434 nm, due to the presence of Ag$_2$V$_4$O$_{11}$ can be seen in the figure inset, where the UV−vis spectrum of Ag$_2$V$_4$O$_{11}$ obtained by hydrothermal synthesis and drop-casting on glass from an ethanol suspension is reported.$^{21}$ It is important to highlight that the UV−vis spectra were acquired after running several cyclic voltammetry (CV) cycles (0.0−0.9 V vs SHE) to dissolve most of the metallic Ag.

In Figure 5, we report the Raman spectra obtained for samples deposited on CP and FTO using Ag$_x$VO$_y$&GO precursor solutions with different amounts of GO. The spectra of the samples with GO, normalized to the intensity at 840 cm$^{-1}$ (excluding the sample containing 1 mg/mL GO). An offset is applied to the spectra for clarity. The Raman spectra acquired after the electrochemical measurements are reported as gray dotted lines.

Figure 3. TEM images of Ag$_x$VO$_y$ (a) and Ag$_x$VO$_y$&GO 0.75 mg/mL (b). Ag$_x$V$_4$O$_{11}$ crystals are characterized by the needle-like shape. Darker spots are due to residual Ag NPs or small amounts of Ag$_x$VO$_y$ (Ag$_x$VO$_y$ sample). (c, d) SEM images and EDX element maps are reported. Large needle-like particles are visible for the Ag$_x$VO$_y$ sample: smaller structures are found in the case of Ag$_x$VO$_y$&GO 0.75 mg/mL.

Figure 4. UV−vis spectra of Ag$_x$VO$_y$ and Ag$_x$VO$_y$&GO deposited on FTO. Both spectra have been obtained after running several CV cycles (0.0−0.9 V vs SHE) to dissolve most of the metallic Ag. The arrows indicate absorption due to Ag$_x$VO$_y$ (430−450 nm) and LSPR of residual Ag NPs (400 nm). In the inset, the UV−vis spectrum of Ag$_2$V$_4$O$_{11}$, obtained by hydrothermal synthesis and drop-casting on a soda-lime glass from an ethanol suspension is reported.

Figure 5. Raman spectra of Ag$_2$V$_4$O$_{11}$ and of samples containing Ag$_x$VO$_y$&GO with various amounts. The spectra are normalized to the intensity at 840 cm$^{-1}$ (excluding the sample containing 1 mg/mL GO). An offset is applied to the spectra for clarity. The Raman spectra acquired after the electrochemical measurements are reported as gray dotted lines.
Raman frequencies are typical of octahedrally coordinated vanadium oxides containing polyanions like V$_x$O$_{2x-}$ or V$_{10}$O$_{28}^-$ . In fact, there are silver vanadates, known as Ag-vanadate bronzes, that are structures deriving from $\beta$-Ag$_2$V$_4$O$_{11}$. The structure of Ag$_2$V$_4$O$_{11}$ consists of infinite chains with the formula [V$_6$O$_{12}$]$_x$. These chains, of a zigzag shape, are double and consist of an edge sharing VO$_6$ distorted octahedra with the V=O bonds distributed in four domains, with the shortest one, a vanadyl bond, equal to 1.67 Å. As well described in the following section, we will assume such a hypothesis when discussing the different electronic properties in the synthesized materials, which can provide different electronic properties in the synthesized materials under polarization conditions. The flat-band position is about 0.95 V. The n-type conductivity is somewhat surprising and opposite to what is usually expected in the case of typical photocatalysts such as Ag$_2$VO$_4$ or Ag$_3$VO$_4$. In particular, Ag$_3$VO$_4$ is the stable phase at room temperature, is expected to be a p-type semiconductor according to the theoretical predictions and confirmed by optical and electrical measurements, because the energy of formation of oxygen vacancies is high and oxygen vacancies do not compensate for the Ag cation vacancies. As a result, holes are formed and therefore Ag-vanadates are usually characterized by a p-type conductivity.

In conclusion of the whole set of physicochemical characterizations, we have strong evidence for the prevalent presence of Ag$_2$V$_4$O$_{11}$ species in the deposited films. In the following section, we will assume such a hypothesis when discussing the PEC measurements.

Mott–Schottky Plots, PEC Measurements, and Electrochemical Sensing of Ethylenediamine. The idea behind the use of Ag-vanadates as electrochemical sensors for the detection of amines is that this material is characterized by (1) surface sites that are effective for the adsorption of N atoms through nonbonded electron pairs (Ag--O sites), (2) a certain number of surface sites at which anodic discharge of water, with the generation of OH radicals, occurs at sufficiently low overpotentials (usually metal oxides or composites of metal oxides) and a good stability at alkaline pH. The mechanism proposed in the literature for the oxidative detection of aliphatic amines, according to the above-mentioned requisites, is the following:

$$S[^-] + H_2O \rightarrow S[OH] + H^+ + e^-$$

They present a typical positive slope characteristic of an n-type behavior. The imperfect linear shape of the plot might be due to the presence of different phases, as already indicated by the Raman and X-ray diffraction (XRD) data, which can provide different electronic properties in the synthesized materials under polarization conditions. The flat-band position is about 0.95 V. The n-type conductivity is somewhat surprising and opposite to what is usually expected in the case of typical photocatalysts such as Ag$_2$VO$_4$ or Ag$_3$VO$_4$. In particular, Ag$_3$VO$_4$ is the stable phase at room temperature, is expected to be a p-type semiconductor according to the theoretical predictions and confirmed by optical and electrical measurements, because the energy of formation of oxygen vacancies is high and oxygen vacancies do not compensate for the Ag cation vacancies. As a result, holes are formed and therefore Ag-vanadates are usually characterized by a p-type conductivity.

Danzhen Li, who synthesized Ag$_2$V$_4$O$_{11}$ by a hydrothermal procedure at low pH (between 4 and 6), obtained a p-type behavior as well, caused by Ag vacancies in the lattice with quite good photocatalytic performances under visible light. Mullins and co-workers prepared Ag$_2$VO$_4$ thin...
films by SILAR obtaining an n-type conductivity after a mild annealing of the deposit at temperatures slightly higher than 150 °C. They measured an increase in the anodic photocurrent up to annealing temperatures of 300 °C, but with a very quick decay of it after only 30 s. This decay was also accompanied by a shift of the flat-band potential to more positive values. The authors concluded that the high values of the initial photocurrents were actually due to the removal of oxygen vacancies created by the annealing procedure. An n-type conductivity was instead found in the case of Ag\textsuperscript{+} ions contained in each sample. The amount of Ag\textsuperscript{+}, after the introduction of GO, can be obtained by multiplying for a conversion factor = 0.195 C/mg Ag\textsubscript{2}V\textsubscript{4}O\textsubscript{11} (C stays for coulomb).

In conclusion, the amount of Ag\textsuperscript{+} determined as metallic Ag contained in the deposit, as shown by XPS and WAXD measurements, is completely dissolved as soon as potentials above 0.5 V versus SHE are applied. To be sure that each sample was free from metallic Ag, several CV cycles were performed (between 0.0 and 0.9 V) before photocurrent determination. Under these conditions, with a pH solution of 8.3, no precipitation of Ag\textsubscript{2}O or Ag\textsubscript{2}CO\textsubscript{3} on the carbon fibers can occur. In conclusion, the amount of Ag\textsuperscript{+} determined as described above corresponds only to the Ag\textsuperscript{+} ions contained in the vanadate. The results of this normalization procedure are reported in Figure 7, wherein it is clear that the best compromise is obtained by using the solution containing 0.75 mg/mL of GO.

The effect of GO on the charge transfer resistance at the electrolyte/electrode interface can be evaluated by electrochemical impedance spectroscopy (EIS) measurements obtained on a pure Ag\textsubscript{3}VO\textsubscript{4} sample and on the one containing 0.75 mg/mL of GO. The Nyquist plots reported in Figure 8 indicate that, apart from the lower resistance of the sample containing GO, the pure Ag\textsubscript{3}VO\textsubscript{4} has a capacitive behavior with a very high resistance.

In Figure 9, we show the Bode plot obtained from 10\textsuperscript{4} to 10\textsuperscript{-1} Hz. The EIS spectra show two time constants, differing in the frequency domain, wherein higher frequencies can be assigned to the double-layer capacitance/charge transfer resistance system, in series with a capacitance/resistance corresponding with the electronic transfer of a thicker inner layer. It is evident that the polarization resistance of the sample containing GO is about two-thirds of that containing pure Ag\textsubscript{3}VO\textsubscript{4} (resistance extracted from the Bode plot at the lowest frequency).

We have simulated the EIS measurements with equivalent circuits, as reported in Figure 9. In the simulation, R\textsubscript{0} represents the solution resistance. Y\textsubscript{1} and Y\textsubscript{2} represent the charge transfer process between the film and the electrolyte within the double layer on the electrode, whereas Y\textsubscript{3} and R\textsubscript{2} represent the capacity and resistance of the film. In both time constants, capacitances were substituted by constant phase elements (CPEs). To take into account their nonideal character, the Brug equation was used to convert CPE into capacitances. The obtained values are, in the case of the pure oxide: C\textsubscript{film} = 1.97 mF, C\textsubscript{DL} = 215 μF, whereas in the case of the Ag\textsubscript{3}VO\textsubscript{4}&GO composite: C\textsubscript{film} = 398 μF, C\textsubscript{DL} = 485 μF. The film resistance (R\textsubscript{2}) reduces from 130 to 28 kΩ after the introduction of GO. Therefore, the
better performance in terms of electronic transfer obtained for
the samples containing GO can be associated with a better
electrical conductivity of the deposit that shows the presence of
a higher amount of Ag$_2$V$_4$O$_{11}$, characterized by n-type electrical
conductivity, as indicated by Raman and XRD spectra. For
now, we can simply associate a lower resistance and a more
efficient charge injection on the electrode surface with the
presence of GO. It is worth pointing out that the two best
performing samples are those that, according to Raman spectra
and XRD, show also the highest amount of Ag$_2$V$_4$O$_{11}$, whereas
samples containing 1.5 and 3 mg/mL GO present a less intense
band at 950 cm$^{-1}$, which we consider as representative of the
presence of short V–O bonds. Therefore, it appears that a
proper ratio between GO and Ag$_2$VO$_3$/NH$_3$ solution is crucial
in favoring the formation of these compounds. To our best
knowledge, in the literature there is another example of
composite Ag$_2$VO$_3$&GO obtained by simply mixing preformed
Ag$_2$VO$_3$ and GO, which does not show the formation of any
Ag$_2$V$_4$O$_{11}$ phase.

As stated in the introduction, Ag$_2$V$_4$O$_{11}$ is a versatile vanadate
and its use as a sensor in the detection of amines and ethanol in
the gas phase has already been tested. The detection of
amines in a water solution, especially biogenic amines, is also an
important task. The detection of biogenic amines and, in
particular, histamine by electrochemical methods requires the
use of polycrystalline boron-doped diamond thin-film electro-
des, gold nanocrystal-modified glassy carbon electrodes, or
thin-film Ni electrodes, as described in refs 40, 41. In our case,
the electrode can be prepared in a few minutes and therefore
can be considered as an interesting alternative to the methods
mentioned above. Ethylenediamine (EDA) is chemically similar
to biogenic amines but easier to handle and can be used as a
tester for biogenic amines.

In Figure 10, we show the response of the Ag$_2$VO$_3$/CP
sample to the addition of small amounts (200 μL) of 0.01 M
EDA solution in 0.1 M KHCO$_3$, by reporting the current at
1.15 V versus SHE (the peak corresponds to the oxidation of
the amine$^{41,42}$) as a function of the EDA concentration. The
electrode showed a good sensitivity to the addition of EDA
with a linear range between about 50 and 300 μm
concentrations. The detection limit, calculated in the response
linear range, considering Δ$I$ as 3 times the standard deviation in
the nonfaradic region, was about 0.2 ppm. This value is comparable to other literature data. Slightly worse results are obtained for the nanocomposite with GO (Figure 10c). In this case, the linear range is also lower than in the case of Ag$_x$VO$_y$ as well as the detection limit. This behavior indicates that the linear range and the response of the electrode strongly depend on the amount of the deposited catalyst (the amount of Ag$_x$VO$_y$ is less in the case of samples containing GO, as

Figure 10. (a) Ag$_x$VO$_y$ electrode response to the addition of 200 µL of 0.01 M EDA solution. (b) Ag$_x$VO$_y$ response to the addition of 200 µL of 0.01 M EDA solution under illumination. (c) Ag$_x$VO$_y$&GO 0.75 mg/mL response to the addition of 100 µL of 0.01 M EDA solution. (d) Ag$_x$VO$_y$&GO 0.75 mg/mL response to the addition of 100 µL of 0.01 M EDA solution under illumination. The current values at 1.15 V vs SHE are reported in the figure insets as a function of the EDA concentration. The bottom LVS curve (red) is the electrode response before EDA addition. The calculated detection limit, considering $\Delta I = 3\sigma$, where $\sigma$ is the standard deviation calculated in the nonfaradic region, is 0.2 ppm in the case of Ag$_x$VO$_y$. The dotted curve (a) is the response of a clean CP electrode in the same solution after 10 EDA additions ($3.8 \times 10^{-4}$ M). (e) CV on a freshly prepared Ag$_x$VO$_y$ sample in KHCO$_3$ solution.
discussed above in this section) and possibly by the presence of GO sheets, which prevents the adsorption of the amines on the vanadate surface.

It must be noted that before performing a sensing measurement, each electrode must be "activated" by applying some CV cycles between 0.0 and 0.9 V versus SHE to strip the amount of metallic Ag (in the form of Ag NPs) that forms during the deposition process (see XRD and XPS characterization) and after exposure of the electrode to light for a few hours. The accumulation of Ag NPs on the surface of Ag-vanadates is well documented and was observed also in the case of Ag₂VO₄ crystals by HR-TEM measurements. Considering the good photoactivity of the films, as described in the previous part of this section (n-type behavior and stable photocurrents up to 1.30 V vs SHE), we carried out the sensing experiments also on a Ag₂VO₄ film under illumination (Figure 10b). As clearly visible from Figure 10b, when the sensing is performed under illumination, the increase in the anodic current (the onset of the photocurrent is above 1.0 V) corresponds to a higher slope of the linear range of the electrode, and this allows a lower detection limit (<0.1 ppm). The linear range is slightly lower than that in the previous case probably because of the formation of Ag NPs induced by the light as testified by the appearance of a weak anodic current at about 0.65 V (Figure 10b). As mentioned above, although the presence of GO improves the photocurrent values, considering the value normalized to the Ag-vanadate content, the sensing efficiency depends instead on the absolute amount of Ag-vanadate and therefore when the sensing experiment is performed using the Ag₂VO₄/GO 0.75 mg/mL sample (Figure 10d), the performances are only slightly better than those obtained under dark conditions (higher slope value in the linear range) and in any case comparable to those obtained with the pure Ag₂VO₄ sample in the dark.

■ CONCLUSIONS

A quick and easy synthesis of Ag₂VO₄ and Ag₂VO₄/GO thin films or nanoaggregates was obtained by aerosol-assisted deposition. The deposition process that allows us to obtain a ready-to-work electrode can be completed in a few minutes, at a difference with the more standard, hydrothermal synthesis, which requires a heat treatment in a closed vessel at 180 °C for about 48 h. The obtained deposit adheres well on CP or FTO and does not require the addition of nafion to prevent material loss during the electrochemical measurements. The precursor solution consisted of an alkaline solution (NH₄OH) containing Ag, V, and O with a Ag/V atomic ratio of 3:1. Different amounts of GO flakes were added to the precursor solution to study the effect of GO on the physicochemical and electrochemical properties of the Ag-vanadate film.

The sample prepared without GO consisted of a mix of Ag₂VO₄ and α-Ag₃VO₄ phases with a large particle size distribution. The addition of GO resulted in a significant increase of the Ag₂VO₄/α-Ag₃VO₄ ratio and a more homogeneous dispersion of the Ag₂VO₄ nanoparticles on the GO sheets. This material was characterized by a stable n-type conductivity. The presence of GO led to the improvement of the electrical conductivity of the film by assisting the electron injection on the electrode surface.

The Ag₂VO₄ samples deposited on CP without and with GO were finally tested as electrochemical sensors for amine detection in solution. The electrodes showed a good sensitivity to the amine with a linear range between about 50 to 300 µm concentrations and with a detection limit of about 0.2 ppm. A lower detection limit could be obtained by performing the sensing measurements under illumination.

■ EXPERIMENTAL SECTION

Aerosol-Assisted Deposition. The precursor solution containing Ag, V, and O in the stoichiometric amount (3Ag/V), named throughout the text as Ag₂VO₄, solution, was prepared according to the following reactions:

\[ \text{AgNO}_3 + 3 \text{Na}_2\text{VO}_4 \rightarrow \text{Ag}_2\text{VO}_4 + 3\text{NaNO}_3 \]

\[ \text{V}_2\text{O}_5 (4.0269 \text{ g}, 22.1 \text{ mmol}) \text{ and NaOH (5.3137 g, 133 mmol)} \]

\[ \text{were dissolved in deionized (DI) water (15 mL) to obtain a Na}_2\text{VO}_4 \text{ solution. AgNO}_3 (22.5581 \text{ g, 133 mmol}) \text{ was dissolved in water (20 mL). Then, both solutions were mixed together and stirred for 15 min to induce the precipitation of Ag}_2\text{VO}_4 \text{ (or other Ag-vanadates). Finally, a concentrated (35% weight)} \]

\[ \text{NH}_4\text{OH solution was added dropwise until a clear solution (Ag}_2\text{VO}_4 100 \text{ mg/mL}) \text{ was obtained. Lyophilized GO obtained by the Hummers method was dissolved in milli-Q water to obtain a solution with a concentration of 2 mg/mL. Then, 5 Ag}_2\text{VO}_4 \text{ solutions (5.0 mg/mL with variable GO contents (0, 0.40, 0.75, 1.50, and 3.00 mg/mL) were prepared (Ag}_2\text{VO}_4/GO).} \]

A commercial medical ultrasonic aerosol generator was used to deposit the composite on a 15 mm round CP (Toray, TGP-H-60) or on FTO (Aldrich, 7 Ω/sq). Volumes of 4 mL of the Ag₂VO₄/GO solutions and 2 mL of concentrated NH₄OH were mixed together and then introduced in the aerosol generator. The resulting vapor was directed by an air stream (flow rate = 60 mL/min) on the CP substrate, which was kept at 250 °C throughout the deposition. The samples were named Ag₂VO₄, Ag₂VO₄/GO 0.4 mg/mL, Ag₂VO₄/GO 0.75 mg/mL, Ag₂VO₄/GO 1.50 mg/mL, and Ag₂VO₄/GO 3.00 mg/mL according to the content of GO in the precursor solution. The procedure followed to deposit Ag₂VO₄ and Ag₂VO₄/GO on FTO was the same but the substrate was kept at 270 °C.

Material Characterization. The nano- and micro-scale morphology of the materials was studied by field electron gun (FEG) SEM, using a Zeiss Supra 35 VP equipment. Micrographs were taken with an acceleration voltage of 5 kV and using an in-lens high-resolution detector. EDX analysis was performed on the same machine with an accelerating voltage of 10 kV. For TEM analysis, the samples were embedded in acrylic resin LRW and allowed to polymerize O.N. at 60 °C. The samples were cut with an LKB ultramicrotome, and 100 nm thick slices were deposited on 200 mesh copper grids. The observation was made by a TEM FEI Tecnai G2 operating at 100 kV. The images were acquired with an OISIS Veleta camera.

XPS measurements were performed on a custom-built UHV chamber (base pressure = 5 × 10⁻¹⁰ mbar) equipped with a nonmonochromatized double-anode X-ray source (Omicron DAR-400), a hemispherical electron analyzer (Omicron EA-125), and a 5-channeltron detection assembly. The electron analyzer acceptance angle was ± 4°, and the diameter of the analyzed area was 3 mm. The spectra were acquired with Al Ka radiation. The binding energy scale was calibrated with respect to the Pt 4f/2, and all reported spectra intensities were obtained after a Shirley background subtraction.

WAXD patterns were recorded in the diffraction angular range of 10–50° 2θ by a Philips XPert PRO diffractometer,
working in the reflection geometry and equipped with a graphite monochromator on the diffracted beam (Cu Kα radiation).

Raman spectra were acquired with a ThermoFisher DXR Raman microscope using a 532 nm laser (5 mW), focused on the sample with a 50X objective (Olympus) obtaining a spot size of about 1 μm. UV–vis spectra were acquired in the absorbance mode on a UV–vis Cary 6E spectrophotometer.

All of the electrochemical measurements were obtained in 0.1 M KHCO₃ solution in a three-electrode electrochemical cell controlled by Autolab PGSTAT204. The Pt electrode and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. PEC measurements were done by visible light LED sources controlled by the optical bench (Metrohm-Autolab) coupled to the Autolab PGSTAT204. All of the potentials mentioned in this article are referred to the standard hydrogen electrode (SHE). EIS data was obtained at the open circuit potential of the samples in the cell without light. The amplitude for EIS measurements is ±10 mV, and the frequency range was set from 10¹ to 10⁻¹ Hz performing 10 points per decade. Stability tests (1 h) were conducted by setting the potential from 0.55 to 1.30 V with mV, and the frequency range was set from 10⁴ to 10⁻¹ Hz. The scan rate was 0.05 V/s.

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**Notes**

The authors declare no competing financial interest.

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**ADDITIONAL NOTE**

“In a 0.1 M KHCO₃ solution (pH = 8.3), where the CO₃²⁻ concentration is about 10⁻¹ M, the precipitation of Ag₂CO₃ occurs for [Ag⁺] higher than 10⁻⁶ M. The stripping of metallic Ag, as deduced from the CV data, always leads to [Ag⁺] ≤ 6 × 10⁻⁶ M. Similar considerations can be applied considering the formation of Ag(OH) and Ag₂O.

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