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Photocatalytic activities of coke carbon/$g\text{-}C_3\text{N}_4$ and Bi metal/Bi mixed oxides/$g\text{-}C_3\text{N}_4$ nanohybrids for the degradation of pollutants in wastewater

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1. Introduction

Population growth, improvements in living standards and the increasing pollution of natural resources are major contributors to environmental problems. From an environmental viewpoint, advanced oxidation processes (AOPs) are one of the most sustainable ways of removing pollutants present in both aqueous and gaseous effluents.\,[1,2] Amongst these, the field of heterogeneous photocatalysis stands out as the one in which technology has undergone the most significant development over the last four decades, owing to its versatility and low cost.\,[3]

The heterogeneous photocatalytic process has been deemed as particularly promising for the removal of certain persistent pollutants that cannot be removed by conventional wastewater treatments.\,[4–8] Several semiconductor photocatalysts have been widely studied in the past decades, mainly TiO\textsubscript{2} and ZnO.\,[9–11] Based on the band gap usually shown by TiO\textsubscript{2} and ZnO compounds, their photocatalytic activity requires ultraviolet light ($\lambda < 400\text{ nm}$), which accounts for only c. 4\% of the global solar radiation. On the other hand, the visible range represents around 42\% of aforementioned global solar radiation, which encourages the development of visible light-driven photocatalysts, such as carbon nitride ($C_3\text{N}_4$). This material has lately been in the spotlight due to its easily tunable band gap, chemical inertness and stability. Although there are several allotropes of carbon nitride, graphitic carbon nitride ($g\text{-}C_3\text{N}_4$) has been shown to be the most stable under ambient conditions.\,[12–17] The reactivity of this polymeric semiconductor, mainly composed of carbon and nitrogen,\,[18] can be tuned without major changes in its overall composition.
It has found application in energy conversion,[19,20] hydrogen and carbon dioxide storage,[21–24] gas sensors,[25,26] solar cells,[15,27,28] water splitting [29–32] and organic pollutants degradation.[14,16,17,33]

Nevertheless, in spite its moderate band gap (~2.7 eV), this polymer tends to exhibit high recombination rates of electron–hole pairs, thus limiting its practical applications. In order to solve these restrictions and to improve its photocatalytic properties, several strategies have been reported, such as the design of heterojunction composites [34] or the modification of the g-C3N4 preparation. [35] The first approach, based on the separation of the electron–hole pairs, is especially suitable to improve the quantum efficiency and photocatalytic performance.

For combination purposes with g-C3N4, as an alternative to TiO2 and ZnO catalysts, metal oxides where the metal has a complete d shell (e.g. Bi2O3, In2O3 or Ga2O3) and complex metal oxides containing cations of d6 and/or d10 electronic configurations (i.e. niobates, vanadates, tinoxides, titanates, tantaletes and germanates) have been reported as very successful photocatalysts. [36–40] These metal oxides or complex metal oxides possess steep absorption edges in the visible-light region, different from the more structured spectrum of TiO2-doped materials.

In this paper, different g-C3N4 composite systems (coke carbon/g-C3N4, Bi2WO6/g-C3N4 and Bi2MoO6/g-C3N4) have been assessed in order to enhance g-C3N4 intrinsic photocatalytic properties in the degradation of methylene blue (MB), as a wastewater pollutant molecule model. This study aims to build on research previously conducted on the graphene/g-C3N4 system by Tian et al. [41] and Li et al. [42] and on the research effort undertaken by other authors on the Bi-W(Mo) mixed oxides/g-C3N4 system, such as Tian et al. [43] on g-C3N4/Bi2WO6; Xiong et al. [44] on g-C3N4/β-Bi2O3; Ohno et al. [45] and Aslam et al. [46] on g-C3N4/WO3; Dong et al. [47] on organic Bi-spheres/C3N4; and Ma et al. [48] on a g-C3N4/RGO/Bi2WO6 catalyst with intermediate composition between the two studied systems.

2. Experimental section

2.1. Materials synthesis

Melamine cyanurate (CAS No. 37640-57-6) was supplied by Nachmann S.r.l. (Milan, Italy) with purity higher than 99%; potassium tungstate (CAS No. 7790-60-5, 94%); potassium molybdate (CAS No. 13446-49-6, 98%); bismuth nitrate (CAS No. 10035-06-0, 98%); potassium methoxide (CAS No. 865-33-8, 95%); sulfuric acid (CAS No. 7664-93-9, ACS reagent), sulfolane (CAS No. 126-33-0, 99%) and methylene blue (CAS No. 122965-43-9, dye content ≥82%, certified by the Biological Stain Commission) were purchased from Sigma-Aldrich Quimica SL (Madrid, Spain). All reagents were used without further purification.

g-C3N4 was synthesized through direct heating of sulfuric acid-treated melamine cyanurate (SATS) – the product of a catalytic and disrupting reaction of a melamine and cyanuric acid adduct with H2SO4 1 M – according to the procedure reported by Dante et al. [49]. Five grams of SATS powder were heated to 550 °C (at a heating rate of 10 °C min−1) for 50 min in a sealed Vycor® glass vial using a convective tubular oven (Carbolite GVA 12/900; power: 5.460 kW, heating length: 900 mm, Tmax: 1200 °C) under nitrogen flow and then cooled at a rate of 10 °C min−1, giving a light-yellow product which consists of dehydrated melamine cyanurate, according to the reaction in [50]:

$$\text{C}_3\text{N}_4\left(\text{NH}_2\right)_3 + \text{C}_6\text{N}_7\text{OH} \rightarrow \text{C}_6\text{N}_7\left(\text{NH}\right)\left(\text{NH}_2\right) + 3\text{H}_2\text{O}$$

A thorough characterization of the resulting material can be found in previous works.[49–51] The choice of 550 °C for the thermal treatment is supported by the superior photocatalytic performance of the g-C3N4 resulting polymerization/condensation reaction at this temperature.[32]

For the preparation of S1 and S2 samples, a mixture consisting of 10% graphitizable carbochemical coke (Ccoke), supplied by ArcelorMittal, and 90% SATS was dispersed in water with 10% sulfolane and, after sonication for 10 min, it was heated under reflux with vigorous stirring at 150 °C for 48 h. The resulting product, washed with water and alcohol and then dried at 60 °C overnight, basically consisted in a composite of Ccoke and melamine cyanurate (S1). Heating of S1 at 550 °C for 50 min yielded composite S2, a mixture of Ccoke and polymeric dehydrogenated carbon nitride (g-C3N4).

The Bi/Bi2WO6/C3N4 composite was prepared by dissolving 0.33 g of potassium tungstate dihydrate (K2WO4·2H2O) and 0.97 g of bismuth nitrate pentahydrate (Bi(NO3)3·5H2O) in 60 ml of 10% potassium methoxide, followed by ultra-sonication for 30 min. The resulting precipitate was centrifuged and washed repeatedly with deionized water and alcohol and then dried at 60 °C overnight. Subsequently, it was mixed in an agate mortar with 0.1 g of Ccoke and heated at 550 °C for 50 min under nitrogen flow. The composite that resulted (S3) was a slightly greenish-yellow product.

The preparation of the Bi/Bi2MoO6/C3N4 composite (S4) was entirely analogous to that of Bi/Bi2WO6/C3N4, but using K2MoO4. This composite showed two phases with greenish-yellow and metallic colors. The specific surface areas of S1, S2, S3, S4 samples were 4.8, 45.8, 1.5, 1.3 m2 g−1, respectively.

2.2. Materials characterization

Infrared spectra were recorded with a Thermo Scientific (Waltham, MA, USA) Nicolet iS50 Fourier transform infrared (FTIR) spectrometer, equipped with a built-in
diamond attenuated total reflectance (ATR) system, in order to identify the chemical functional groups.

X-ray powder diffractograms of the samples were obtained using a Bruker (Billerica, MA, USA) D8 Advance Bragg-Brentano diffractometer, in reflection geometry.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were collected with an FEI (Hillsboro, OR, USA) Quanta 200FEG microscope equipped with a Genesis energy-dispersive X-ray (EDS) spectrometer system and with a JEOL (Akishima, Tokyo, Japan) JEM-FS2200 HRP microscope equipped with an Oxford instruments INCA Energy TEM 250 EDS probe, respectively.

The diffuse reflectance spectra of the samples were obtained by means of a UV-visible Agilent (Santa Clara, CA, USA) Cary 3 spectrometer equipped with an integration sphere. The materials were not diluted in any matrix to avoid a decrease in the absorbance. The spectra were recorded in diffuse reflectance mode and transformed by the instrument software to equivalent absorption Kubelka-Munk units.

3. Results and discussion

3.1. Materials characterization

3.1.1. X-ray powder diffraction analysis

As depicted in Figure 1(a), the diffractogram of sample S1 (solid black line) shows a good agreement with that of melamine cyanurate (dotted black line): the peaks appear at the expected theta angles, and differences in

![Figure 1](https://example.com/figure1.png)

**Figure 1.** X-ray powder diffraction patterns of: (a) coke/melamine cyanurate (S1), (b) coke/g-C\(_3\)N\(_4\) (S2), (c) Bi/Bi\(_2\)WO\(_6\)/g-C\(_3\)N\(_4\) (S3), and (d) Bi/Bi\(_2\)MoO\(_6\)/g-C\(_3\)N\(_4\) (S4) composites. JCPDS patterns have also been included for comparison purposes.
3.1.2. TEM and SEM images

The texture of the C_{coke}/g-C_{3}N_{4} sample (S2) was studied by TEM (Figure 2). The micrographs evidence the graphenic structure of the composite and provide details on flakes, mosaic structures and domains. It can be observed that the nanosheets of polymeric carbon nitride tend to form crumpled surfaces. These conformations seem to originate from the curled surfaces, which tend to roll up and then shrink by effect of the stabilization needed by the particle sheets, which were constituted by several layers.

The SEM analysis of S3 (Figure 3, left) and S4 (Figure 4, left) composites showed a large quantity of solid Bi-nanospheres in both composites, analogous to those reported by Dong et al. 

3.1.3. Vibrational characterization

The bands in the ATR-FTIR spectrum of S1 (Figure 5(a), black line) correspond to SATS: the peaks at 3381 and 3225 cm\(^{-1}\) can be assigned to the asymmetric and symmetric NH\(_{2}\) stretching absorptions of melamine, respectively. The broad band around 2600 cm\(^{-1}\) with
The main effects of the sulfuric acid treatment are the shifting of the cyanuric acid from the amide tautomer to the imidic acid one and the forming of strong hydrogen bonds between the amino groups of melamine and the oxygen of sulfate.

The spectra of S2 (Figure 5(a), red line) shows the pristine g-C$_3$N$_4$ peaks at 1628, 1535, 1454, 1394, 1313 and 1230 cm$^{-1}$, which correspond to the typical stretching modes of C–N heterocycles. In addition, the characteristic stretching mode of triazine units at 806 cm$^{-1}$ appears with clarity. The absence of C$_{coke}$ bands may be two peaks (2693 and 2500 cm$^{-1}$) corresponds to amide NH interacting via hydrogen bonding with oxygen within cyanuric acid. The strong peak at 1732 cm$^{-1}$ is allocated to NH$_2$ scissoring,[55] while that at 1659 cm$^{-1}$ relates to a NH$_2$ bending vibration, as a result of the intermolecular interaction through the NH$_2$ groups of the melamine molecule. The benzene ring has two intense absorption bands at 1531 cm$^{-1}$ and 1445 cm$^{-1}$, associated with the vibrations of C=N and C-N bonds, respectively. The position of the $\nu$(C=O) band at 1780 cm$^{-1}$ suggests some strengthening of the bond in the carbonyl group.[56] The peak at 1199 cm$^{-1}$ corresponds to the bridging C-NH-C units.[57] The bands at 1085 cm$^{-1}$ and 913 cm$^{-1}$ originate from ring-breathing vibrations and the band at 762 cm$^{-1}$ is due to CH wagging in the aromatic ring. The peak at 518 cm$^{-1}$ is attributed to the side chain in-plane C–N bending vibration.

The spectra of S2 (Figure 5(a), red line) shows the pristine g-C$_3$N$_4$ peaks at 1628, 1535, 1454, 1394, 1313 and 1230 cm$^{-1}$, which correspond to the typical stretching modes of C–N heterocycles.[49] In addition, the characteristic stretching mode of triazine units at 806 cm$^{-1}$ appears with clarity. The absence of C$_{coke}$ bands may be...
The UV–vis diffuse reflectance spectra of the samples are depicted in Figure 6. It can readily be observed that, whereas S1 and S2 composites only absorb in the UV region (at \( \lambda < 252 \) nm and \( \lambda < 410 \) nm respectively), S3 and S4 composites cover most of the visible spectrum, starting at \( \lambda < 620 \) nm. The estimated bandgap values \( E_g \) (calculated by Tauc plot method with exponent \( r = 1/2 \) \([59,60]\)) are summarized in Table 1. While the value obtained for S2 is in the expected range for pure g-C\(_3\)N\(_4\) and is typical of a wide-bandgap semiconductor, with Bi/Bi\(_2\)MoO\(_6\)/g-C\(_3\)N\(_4\) (S3) and Bi/Bi\(_2\)WO\(_6\)/g-C\(_3\)N\(_4\) (S4) composites and Bi\(_2\)WO\(_6\) (included for comparison purposes).

FTIR spectra of S3 and S4 composites (Figure 5(b)) provide some additional evidence of the presence of g-C\(_3\)N\(_4\), Bi\(_2\)O\(_3\), and either Bi\(_2\)WO\(_6\) or Bi\(_2\)MoO\(_6\). The peak at 1394 is related to the stretching modes of CN heterocycles in g-C\(_3\)N\(_4\). The peak at 878 cm\(^{-1}\) is close to the calculated \( \beta-C_3N_4 \) IR active mode at 891 cm\(^{-1}\), and the peak at 834 cm\(^{-1}\) can be ascribed to the characteristic breathing mode of triazine units. Nonetheless, the bands at 878 and 834 cm\(^{-1}\) may also be assigned to \( \nu_1 \) and \( \nu_2 \) of molybdate, respectively. The absorption peaks around 571 and 624 cm\(^{-1}\) correspond to the stretching vibrations of Bi-O, Mo-O and Mo-O-Mo and that 511 cm\(^{-1}\) to \( \nu(Bi-O-Bi) \).

**Figure 5.** ATR-FTIR spectra of: (a) C\(_{coal}\)/melamine cyanurate (S1) and C\(_{coal}\)/g-C\(_3\)N\(_4\) (S2) composites; (b) Bi/Bi\(_2\)WO\(_6\)/g-C\(_3\)N\(_4\) (S3) and Bi/Bi\(_2\)MoO\(_6\)/g-C\(_3\)N\(_4\) (S4) composites and Bi\(_2\)WO\(_6\) (included for comparison purposes).

**Figure 6.** UV-vis diffuse reflectance spectra of (a) S1; (b) S2; (c) S3 and (d) S4 composites.

**3.1.4. Electronic and optical gap characteristics from UV–vis spectra**

The UV–vis diffuse reflectance spectra of the samples are depicted in Figure 6. It can readily be observed that, whereas S1 and S2 composites only absorb in the UV region (at \( \lambda < 252 \) nm and \( \lambda < 410 \) nm respectively), S3 and S4 composites cover most of the visible spectrum, starting at \( \lambda < 620 \) nm. The estimated bandgap values \( E_g \) (calculated by Tauc plot method with exponent \( r = 1/2 \) \([59,60]\)) are summarized in Table 1. While the value obtained for S2 is in the expected range for pure g-C\(_3\)N\(_4\) and is typical of a wide-bandgap semiconductor, with Bi/Bi\(_2\)MoO\(_6\) (M = W, Mo) on g-C\(_3\)N\(_4\), there is an obvious enhancement of light absorbance. It is worth noting that the \( E_g \) values of S3 and S4 composites are even smaller than that of \( \beta-Bi_2O_3 \) (\( E_g = 2.50 \) eV) and close to those reported for WO\(_3\)/g-C\(_3\)N\(_4\) composites by Kailasam et al. \([61]\). As described in the literature,\([62,63]\)
that of the C\textsubscript{coke} based composites (Figure 7). Conversely, under UV irradiation, S1 and S2 composites were more efficient than under visible irradiation. The results are in good agreement with the reported bandgap values.

From the point of view of the global decontamination of an effluent, it is also important to study the adsorption of the pollutant on the catalyst surface provided that, although it is a necessary phenomenon for the occurrence of photo-oxidation, the aim of an AOP is to completely degrade the pollutant by photo-oxidation and not to transfer the pollutant from the effluent to the solid photocatalyst, since otherwise the problem of the removal of the pollutant would not have been solved.

In the C\textsubscript{coke}-based samples (S1 and S2), the adsorption phenomenon (experiments conducted in the dark) can be deemed as negligible (<4%). On the other hand, for the samples with Bi/Bi\textsubscript{2}MO\textsubscript{6} (M = W, Mo), i.e. S3 and S4, a high adsorption of the dye was detected (more than 50% within the first minute of the experiment). Consequently, the decrease in the pollutant concentration cannot be exclusively ascribed to the photocatalytic phenomenon.

4. Discussion

The use of a low initial C\textsubscript{coke} content in the preparation of S1 and S2 has led it to behave as a reductor for polymeric carbon nitride and to the formation of C\textsubscript{coke}/C\textsubscript{N}\textsubscript{4} composites with very low amounts of C\textsubscript{coke}. On the other hand, for the samples with Bi/Bi\textsubscript{2}MO\textsubscript{6} (M = W, Mo), i.e. S3 and S4, a high adsorption of the dye was detected (more than 50% within the first minute of the experiment). Consequently, the decrease in the pollutant concentration cannot be exclusively ascribed to the photocatalytic phenomenon.

5. Conclusions

The C\textsubscript{coke}/g-C\textsubscript{3}N\textsubscript{4} hybrid (S2), rich in heptazines, produced by thermal treatment at 550 °C of a composite made from coke and melamine cyanurate (S1), exhibited a UV-light driven photocatalytic activity but not the desirable visible-light response (with an absorption
edge at 410 nm) which could allow a more efficient degradation of MB.

On the other hand, S3 and S4 composites, produced by thermal reduction of Bi2WO6 or Bi2MoO6 by g-C3N4, consisted of Bi spheres, Bi mixed oxides and g-C3N4 (Bi/Bi2WO6/g-C3N4 and Bi/Bi2MoO6/g-C3N4 composites). These nanohybrids exhibited a high and stable visible-light photocatalytic performance for the removal of MB, notwithstanding the fact that the adsorption of the contaminant could also play a role.

The use of Bi semimetal in S3 and S4 as a plasmonic cocatalyst for boosting visible light photocatalysis (in a similar fashion to Au and Pt) may provide a more economical alternative to the use of noble metals so as to advance photocatalysis efficiency.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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