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Short Communication

Photocatalytic CO₂ reduction in gas–solid regime in the presence of H₂O by using GaP/TiO₂ composite as photocatalyst under simulated solar lightGiuseppe Marci^{*}, Elisa I. García-López, Leonardo Palmisano*"Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'informazione e modelli Matematici (DEIM), Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy*

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ABSTRACT

GaP/TiO₂ composites exhibited a remarkable photocatalytic activity for CO₂ reduction in the presence of water vapor producing methane. By decreasing the GaP:TiO₂ mass ratio an increase in the photocatalytic activity of the composite was observed for up to a 1:10 mass ratio. The photocatalytic activity of the composite can be attributed to the band structures of the solids as well as to the efficient charge transfer between GaP and TiO₂ heterojunction.

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1. Introduction

The increasing CO₂ level in the atmosphere is a global environmental problem, therefore an efficient photoreduction of CO₂ is a challenging task of applied catalysis [1]. Heterogeneous photocatalysis is an attractive technology for this purpose [2]. Inoue et al. already reported in 1979 that small amounts of formic acid, formaldehyde, methyl alcohol and methane can be formed under irradiation of CO₂ in aqueous suspensions of TiO₂, ZnO, CdS, WO₃ and SiC [3]. Since then great efforts have been made to increase the amount of reaction products in the photocatalytic CO₂ reduction, especially by using TiO₂ or related titanium containing solids [2], silica containing highly dispersed Ti-oxide species [4], composites containing MgO and TiO₂ [5], graphene oxide [6] or WO₃/graphene composite [7].

Gallium phosphide, GaP with a band gap of 2.3 eV [3,8] presented as water-insoluble slightly orange crystals has been rarely used as a photocatalyst [9] due to the low oxidizing power of its valence band (VB). The position of its conduction band (CB), instead, should allow the CO₂ to be reduced; indeed, it is ca. 1.3 V more negative than that of CO₂/CH₄ redox couple [10].

GaP has already been used in the photoelectrochemical reduction of carbon dioxide and in 1978, the photoelectrochemical reduction of aqueous CO₂ was already obtained by using GaP in liquid junction solar-cells [11]. Recently, Barton et al. have demonstrated the highly selective reduction of CO₂ to methanol in water when a GaP electrode was used with pyridine as co-catalyst [12].

Bare GaP is ineffective for photocatalytic CO₂ reduction as, although the electrons from the GaP conduction band are able to reduce CO₂ to CH₄, the oxidative counterpart should be also considered for the successful occurrence of the photoreaction. H₂O vapor, often chosen as a hole trap, cannot be used because the reduction potential of the GaP valence band is unable to oxidize H₂O.

In this paper, the results obtained with a composite material formed by GaP and TiO₂ are reported for the first time for the photocatalytic CO₂ reduction. The appropriate position of the valence and conduction bands of the components, not only allows the efficient separation of the photo-produced electron–hole pairs, but also allows both the reduction of CO₂ and the oxidation of H₂O.

2. Experimental

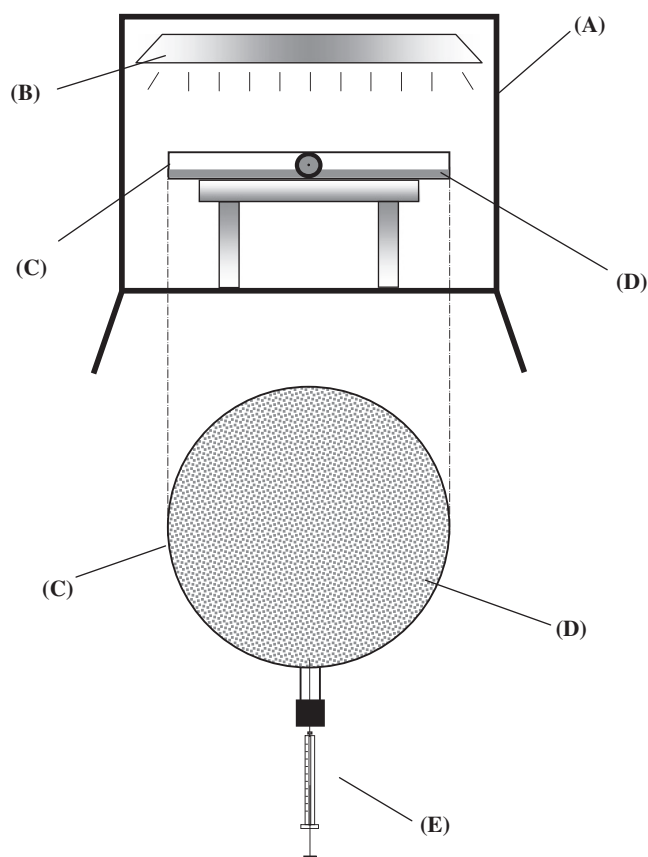
Commercial TiO₂ Evonik P25 and GaP Aldrich powders were used as the starting materials to obtain GaP/TiO₂ powders, prepared by mechanically milling both solids with a Retsch RM200 mortar grinder provided with grinding tools in agate that mixed and triturated by pressure and friction with a speed of 100 rpm at room temperature. 0.5 g of GaP, as commercial pellets, was first finely grinded for 20 min. Subsequently ca. 0.1 g of Degussa P25 TiO₂ powder was added to the GaP powder and both solids were again grinded for 10 min before the addition of other aliquots of TiO₂ until the needed total amount of TiO₂ was achieved. The samples contained a mass ratio GaP:TiO₂ in the range 10:1 to 1:20 and were labeled as GaP/TiO₂ preceded by the GaP:TiO₂ mass ratio. Moreover Pd and Pt-loaded GaP/TiO₂ samples with different noble metal contents were also prepared with the aim to increase the reactivity. Two sets of samples were obtained by

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following two methodologies, i.e. by depositing the noble metal on the 1:10-GaP:TiO₂ composite or on the bare GaP before mixing with TiO₂ to obtain the 1:10-0.2%(Pt or Pd)-GaP:TiO₂ samples (see ESM for details). Some characterization techniques have been used to better understand the features of the composite materials (see ESM).

The photocatalytic CO₂ reduction was carried out in a gas–solid Pyrex batch photoreactor of cylindrical shape ($V = 100$ mL, $\Phi = 94$ mm, height = 15 mm) containing the photocatalyst (0.3 g) dispersed as a thin layer. In this tightly closed reactor the desired water amount (3 μ L for most of the runs, corresponding to $1.7 \cdot 10^{-3}$ M) was injected by a microsyringe after purging with ultrapure CO₂ for 60 min under dark conditions at room temperature (CO₂ concentration $4.2 \cdot 10^{-2}$ M). Some selected runs were carried out by using the maximum amount of water that can be vaporized in the photoreactor under the used experimental condition, i.e. $1.1 \cdot 10^{-2}$ M (injection of 20 μ L of liquid water).

The photoreactor was horizontally positioned and illuminated from the top inside a SOLARBOX apparatus (CO.FO.ME.GRA.) equipped with a solar light simulating lamp (1500 W high pressure Xe lamp). The set-up of the photoreactivity system is shown in Scheme 1. The maximum temperature reached inside the reactor was ca. 70 °C. The irradiance reaching the photocatalyst (measured by UVX Digital Radiometer) was 1.0 mW \cdot cm⁻² in the 315–400 nm range, and 100 mW \cdot cm⁻² in the 400–950 nm range. The runs lasted ca. 48 h and the reacting fluid was analyzed by withdrawing gas samples from the photoreactor with a gas-tight syringe. The evolution of the reaction was followed by gas chromatography (see ESM for details). The possible presence of products deriving from C impurities was checked by treating the GaP/TiO₂ composites under irradiation (before the photoactivity experiments in the presence of CO₂) with a flow of humid He according to Strunk et al. [13], which allowed also to clean the surface. Notably



Scheme 1. Set-up of the photoreactive system: (A) Solarbox; (B) lamp; (C) photoreactor; (D) powdered photocatalyst; (E) gas-tight syringe.

only insignificant amounts of CH₄ (less than 0.1 μ M) were observed during the treatment.

3. Results and discussion

Table 1 reports the B.E.T. specific surface area (SSA) of the samples. Bare commercial GaP and TiO₂ show SSAs of 2 and 50 m² \cdot g⁻¹, respectively. The presence of GaP in the samples gave rise to a decrease of the SSA. EDX mapping analysis confirmed the nominal GaP:TiO₂ mass ratio, although the content of the two components in the agglomerates was not always constant, and this finding pointed to a certain inhomogeneity of the materials. Notably when Pt or Pd were present in the samples it was not possible to detect them by EDX due to their low amount. Diffuse reflectance spectra (DRS) spectra were used to determine the band gap energy of GaP, 2.3 eV, and TiO₂, 3.0 and 3.2 eV, containing anatase and rutile polymorphs, respectively, in agreement with literature data (see ESM for characterization details).

Blank tests indicated that no organic compounds were produced in the absence of catalyst as well as under dark conditions. Both bare TiO₂ Evonik P25 and GaP were inactive for CO₂ reduction in our experimental conditions also in the presence of light and H₂O. On the contrary, the presence of methane was observed during the photocatalytic tests in the presence of cleaned GaP/TiO₂ composites. By increasing the TiO₂ content, methane increased reaching a maximum value by using the 1:10-GaP/TiO₂ sample. A further increase of TiO₂ caused a decrease in methane production. No reactivity was observed for the 1:20-GaP/TiO₂ sample. Other organic molecules different from CH₄ were absent in the photoreactor, at least in amounts comparable to the main product. The presence of CO was also checked but excluded probably because its concentration was below the analytical detection limit. The maximum activity for 1:10-GaP/TiO₂ sample can be attributed to an optimum coverage that allowed an optimal light activation of both components. Noticeably, the SSA (45 m² g⁻¹) of the 1:10-GaP/TiO₂ sample is only slightly lower with respect to that of the bare TiO₂, whereas the low SSAs of the 1:1-GaP/TiO₂ and the 10:1-GaP/TiO₂ samples (15 m² g⁻¹ and 7 m² g⁻¹, respectively) can severely limit their photocatalytic activity.

Fig. 1 shows methane concentration versus irradiation time for runs carried out under different experimental conditions by using both bare and Pt- or Pd-loaded 1:10-GaP/TiO₂ samples.

The maximum concentration of methane, 118 μ M per gram of catalyst, was obtained by using the 1:10-GaP/TiO₂ sample after 10 h of irradiation in the presence of $1.7 \cdot 10^{-3}$ M water concentration. Methane production was of the same order of magnitude or higher with respect to values previously reported in literature under various irradiation conditions [14].

Nevertheless, in the present work CH₄ concentration reached a plateau and remained constant in the reaction system even after 48 h of irradiation. The plateau can be due to a partial catalyst deactivation

Table 1

Maximum methane concentration found in the CO₂ reduction photocatalytic runs (water amount = $1.7 \cdot 10^{-3}$ M).

Photocatalyst	SSA [m ² g ⁻¹]	CH ₄ concentration per mass of photocatalysts [μ M g ⁻¹]
TiO ₂ Evonik P25	50	Negligible
GaP Aldrich	2	Negligible
10:1-GaP/TiO ₂	7	Negligible
1:1-GaP/TiO ₂	15	10.38
1:10-GaP/TiO ₂	45	118.18
1:15-GaP/TiO ₂	50	47.04
1:20-GaP/TiO ₂	50	Negligible
1:10-0.2%Pt-GaP/TiO ₂	50	12.59
1:10-0.2%Pd-GaP/TiO ₂	50	28.89
1%Pt-1:10 GaP/TiO ₂	50	Negligible
1%Pd-1:10 GaP/TiO ₂	50	Negligible

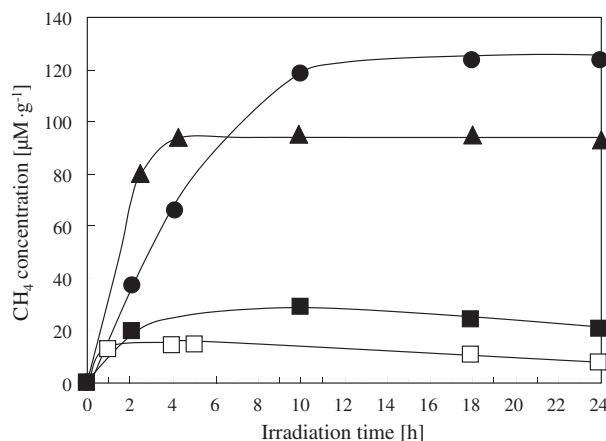


Fig. 1. Methane concentration per gram of photocatalyst during CO₂ reduction under different experimental conditions: (●) 1:10-GaP/TiO₂ (3 µL H₂O); (▲) 1:10-GaP/TiO₂ (20 µL H₂O); (□) 1:10-0.2%Pt-GaP/TiO₂ (3 µL H₂O); (■) 1:10-0.2%Pd-GaP/TiO₂ (3 µL H₂O).

(the catalytic activity was lower, ca. 30% after reusing twice the photocatalysts) and to the fact that O₂ was also produced from water oxidation during the formation of CH₄. O₂ could efficiently trap electrons preventing CO₂ reduction giving also rise to the re-oxidation of CH₄ to CO₂. In this way a sort of equilibrium was reached. It is worth noting that the formation of O₂ was detected, by GC analysis, during the photocatalytic reaction although it was not quantified.

As shown in Fig. 1, an increase of water concentration gave rise to a more rapid achievement of the plateau, but its value was lower than that observed in the presence of smaller concentrations of H₂O.

The maximum amount of methane decreased when the GaP/TiO₂ samples were loaded with Pt or Pd.

In particular, samples loaded with 1% of Pt or Pd on the 1:10-GaP/TiO₂ composite showed a negligible activity, whereas methane concentration began to decrease after ca. 10 h in the presence of 0.2% of noble metal, suggesting that the oxidation reaction could take place in a higher extent with respect to the bare composite samples.

In order to explain the photoreactivity of the various samples, we should consider that, from a thermodynamic point of view, the reduction of CO₂ requires that the bottom energy level of the conduction band of the semiconductor is lower than the reduction potential of the various processes leading to products of CO₂ reduction. Fig. 2 shows the alignment of the conduction bands of anatase [15], rutile [16] and GaP [5,8] with the reduction potentials of the CO₂/CH₄ couple [17]. The reduction of carbon dioxide to methane is the most thermodynamically favorite process among all the possible ones [18].

A perusal of Fig. 2 shows that the potentials of the CB in TiO₂ rutile and anatase are only slightly lower than that of the CO₂/CH₄ couple. This could justify why the TiO₂ sample was inactive for the CO₂ reduction, also considering the CO₂ overpotential that we did not quantify in the current experimental conditions but that was always present. On the contrary, the potentials of the VB of the two TiO₂ polymorphs are higher enough to oxidize water to O₂. The CB potential of GaP, instead, is suitable for CO₂ reduction to CH₄ but the potential of VB does not allow water to be oxidized, and consequently this could justify why bare GaP was inactive for CO₂ photoreduction. By considering the relative position of CB and VB of both TiO₂ and GaP, the two semiconductors can be coupled with the aim to obtain a cooperative photo-redox process.

The photoproduced (UV light) electrons in the CB of TiO₂ can be trapped by the photoproduced (visible light) holes in the VB of GaP (see Fig. 2). This mechanism works separating efficiently the holes in the VB of TiO₂ from the electrons in the CB of GaP, making water oxidation and CO₂ reduction possible. The circuit is closed analogously to what reported in the so-called Z-scheme [19].

SEM analyses (see ESM) support the hypothesis above presented to explain the highest photocatalytic activity of 1:10-GaP/TiO₂ sample and the inactivity of the 1:20-GaP/TiO₂ sample. In fact, it can be noticed that GaP is not completely in contact with TiO₂ in the samples containing an amount of TiO₂ lower than that present in the 1:10-GaP/TiO₂ sample where GaP is in full contact with TiO₂, whereas in the 1:20-GaP/TiO₂ sample the high amount of TiO₂ on GaP does not allow light to reach satisfactorily the GaP surface. In order to explain the behavior of the Pt- and Pd-loaded samples, we consider that when the noble metals are deposited on the 1:10-GaP/TiO₂ sample they are mainly present

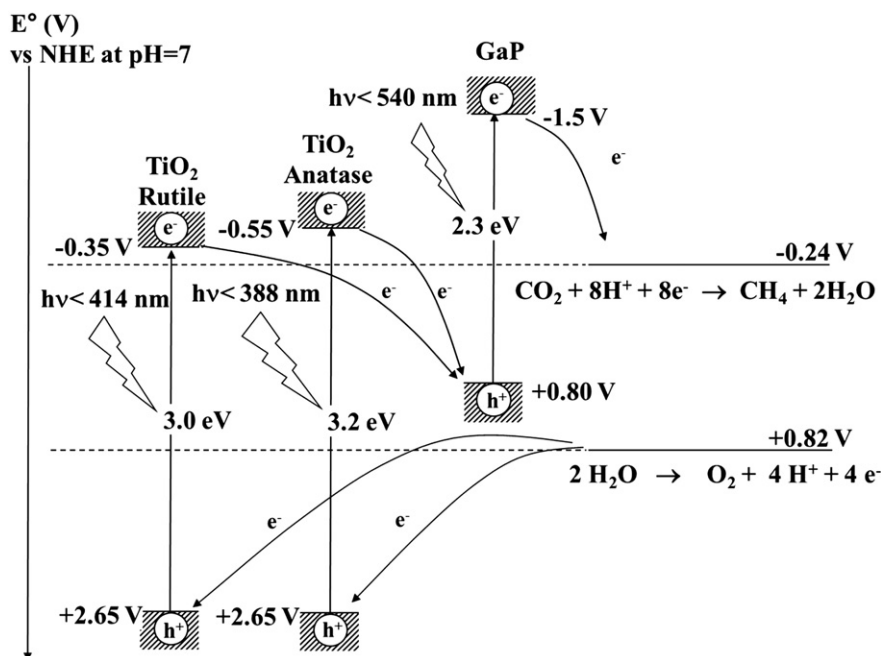


Fig. 2. Relationship between the band structures of TiO₂ and GaP and the reduction potentials (versus NHE at pH = 7) for the most favorite processes of oxidation and reduction.

onto the TiO₂ surface, trapping the photoproduced electrons and inhibiting the GaP role as an electron sink. On the contrary, for the 1:10–0.2%Pt-GaP/TiO₂ and 1:10–0.2%Pd-GaP/TiO₂ samples, where Pt or Pd are mainly deposited on GaP, two contrasting effects can occur: the noble metals can favor the CO₂ reduction as they favor trapping of electrons in the CB of GaP but at the same time more holes are available in the VB of TiO₂ and this phenomenon can produce the re-oxidation of CH₄ to CO₂ as observed after 10 h of irradiation (see Fig. 1), reducing the global efficiency of the process.

4. Conclusions

The photocatalytic reduction of CO₂ has been performed with various GaP/TiO₂ photocatalysts mechanically prepared by mixing commercial GaP Aldrich and TiO₂ Evonik P25. Both bare GaP and TiO₂ samples resulted completely inactive, whereas the GaP/TiO₂ composites gave rise to the reduction of CO₂ mainly to CH₄. The extent of photoactivity depended on the amount of GaP with respect to TiO₂, with a maximum CH₄ formation observed for the 1:10 GaP/TiO₂ sample. Higher or lower amounts of GaP were detrimental. The presence of 1% or 0.2% of Pd or Pt on the surface of the most photoactive GaP/TiO₂ sample (ratio 1:10) was also detrimental. These composite GaP/TiO₂ materials prepared in a very simple way appear to be promising new candidates for reduction of CO₂ in the presence of H₂O.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2014.04.024>.

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