Band alignment investigations of heterostrcuture NiO/TiO_2 nanomaterials used as efficient heterojunction earth-abundant metal oxide photocatalysts for hydrogen production

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In the broad context of environmental issues related to the continuous energy demand increase arising from the global population growth, semiconductor heterogeneous photocatalysis appeared to be a versatile concept for green technology, and was directed to a wide range of purposes as hydrogen production, and depollution. Nonetheless, the recombination of charge carriers constitutes one of the main limitations to achieve high photocatalytic efficiencies. Development of heterostucture photocatalysts by coupling two semiconductors with suitable band edge position, such as p-type and n-type semiconductors, can reduce recombination phenomena by vectorial transfer of charge carriers.[1] On the other hand, the scarcity of some elements requires the development of photocatalysts with earth-abundant elements and a careful control of the polymorphs obtained is needed to rationalize the photocatalytic properties.

In this context, earth-abundant NiO/anatase TiO_2 heteronanostructures were prepared by a straightforward one pot sol-gel synthetic route followed by a suitable thermal post-treatment. The resulting 0.1-4wt% NiO-decorated anatase TiO_2 nanoparticles were characterized by X-ray diffraction, electron microscopy, Raman and UV-visible spectroscopy and N_2 sorption analysis, and showed both high crystallinity and mesoporosity. The careful determination of the energy band alignment diagram by a suitable combination of XPS/UPS and absorption spectroscopy data revealed significant band bending at the interface of p-n NiO/anatase TiO_2 heterojunction nanoparticles. Furthermore, these heterojunction photocatalysts exhibited improved photocatalytic activity in organic dye degradation and H_2 production by methanol photoreforming compared to pure anatase TiO_2 and commercial P25 and could be recycled several times without any noticeable change in photocatalytic activity. Thus, an average H_2 production rate of 2693 $\mu mol\ h^{-1}g^{-1}$ was obtained for heterojunction 1 wt% NiO/anatase photocatalyst, which is one of the most efficient NiO/anatase TiO_2 system ever reported. Enhanced dissociation efficiency of photogenerated electron-hole pairs resulting from internal electric field developed at the interface of the NiO/anatase TiO_2 p-n heterojunctions was found to be at the origin of this unprecedented photocatalytic activity.

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References:

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