Fast One-Pot Synthesis of MoS_2/Crumpled Graphene p-n Nanonjunctions for Enhanced Photoelectrochemical Hydrogen Production

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Abstract Besides being a material with exceptional electrical conductivity, outstanding mechanical toughness and remarkable optical properties, graphene is, at its very nature, a perfect and soft 2D atomic sheet. This combination of confinement to nanodimension and easy mechanical pliability makes it an incredibly versatile material that can be shaped in almost any form. This great potential for manipulation paves the way toward the development of advanced architectures that combine graphene intrinsic properties with nanodesign optimized for specific functions.[1] Interestingly, the two-dimensional nature of graphene implies the ability to undergo easy folding and bending, just like macroscopic objects, thus graphene sheets can be opportunely crushed to form crumpled nanoballs.[2,3] This special conformation is quite intriguing since it prevents the re-stacking of single sheets, allowing the preparation of high surface area systems Moreover, mechanical strain induced in the material by wrinkles and folds can promote unexpected chemical reactivity and better electrochemical performances.[4,5] Aerosol processing allows preparing in high yield and short time hierarchical graphene nanocomposites with special crumpled morphology, employing aqueous suspensions of graphene oxide(GO)[2]. By modular insertion of suitable precursors in the starting solution, it is possible to synthesize different types of graphene based materials ranging from heteroatoms doped graphene nanoballs, to hierarchical nanohybrids made up by nitrogen doped crumpled graphene nanosacks that wrap finely dispersed MoS_2 nanoparticles. These materials are carefully investigated by microscopic (SEM, standard and HR TEM), grazing incidence X-ray diffraction (GIXRD) and spectroscopic (high resolution photoemission, Raman and UV-visible spectroscopy) techniques, evidencing that nitrogen dopants provide anchoring sites for MoS_2 nanoparticles, whereas crumpling of graphene sheets drastically limits aggregation. The activity of these materials is tested toward the photo-electrochemical production of hydrogen, obtaining that N-doped graphene/MoS_2 nanohybrids are seven times more efficient with respect to single MoS_2 because of the formation of local p-n MoS_2/N-doped graphene nanojunctions, which allow an efficient charge carrier separation.

References

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Figures