Remarkably enhanced photocatalytic activity of laser ablated Au nanoparticle decorated BiFeO$_3$ nanowires under visible-light†

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Hybrid photocatalysts consisting of single crystalline BiFeO$_3$ nanowires and laser ablated Au nanoparticles were synthesized by a functionalization-step-free solution process. The 1.0 wt% Au nanoparticle decorated BiFeO$_3$ nanowires exhibit ~30 times higher photocatalytic activity for water oxidation than that exhibited by the parent wires during the first 4 h.

Photocatalytic water splitting with semiconductor materials has been investigated as a clean and renewable process for converting sunlight into chemical energy.1 Multiferroic materials have recently been used for applications in both photovoltaics (PV) and photocatalysis due to their ferroelectric properties and relatively narrow band gaps, which allow them to harness the majority of solar radiation in the visible range.2,3 As a typical multiferroic material, BiFeO$_3$ (BFO), has been recognized as a potential system for PV and visible-light photocatalysis applications, thanks to its suitable band gap (2.2–2.8 eV) and good chemical stability.2,3 However, the investigations of BFO nanomaterials for photocatalytic water splitting are still limited.3

The use of one-dimensional (1D) semiconductors has attracted considerable attention for solar water splitting.1,4 In comparison with bulk materials, photocatalysts in the form of 1D nanostructures, such as nanowires (NWs), nanotubes and nanobelts, have demonstrated enhanced efficiencies for photocatalytic water splitting.4,5 The reduced radial dimension and the extremely large surface-to-volume ratio promote rapid diffusion of photogenerated electrons/holes to the NW surfaces before recombination can occur, and thus can increase separation efficiency of charge carriers.4 Most importantly, single crystalline NWs are deemed to be more active since ballistic charge transport along the wire axis is significantly more efficient than the diffusive transport in powdered or polycrystalline materials. Therefore, BFO NWs in single-crystalline form are expected to be highly active photocatalysts for solar water splitting.

On the other hand, the photocatalytic performance of semiconductor materials can be enhanced by combination with noble metal (e.g. Ag, Au, Pt, etc.) nanostructures.6 Among them, gold nanoparticles (AuNPs) are very promising because they exhibit excellent chemical stability and a characteristic absorption peak in the visible wavelength range.7 The enhanced photoactivity is attributed to the roles of the AuNPs as electron-trapping centres and/or the LSPR effect.6,7,a In addition, it has also been discovered that AuNPs exhibit a dual role as light harvesters injecting electrons into the semiconductor and also as catalytic sites for gas generation.6,7,b,c Pulsed laser ablation in liquid phase (PLAL) on a Au bulk target produces relatively “bare and clean” AuNPs,8 which have been proved to facilitate catalytic reactions as the reactive sites on the NP surface are mostly exposed and readily accessible to reactants,9 thus prompting us to expand the applications of PLAL-AuNPs in solar water splitting.

Herein, we employed a simple and functionalization-step-free solution process to synthesize the Au-BFO nanocomposite. First, AuNPs were synthesized by laser ablation using a bulk Au target in pure water,9 and single-crystalline BFO NWs were obtained by a hydrothermal approach.10 Second, the as-prepared PLAL-AuNP solution was simply mixed with the BFO NWs to assemble AuNPs onto the surface of the NWs (see the Experimental section of ESI† for details). The formation process is conceptually displayed in Scheme 1.

The rhombohedral perovskite structure of the BFO NWs was confirmed using X-ray diffraction (XRD) (Fig. S1, ESI†). As shown in a scanning electron microscopy (SEM) image (Fig. 1a), the length of the as-synthesized BFO NWs is up to several micrometers with diameters around 40–200 nm. Fig. 1b and c show transmission electron microscopy (TEM) images of BFO NWs and the PLAL-AuNP (1.0 wt%)-BFO NW nanocomposite, respectively. Uniform AuNPs with an average diameter of about 3 nm were distributed evenly on the surface of BFO NWs. The Au-BFO hybrid nanostructures were further characterized using high-resolution TEM (HRTEM), as shown in Fig. 1d. The lattice fringes of attached AuNPs and the BFO NW surface were clearly observed, with a spacing of 2.38 Å corresponding...
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Fig. 1a shows the UV-vis absorption spectra of BFO with and

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stem to that of the (111) plane of face-centered cubic Au, and a lattice
spacing of 1.35 Å matching that of the (422) crystal planes of
perovskite structured BFO. These results regarding crystalline structures are in good agreement with those obtained from the selected area electron diffraction (SAED) patterns (Fig. 1e).

Our synthesis approach differs from conventional methods for synthesizing metal–semiconductor nanocomposites, where the support semiconductor materials and/or metal NPs need to be first functionalized with functional groups to promote their coupling. Indeed, it does not require pre-functionalization of either the BFO NWs or the AuNPs. The effective immobilizing process is associated with the surface chemistry of the PLAL-AuNPs and BFO NWs. Zeta-potential measurement (Fig. S2, ESI†) reveals that the Isoelectric Point (IEP) of BFO NWs is about 6.5. As the pH value of the incubation solution (pure water) is ~ 6.0, the surface of BFO is slightly positively charged. On the other hand, the PLAL-AuNPs are negatively charged at this pH value, which is due to the adsorption of –OH groups. As a result, the electrostatic interaction between them leads to the formation of a hybrid Au–BFO structure.

To gain more detailed insight into the interaction between AuNPs and the BFO NW support, the valence state of Au4f in the PLAL-AuNP–BFO NW nanocomposite and pristine AuNPs was investigated using X-ray photoelectron spectroscopy (XPS). As shown in Fig. S3 (ESI†), the XPS peaks observed for PLAL-Au (1.0 wt%)-BFO confirm the presence of Au(0) with binding energies of 87.1 and 83.5 eV that are somewhat shifted towards lower values than binding energies of pristine AuNPs (87.8 and 84.2 eV). This suggests the occurrence of charge transfer between the BFO NW support and the AuNPs, as reported previously in other counterpart noble metal NP–semiconductor systems.7c,11

Fig. 2a shows the UV-vis absorption spectra of BFO with and without AuNPs. The optical spectroscopy of BFO NWs shows an absorption edge which is due to the bandgap transition. The direct band gap of BFO NWs is about 2.35 eV (Fig. S4, ESI†) calculated from the absorption spectrum. As expected, the UV-visible spectrum of the Au–BFO samples exhibits the typical Au surface plasmon band in the visible region between 500 and 600 nm. The capability of our BFO NWs to drive oxygen evolution from water oxidation under visible light (λ > 380 nm) illumination was analyzed using FeCl3 as a sacrificial electron acceptor. Fig. 2b shows oxygen evolution over time for the pristine BFO NWs and a series of Au–BFO samples. Table 1 lists parameters for photocatalytic activity of all samples under study. The BFO NWs exhibit much better photocatalytic activity than the previously reported BFO nanocubes under similar conditions (the same loading of catalysts),18 which can be attributed to high surface area and unique morphology of the NWs. Interestingly, the amount of oxygen produced using the PLAL-Au–BFO photocatalyst with 1 wt% Au loading is ~ 30 times higher than that produced using the parent wires during the first 4 h (Fig. 2b), indicating remarkable influence of AuNPs on water oxidation activity under visible light. Such enhancement of photocatalytic activity is much more significant than that (~ 2–10 times) of the reported Au–semiconductor systems.7a,b,12 For comparison, a nanocomposite photocatalyst consisting of BFO NWs and 1.0 wt% of chemically synthesized, citrate ligand-capped AuNPs (Chem-AuNPs) with an average diameter similar to that of the PLAL-AuNPs was prepared (see details in ESI†) and its photocatalytic activity was tested under the same conditions. The initial reaction rate (r0) of the Chem-AuNP (1.0 wt%)-BFO nanocomposite is 0.171 μmol min⁻¹, about 1.5 times smaller than that (0.309 μmol min⁻¹) of the PLAL-AuNP (1.0 wt%)-BFO sample (Table 1). The PLAL-AuNPs and Chem-AuNPs have similar average size, size distribution (Fig. S5, ESI†) and the Au/support ratio, therefore the distinct difference in photoactivity should be related to their inherent difference in surface-chemistry features. The photocatalytic activity decreased upon increasing the Au loading to 5.0 wt% (TEM image shown in Fig. S6, ESI†). It was reported that
AuNPs by themselves do not exhibit any photoactivity.\textsuperscript{13} Therefore, the cooperative effect of the AuNPs and the support surface on the reaction can be used to describe our results. The balanced combination of several factors (e.g. surface coverage of the support semiconductor, population of residual hydroxyl groups, and metal dispersion, \textit{etc}.) that are influenced by the Au loading amount determines the maximum photocatalyst efficiency. AuNPs would also serve as electron–hole recombination centers when the support surface is largely covered by AuNPs, and thereby reduce the photoactivity.\textsuperscript{14}

To understand the mechanism of enhanced photocatalytic activity, we investigated the photoluminescence (PL) spectra of BFO NWs and the PLAL-Au–BFO nanocomposite (Fig. S7, ESI\textsuperscript{†}). Two emission peaks were detected at around 485 and 540 nm in the case of BFO NWs, consistent with those reported in the literature.\textsuperscript{15} The PL emission of BFO is drastically quenched in the presence of PLAL-AuNPs, suggesting the occurrence of efficient charge and/or energy transfer from BFO NWs to AuNPs. Energy transfer may also occur since the absorption spectrum of Au overlaps with the emission spectrum of BFO. The charge transfer process is closely related to the distance between the two materials involved. It is known that when both transfer processes are present, charge transfer usually dominates at short distance.\textsuperscript{16} In our case the AuNPs and BFO NWs were tightly attached to each other, therefore the observed quenching of the PL peak is most probably due to the electron transfer instead of energy transfer. In addition, this charge transfer mechanism is also consistent with the improved photocatalytic performance.

Scheme 2a illustrates the proposed dominating mechanism in the present photocatalyst system. The Fermi level of Au is more positive (+0.5 V versus NHE), compared to the conduction band energy of BFO (+0.1 V versus NHE),\textsuperscript{17} as shown in Scheme 2b. Thus, the charge transfer from the excited BFO to AuNPs would be thermodynamically favorable. After combining them together, the photogenerated electrons will transfer from the conduction band of BFO to AuNPs to reach a new common Fermi level ($E_F^*$) due to electron accumulation around their interface. This charge transfer process can reduce the recombination rate of $e^–$–h$^+$ pairs, thus enhancing photocatalytic activity. To further verify the contribution of the LSPR effect of AuNPs to the photoactivity, we tested the dependence of the photocatalytic reaction rate on radiation wavelength (Fig. S8, ESI\textsuperscript{†}). The enhancement of photoactivity at a wavelength of 530 ± 5 nm is more significant (~3 times) than that at 630 ± 25 nm compared with pristine BFO NWs, suggesting that the LSPR effect of the AuNPs also plays an important role in the remarkably enhanced efficiency of Au–BFO samples.

In summary, we have demonstrated the potential of a hybrid PLAL-AuNPs–BFO photocatalyst synthesized by a functionalization-step-free solution process for solar water splitting. Their superior catalytic activity is likely due to the role of the AuNPs as electron-trapping centres as well as the unique surface-chemistry features of the PLAL-AuNPs that can strengthen the interaction and promote charge transfer from BFO to AuNPs. More systematic studies of different semiconductors decorated with laser ablated metal nanostructures are underway.

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Notes and references